

Exploring the Chemistry of Metallic Solids, including Superconductors

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Dedication

To the memory of a great chemist, educator, humanitarian, and gentleman



Linus Pauling

Born February 28th , 1901 , Portland , Oregon

Died August 19th , 1994 , Big Sur , California

Much of the discussion of the structural chemistry in this book is based on Professor Pauling's theory of orbital hybridization, the "directed valence bond" (VB) theory, which I have found invaluable in my study of metallic solids. In that sense, this work deserves to be dedicated to the creator of the valence bond theory. I am proud to have extended the application of VB to the description of many lattice (nonmolecular) structures.

The photograph of Professor Pauling above is copyright \bigcirc The Nobel Foundation , and is used by permission of the copyright holder . I would like to thank Ms. Kristina Fallenius for consenting to the reproduction of the photograph in this work .Visit the Nobel e-Museum online to read about the many Nobel laureates , at the URL <u>http://www.nobel.se</u> ; and more specifically at <u>http://www.nobel.se/chemistry/laureates/1954/index.html</u> , where you will find an informative biography of Linus Pauling .

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Foreword

"By definition science welcomes new evidence , new ways of thinking . It has no final truths . It is a continuous quest and exploration".

- Baruch Blumberg (Nobel Laureate, 1976, Medicine or Physiology)

There are many ways of understanding the world around us . Everyone has their own way of doing so , depending on their nature and abilities . Observers will often agree with the overall picture , while they sometimes disagree about specific details .

Scientific endeavor is much the same . Accumulated scientific knowledge is by general consensus accepted , while in many contentious areas there is some disagreement , or clarification is needed . Most important , however , are the following points :

- There is no "absolute truth" in science . Everything changes , including scientific knowledge and the textbooks (this book also) that delineate such learning . Chemistry textbooks gradually change , becoming obsolete and disappearing , as this one will surely do . Science and chemistry evolve , moving continuously forward .
- Two or even more pictures (hypotheses, theories, or models) may reasonably describe the same phenomenon. For example, an electron may be described either in wave or particle terms. Often, the two different pictures describing the same phenomenon may complement and reinforce each other.

The ideas presented in this work are the pictures I have of metallic solids : what they are and how to explain their properties . As I am most comfortable in my own area of interest and training – chemistry – the pictures of these materials are based in chemistry , and not in condensed matter physics .

For example, I discuss the "metallic bond", and not the "conduction band", which are essentially two different ways of describing the same thing, the electrical conduction pathway in metallic solids. Both are valid approaches to the subject.

I have tried very hard to keep the discussions as simple as possible, avoiding the abstract in favor of the "practical" and "concrete". The text is liberally illustrated with sketches and crystal models, and included in it are hundreds of suggested experimental reactions, which I trust will be helpful and interesting to the reader.

While I hope this ebook will eventually enjoy a wide readership, I will be happy and satisfied if only a few people find something useful in it . In this regard, there is little doubt that the Internet, and its offshoot, the World Wide Web, are truly revolutionary in the way they have broadened access to human communication, and to scientific communication in particular. So I am confident that when made available in ebook form on the "Web", this exposition on metallic solids should find a wider audience than it would in hard copy (paper) format.

The practice of science is studying Nature , asking questions about it , and trying to answer them by theory and experiment . That's what I have done in studying metallic solids : wondering about them , asking questions about them , trying to find the answers in the scientific literature , then proposing my own answers in the form of pictures and experimental tests to verify them . In the process I have raised yet more questions and puzzles for the reader to ponder . These pictures are my point of view ; they are neither absolutely right , nor absolutely wrong . It is the responsibility of the reader to keep an open mind when reading this and other books , and to search for and find the truth in them .

"Chemistry has been called , by its votaries , a fascinating science , and with some truth , for it certainly affords more recreation than any other ; that it is the most useful of all sciences cannot be denied , nor can there be a doubt that it has a tendency almost to enchant those who devote their attentions to it . Its powers are almost infinite , and in some instances , produce effects which appear magical : a great number of those conjuring tricks , which have astonished our contemporaries as much as our forefathers , have been affected solely by its agency".

anon., "Chemical Amusements", <u>The Boy's Own Book</u>, fifth edition (revised); DeWolfe, Fiske (Boston, MA, ca. 1889); from page 125.



EXPLORING the CHEMISTRY of METALLIC SOLIDS, including SUPERCONDUCTORS

Introduction

The aim of this report is to demonstrate how simple chemical principles , generally of no greater complexity than are taught at mid-level undergraduate college chemistry , can be applied to the study of metallic solids as chemical substances , in order to understand them from a chemist's viewpoint , so that we will be able to predict with some confidence the design and synthesis in the laboratory of new compounds with metallic properties .

When I began this study around 1990 my original aim was to understand the nature of superconductors in easily understood chemistry terms, as this scientific field was almost entirely dominated at that time by condensed matter physicists. As my research progressed, I learned that superconductors are a special class, or subset, of a much broader group of materials, the metallic solids. Generally, all superconductors are metallic solids are superconductors. Why is this?

As this report unfolds, I will offer simple "pictures" to illustrate the various aspects of metallic solids and superconductors, and will try to suggest possible answers to the above fundamental question and others that surround the phenomenon of superconductivity. The discussion will center about many instructive examples of crystal systems from the literature of solid state chemistry. I will also use this forum to pose what I hope will be relevant and perceptive questions to the reader, and to propose the design and synthesis – sometimes by several different routes – of many compounds and crystal systems. From the principles and examples discussed, we

will expect them to be metallic solids with interesting properties, among which – in certain cases – new superconductors may be found.

Superconductivity was discovered in 1911, and for much of the twentieth century it remained the exclusive preserve of condensed matter physicists. Chemistry had little or no role to play in its study and understanding. On occasion, inorganic or solid state chemists would prepare a new compound or crystal system which would arouse the interest of physicists working in superconductivity research.

High temperature superconductivity (usually understood to mean that the material in question becomes superconducting above the boiling point of liquid nitrogen, at 77 K) arrived in 1986-87 with discovery of the mixed-valent cuprates. This important, even critical breakthrough in the field resulted in a sudden popularity of solid state chemistry and chemists, as they were urgently required for "cooking" batches of chemical reagents in recipes almost reminiscent of medieval alchemy.

More and more these days a good grounding in chemistry is required for any researcher in the field of superconductivity. Clearly, the chemical composition and properties, and the crystal and electronic structures of the new materials, will have a direct and possibly critical effect on their physical properties, with particular reference to their metallic nature and superconducting behavior.

It should also be evident by now that new candidate materials with these desired properties can only be designed and synthesized by the application of chemical principles and theories . A purely physical theory cannot be used to design a new chemical compound . A "translation" of the physical theory into a chemical theory (or approach , or picture) is required for the preparation of new materials that have a reasonable chance for being metallic solids and possibly also superconductors .

That this is the case for any new high transition temperature (T_c) superconductors is only gradually – and I suspect, reluctantly – being

acknowledged, as is illustrated by the title of a review paper, "A New Era for Chemical Superconductors" [my emphasis] (ref. 1, page 390). Of course, scientists can certainly wait for someone to stumble onto a new compound that has extraordinary and exciting properties in their field of interest, then duplicate it and study it minutely. This is sometimes referred to as "serendipity", and indeed most, if not all of the synthetic and molecular metals (several of which will be looked at later) were discovered in such a manner.

A second possibility is the "edisonian approach", in which vast numbers of compounds are prepared and studied in the laboratory ; these are usually variants, or analogues, of successful materials discovered earlier in a serendipitous manner. The term "edisonian", by the way, is derived from the name of the great American industrial inventor, Thomas Alva Edison (1847-1931), who is said to have carried out 8000 experiments before completing a functioning design of the "Edison Cell", a rechargeable alkaline iron/nickel peroxide storage cell for the newly emerging automobile industry in Detroit . Japanese and British researchers have done this sort of "hit-and-miss" investigation, in some cases with the aid of laboratory robots to relieve the tedium (and aching feet and backs !) for human workers in attempts to prepare new high T_c superconductors.

Personally, I think edisonian research is a tacit admission by scientists that they don't really understand the chemistry underlying the nature of the materials they are aiming to prepare ; and I would think it would be difficult to obtain funding for any project based purely on serendipity. The objective of many materials science projects is to produce new compounds or crystal systems that have certain desired physical properties ; the prerequisite must then be to understand the chemical nature of those substances that we know from experience will result in them having such properties . Thus , chemistry must precede physics , at least in the design and synthesis of new candidate materials for whatever physical application .

Actually, several experienced scientists have argued persuasively for the necessity of an interdisciplinary approach to the study of complex

natural phenomena such as superconductivity. That is, they suggest that teams of physicists, crystallographers, chemists, and technicians, in both academic and industrial settings, are essential to the unraveling of the mysteries of superconductivity, and for the development of its technology. W.A. Little, who in the 1960s aroused a slumbering community of superconductivity researchers with his bold predictions of an ambient superconductor, commented in 1970 (ref. 2, page 390),

"To bring any of this [organic superconductors] about I think what is needed here is a continuous dialogue between the physicist and the chemist to know what it is which is possible to make , and if it is possible to make , if it is of any use In conclusion I would like to stress that in this field there is a desperate need for an interdisciplinary approach".

Little's colleague at this colloquium, R. West, concurred and added that the major industrial research laboratories and the National laboratories should become involved in superconductivity research (ref. 3, page 390) :

"This problem [organic superconductors] is so broadly interdisciplinary, that it will require the contribution of chemists, physicists, electronic specialists, and probably also engineersthis discovery could take place in a large and well-financed industrial laboratory....The synthesis of organic superconductors could well become an important mission of one of our National laboratories".

West's recommendations proved to be prescient, because prominent industrial research facilities such as Bell Labs (Lucent Technologies), and U.S. government establishments such as the Argonne National Laboratory, have indeed carried out important superconductivity research during the three decades since he spoke at that scientific conference.

More recently, the prominent solid state chemist A.W. Sleight has underlined the growing influence of chemists in superconductivity research and development (ref. 4, page 390) : "Chemists have played a critical role in the area of oxide superconductors . Creative synthesis routes were developed in several cases A continuing role for chemists is to provide improved synthesis of the known oxide superconductors . An even more important role lies in the search for new superconductors , which may not be oxides and may not contain copper . Given the status of the theory of superconductivity , exploratory synthesis holds the best promise for producing the next good surprise in superconductivity ".

Superconductivity as a research field has experienced periods of activity induced by breakthrough discoveries , followed by stretches of apparent dormancy during which the initial results were investigated in detail . One such dormant period occurred between 1968-1986 , after it was mathematically proven , from the highly respected BCS theory , that the maximum superconductor T_c obtainable in any system was around 30 K (note that W.A. Little , cited on the previous page , had predicted the possibility of an ambient superconductor in 1964 , but maybe the physics community thought that was just science fiction). Fortunately , the BCS theory doesn't seem to apply very well – if at all – to high T_c superconductors , so the field was rescued from stagnation again by another breakthrough , this time by the Swiss-German researchers J.G. Bednorz and K.A. Müller with their serendipitous discovery , in 1986 , of the barium lanthanum mixed-valent cuprates with a peak T_c of around 30 K .

These remarkable findings stimulated a rapid increase in high temperature superconductivity research worldwide , which reached a fever pitch after the announcement of the discovery of the first "liquid nitrogen range" superconductor , an yttrium barium mixed-valent cuprate with a T_c of about 93 K , by the C.W. Chu and M.-K. Wu teams in March , 1987 . An excellent account of these exciting , frantic days in the high T_c superconductivity field is given by Hazen (ref. 5 , page 390) , who participated in the analysis of the crystal structures of several of the new compounds .

Since 1987 the field has again slowed down to the point of tranquility, if not dormancy. A vast amount of research has been carried out in the chemistry of the cuprates, with impressive advances being made in high temperature

superconductor materials and in their transition temperatures (a review of the significant high T_c superconductor compounds begins on page 184). Still, the peak T_c obtained to date hasn't moved much higher than that (133 K) for a mercury-containing cuprate prepared in 1993. "Tweaking" the chemical composition of these mercury cuprates, for example by substituting some thallium for part of the mercury content, has raised their T_c values only a few kelvins. In short, I suspect researchers have run out of ideas as to where to look for new superconductor compounds.

One of my objectives in this book will be to propose many new compounds and crystal systems as potential superconductor candidates . A broader aim , however , will be to discuss the chemistry of metallic solids , a wider class of materials that encompasses superconductors . I have discovered that an understanding of the nature of metallic solids is invaluable in the study of superconductor chemistry . I have also found that metallic solids in general are truly fascinating materials in their own right , and deserve much more attention from researchers than they have received in the past . Hopefully , this account will inspire more chemists to devote their research efforts to the solid state chemistry of metallic solids , including superconductors . The Metallic Bond

A metallic solid is any solid that contains a metallic bond . I prefer , and use in this text , the general term "metallic solid" rather than the familiar "metal" . This latter word is more useful in conjunction with adjectives such as molecular , synthetic , metallurgical , and industrial . I will be discussing several interesting and educational molecular and synthetic metals later on , but I would prefer to leave any consideration of metallurgical and industrial metals to the metallurgical engineering texts in the university library . The metallic bond is quite functional in liquid metals such as mercury , gallium , and cesium , in molten metals at higher temperatures , and in certain amorphous glasses . However , this study will be confined to crystalline solids , which is wide enough in scope for anyone's ambitions .

You rarely see any mention of the term , "metallic bond", in the literature any more . It seems to have been supplanted almost entirely by the band theory , from solid state physics , to describe the nature of metallic solids . Band theory is too mathematical and abstract for me ; I understand it in broad outline but not in detail . That leads me back to the earlier , simpler, and more chemistry-relevant concept (to me) of the metallic bond .

A bond , in the chemistry sense , is any force joining together two or more atoms . There are five generally recognized chemical bonds :

- The covalent bond , including the coordinate covalent bond , in which an electron pair is shared between two atoms ;
- The van der Waals dipolar bond , in which an unequal distribution of electronic charge in atoms or molecules creates electrical dipoles in them , resulting in a sort of "electrostatic cling";
- The hydrogen bond , in which the hydrogen atoms in molecules interact with other neighboring atoms , has aspects resembling both covalent and dipolar bonds ;

- The ionic (or electrostatic or coulombic) bond is the binding force between anions and cations in a crystal. These ions have full negative or positive charges, compared to partial electrostatic dipolar charges in van der Waals dipolar bonds; and finally, the fifth type of chemical bond, and the star of our show,
- The metallic bond.

All five types of bonds can occur in crystalline solids , usually in combination . For example , in some structures it may be possible to have a "blend" of covalent and ionic bonds in varying degrees in the crystal . Some crystal systems have virtually only one type of bond holding the atoms together ; the ionic bond in sodium chloride , the covalent bond in diamond , and the metallic bond in the alkali metals are examples . More complex structures may have combinations of several of the bond types . The interesting synthetic metal "KCP" [$K_2Pt(CN)_4Br_{0.3}$. $3H_2O$] (page 87) is bonded by all five types of chemical bonds (ref. 6 , page 390) .

Most of the elementary (metallurgical) metals have a combination of covalent bonds and a metallic bond . Often these covalent bonds are quite strong , and impart the properties of mechanical toughness and refractoriness to them . The metallic bond , by contrast , is very weak and contributes little to the metal's strength . Compare the alkali metals (with the possible exception of lithium , which is stiffer than the others) , having the consistency of firm putty , with some of the transition metals like titanium or the fantastically refractory tungsten (m.p. 3387 °C , b.p. 5927 °C) . On the other hand , the presence of covalent bonds in a metallic solid is no guarantee of strength , either , as we will see when we take a look at the bonding in tin (page 164) , a relatively soft , low-melting metal . Of course , the characteristics of strength and toughness of metals are also a function of the macroscopic crystal structure of the materials , as described by their metallurgy , which is beyond the scope of this study .

The valence electrons and their orbitals jointly comprise the metallic bond in a solid . All electrons in matter are in – or possibly form , according to one's philosophy – orbitals about their atomic nuclei . Because of the quantum nature of electrons , these orbitals can be thought of as their wave patterns

and also as the mathematical function of their probability density . It is possible to combine two or more native orbitals to produce a new , composite hybrid orbital on an atom , or molecular orbital in a molecule , or crystal orbital across the dimensions of a crystal . The four types of native atomic orbitals , s (sharp) , p (principal) , d (diffuse) , and f (fine) , can combine with themselves and each other in many different combinations . The native , hybrid , molecular (MO) and crystal (XO) orbitals all have unique geometries and shapes . The molecules and crystals, which are bonded together by valence electrons in these various orbitals, will thus have a vast multitude of distinct atomic architectures .

The covalent and metallic bonds are orbital in nature . Dipolar and hydrogen bonds aren't directly orbital-related , but occur in molecules that are already joined by covalent bonds . Ionic bonds are omnidiectional electrostatic forces unrelated to orbitals . The atomic architecture of ionic crystals is governed by the magnitude of these forces , the size of the ions involved , and by the most energetically favorable packing pattern of the ions in the solid .

There are several ways of classifying metallic solids . One possible way might be to assign them to one of three general categories : molecular , macromolecular (polymeric) , and nonmolecular . The latter type would include both the elementary metals and their alloys , and the extended atomic lattice compounds , which I will refer to more simply as the lattice compounds . Although I will touch briefly on several informative examples of molecular and polymeric metallic solids later on , the focus of this work will be on the lattice type of compounds .

A more general approach to classifying metallic solids is by their orbital topography, a concept first introduced by H. Krebs in the mid-1970s with respect to superconductors. The word "topography", which I believe was first applied to orbitals by A. Simon (ref. 7, page 391), refers to the presence or absence in crystal orbitals of nodes, which fundamentally affect the electronic properties of metallic solids. Nodes are regions of zero or low electron probability density occurring around atomic kernels in molecular and crystal orbitals when they are formed from the overlapping of two or

more native or hybrid orbitals . It is also possible to form certain types of MOs and XOs that are nodeless along at least one crystal axis , for example with s-s sigma , face-to-face p-p pi , and face-to-face d-d delta overlap .

Krebs is one of the few solid state chemists I know who extensively used orbital theory in the analysis of crystal structures, for example in his excellent textbook (ref. 8, page 391). In what I regard to be a key paper in superconductivity chemistry theory (ref. 9, page 391), he stated,

"The rule that superconductivity is only possible if there exists at least one space direction not intersected by plane or conical nodal surfaces can only be verified for a limited number of superconductors . On the other hand , in no case does anything point against the validity of this rule . In those cases in which the condition of the rule is fulfilled , superconductivity is found with very few exceptions . We can thus assume that the principle condition for the occurrence of superconductivity is in fact the absence of these nodal surfaces".

I refer to Krebs's "principle condition" above as Krebs's Theorem, and extend it broadly over the entire class of metallic solids . When this is done, another general classification of metallic solids is possible, based on the orbital configuration of their metallic bond. In the current literature two fundamental varieties of metallic solids are recognized : "metallic conductors" and "semiconductors". These two types of materials have recognizably different electrical conductivity characteristics.

Metallic conductors usually have excellent electrical conductivities whose magnitudes are inversely proportional to their absolute temperature . They may or may not also become superconducting when cooled to near absolute zero . Semiconductors mostly have low electrical conductivities that are directly proportional to their absolute temperature , and by definition they never become superconducting , since they tend to become insulators at low temperatures .

Where I have been able to obtain suitable data from various literature sources, I have drawn graphs of the electrical conductivity versus

absolute temperature for a number of metallic solids . With the obvious variations , the graphs always appear the same for the two general types of material : the "metallic conductors" have curves with an asymptote at either end , and a short linear section in the middle ; a typical example is that of gold , the paragon of metals , whose conductivity is shown in Figure 1 :



Data for this graph were taken from the <u>Handbook of Chemistry and Physics</u> (ref. 10, page 391).

Graphs for several semiconductors I looked at could be liberally interpreted as linear, terminating on the x axis, as illustrated by a typical example, that of the gray tin allotrope in the following Figure 2:



In the above graphs, the unit "ohm~1cm~1" is actually ohm⁻¹cm⁻¹, which is my preferred unit of electrical conductivity (and the only cgs unit I use in my work ; I always employ MKS-SI units elsewhere) ; the graphing and graphics software lacked subscripts and superscripts in their text labeling. I also prefer to use units of electrical conductivity rather than resistivity, as referring to how well a metallic solid conducts electricity, rather than how poorly it does so. I suppose this is just a matter of perspective, though.

The data for the gray tin graph were taken from Ewald and Kohnke's Fig. 2 (ref. 11, page 391).

The electrical conductivity of gray tin is 2090 ohm⁻¹cm⁻¹ at 273 K, which is substantial for a "semiconductor" (that of white tin, a typical "metallic conductor", is 87,000 ohm⁻¹cm⁻¹ at 273 K, and it becomes superconducting at 3.7 K). On the other hand, YBCO, the famous ceramic high T_c superconductor mentioned above on page 5, has a rather feeble room temperature conductivity of around 500 ohm⁻¹cm⁻¹ or so (Table X-1, p.198, in ref. 12, page 391). The classification of metallic solids purely by the magnitude of their electrical conductivities can thus be deceptive. A more accurate classification of these materials will be provided by a graph of their conductivity versus absolute temperature, which will quickly assign them to the "inverse" (metallic conductors) or "direct" (semiconductors) category.

Since the numerical value for the ambient conductivity of a metallic solid is really irrelevant to its general classification, I prefer to call the metallic conductors true metals, and the semiconductors pseudometals. White tin (a metallurgical metal and good conductor) and YBCO (a ceramic and poor ambient conductor) are thus true metals, while gray tin (a good semiconductor) is a pseudometal, based on their conductivity behavior over a wide range of temperatures.

Krebs's Theorem , extended to metallic solids in general , could be phrased something like this :

"True metals will have a metallic bond consisting of a nodeless crystal orbital along at least one crystal axis, while in pseudometals the metallic bond will consist of at least one crystal orbital that is periodically intersected by nodes".

Note that true metals may also have , simultaneously , other conduction pathways that utilize nodal crystal orbitals , but the XO that makes them a true metal will always be nodeless . Pseudometals , by comparison , have no nodeless XOs at all . Superconductors are a special subclass of true metals , with a nodeless XO along at least one crystal axis ; thus they conform to Krebs's original rule for the appearance of superconductivity in metallic solids . Unfortunately , the theorem doesn't distinguish between true metals that are and aren't superconductors . We will have to search elsewhere for the reason why superconductivity can appear in some , but not all true metals .

As for the reason underlying Krebs's Theorem itself, we will have to turn to metals physics for an explanation. Since I am well out of my depth in this area, I will offer only a brief suggestion here, and hope that readers more familiar with the subject will be able to fill in the blanks, so to speak.

The flow of electricity in a metallic solid is the movement of mobile valence electrons in the metallic bond from a region of high potential energy, to a region of low potential energy (usually the "ground"). These mobile electrons, both as particles and as waves, transfer the electrical energy from the high potential region to that of lower potential.

In any given sample of a metallic solid there is only one metallic bond throughout the entire mass of material. This in contrast to the other types of chemical bonds listed above on pages 7 and 8, which are localized ; the metallic bond is delocalized, or spread out throughout the entire volume of the crystal.

The crystal orbital spanning the macroscopic dimensions of the crystal contains all of the valence electrons participating in the metallic bond . Again , this is in contrast to a conventional covalent bond , which consists of a single molecular orbital (MO) containing a pair of valence electrons . Accompanying each low energy MO is a higher energy antibonding molecular orbital (ABMO) , which is generally vacant under ambient conditions .

The question naturally arises : how can you fit all those valence electrons into a single XO, contrary to the Pauli exclusion principle ? The answer – expressed in very simple chemistry terms – is that the valence electrons are indeed in a single XO, the metallic bond, in physical space, but they are

paired off in a vast number of separate levels in energy space. Each pair of energy-matched valence electrons is at an increasingly higher energy level, in effect acting as a "sub-covalent bond" within the overall single metallic bond.

At a certain energy level, the valence electrons are no longer paired off, but are singlets in the successive energy levels above that point, which is called the Fermi level. These singlet electrons at and above the Fermi level are considered to be the ones responsible for the characteristic properties of metallic solids, such as electrical conductivity, good heat conduction, and metallic luster. They are usually very mobile, both "vertically" (rapidly oscillating in the energy levels above the Fermi level, resulting in the typical shininess of fresh, unoxidized metal surfaces) and "horizontally", that is, being able to move throughout the physical dimensions of the XO.

These mobile singlet valence electrons in a metallic solid are often collectively referred to as the Fermi sea of free electrons in the crystal . Actually, credit for the first description of the metallic bond should be given to the German metals physicist Paul Karl Ludwig Drude (1863-1906) who published his theory of the mobile free electrons in metals in 1900 :

"Drude....developed an electron theory of metals ; every metal contains a large number of free electrons (which he treated as a gas) , nonconductors containing relatively few ; only negative electrons are mobile ; although average kinetic energy is high , velocity is limited by their very small mean free path (due mainly to collisions with atomic centers) . He used this theory to explain the optical , thermal , and electrical properties of metals" [from Katz , ref. 13 , page 392] .

Recall that electrons, while being theorized about since the times of the ancient Greeks ("electron" is from "amber", in Greek; rubbing amber produced static electricity), were formally discovered only three years earlier, in 1897, by Sir Joseph John [J.J.] Thomson (1856-1940) in his studies of cathode rays. It was a brilliant idea by Drude to connect these mysterious cathode rays with the static electricity of amber, the flow of electricity in substances, and the other characteristic properties of metals.



Figure 3 : Paul Drude , "father of the metallic bond". This photograph is copyright \bigcirc by the Paul-Drude-Institut für Festkörperelektronik , Berlin , Germany , and is used by permission of the copyright holder . It was reproduced from their web page , <u>http://www.pdi-berlin.de/drude.shtml</u>.

In Drude's picture of the metallic bond the free electrons were treated as hard spheres behaving like gaseous atoms obeying classical gas laws . However, there were several significant discrepancies in Drude's theory, which led, in the late 1920s, to its radical overhaul using the newly developed quantum physics. The discrepancies were understood and resolved, and from this era the modern electron theory of metals emerged. Drude's pioneering work with metals should not be forgotten, though.

So much for some background on the metallic bond ; we can now look at a possible rationale for Krebs's extended theorem . Regardless of the nodal nature of the XO in a metallic solid , the electron waves can propagate unimpeded across the crystal dimensions . However , the free electrons as particles perhaps cannot drift across the nodes around the atomic kernels under the applied potential difference . There are two conceivable ways to get the electrons across the nodes in the pseudometals .

First, they might tunnel through them. Electron tunneling in solids is a well-known physical phenomenon; for example, the Josephson effect is based on the tunneling of Cooper pairs of electrons in superconductors through a very thin insulating barrier placed between the two layers of superconductors; the entire assembly is called a "Josephson junction". Question: would the tunneling of free electrons in a nodal XO require energy input from the environment? If so, then we can understand the electrical conductivity behavior of pseudometals. The higher the temperature of the material, the greater the population of tunneling free electrons in the nodal XO, and the higher its electrical conductivity will be.

Second , they might bypass the nodes through a higher energy level nodeless XO . For example , the semiconducting metalloid silicon has the diamond crystal structure , with a tetrahedral sp³ coordination about each atom . Silicon is a 3 s-p element $(3s^2 3p^2 \text{ configuration})$ with all four valence electrons involved in sigma covalent bonds forming the crystal skeleton . Some of these 3 s-p skeletal electrons can be thermally raised to a higher energy level ; even at room temperature a very small population of them are promoted (Note 1 , page 374) . The 3 s-p sigma* ABMO and the 4s sigma XO are two possible destinations for them . The ABMO will be a dead end , because all ABMOs are nodal in nature . However , the nodeless 4s sigma XO is a good candidate for a "bypass" conduction pathway in silicon . In this case , heat from the environment will be required to promote a small population of 3 s-p skeleton electrons up into the 4s sigma XO .

Energy levels become more and more closely spaced with increasing shell number (period), as is illustrated in Figure 3 at the top of the next page. Under normal chemical conditions, promotion of a valence electron from the 2 s-p to the 3 s-p level is very difficult (as in diamond); that from the 3 s-p to the 4 s-p level is less so (as with silicon), and so on, decreasing again with germanium and least of all with the gray tin allotrope (5 s-p to 6 s-p level). We would therefore expect increasing ambient electrical conductivities from diamond through to gray tin, which is observed. The band gap, a measurement of the energy required to promote a valence electron from the low energy skeletal MOs to the higher energy conduction XO, also decreases dramatically from diamond to gray tin (Table 1):



Figure 4 : the increasing energy levels of the s, p, d, and f native atomic orbitals as a function of their shell number (period). The drawing is not to scale; it is for illustration purposes only. This figure is shown in many forms in a number of standard texts; I copied the design from the excellent book by Basolo and Johnson on coordination chemistry (ref. 15, page 392, their Figure 2-1, p. 28).

Table 1 : Electronic Properties of Several Group 4A Elements			
<u>Element</u>	Valence Shell	<u>Electrical Conductivity</u>	Band Gap
Diamond	$2s^2 2p^2$	10 ⁻¹⁶ ohm ⁻¹ cm ⁻¹	5.4 eV
Silicon	$3s^2 3p^2$	4.35 x 10⁻ ⁶	1.107
Germanium	າ 4s ² 4p ²	0.019	0.67
Gray Tin	5s ² 5p ²	2090	0.08

Data for the band gaps in Table 1 were taken from the <u>Handbook of</u> <u>Chemistry and Physics</u> (ref. 10, page 391). Data for the ambient electrical conductivities were from the <u>Kirk-Othmer Encyclopedia of Chemical</u> <u>Technology</u> (ref. 16, page 392, diamond, silicon and germanium), and from Ewald and Kohnke (ref. 11, page 391, gray tin).

Table 1 shows that in the diamond-structure 4A elements their electrical conductivities are an inverse function of their band gaps ; we would expect this from a consideration of the energy level separations shown in Figure 3 . However , three of the elements listed are pseudometals , with direct conductivity-temperature relationships (pure , undoped diamond is an insulator) . Moore (Seven Solid States , listed in ref. 14 , page 392) , in his Fig. 3.3 , p. 77 , shows a graph of the electrical conductivities of silicon and germanium over a wide temperature range . Both clearly have a direct conductivity-temperature relationship , hence can be classified as pseudometals , as is gray tin , as we saw earlier on page 29 .

The two conduction mechanisms of tunneling and bypassing must both be at work in pseudometals . When the small population of thermally excited skeletal electrons are promoted to the next higher sigma XO , holes are left in the skeletal MOs , permitting these lower energy electrons to migrate downfield under the potential difference , too (the common convention is to consider the empty holes as "positive charges" migrating upfield in the p.d. , but in this simplified chemistry approach I would like to stay with "plain , ordinary" valence electrons in the pictures I present ; see Note 2 , page 375) . I don't know what the relative contributions are of each conduction pathway in the pseudometals to their overall electrical conductivities , though .

As for true metals, their inverse conductivity-temperature relationship is usually attributed to scattering of the free electrons off the vibrating atomic kernels ("phonons"). As the temperature of the metallic solid increases, the phonon amplitudes rise and they become more and more efficient at blocking the passage of the migrating electrons. The picture I have of this process is that of the game of pinball, with the ball – usually a chrome ball bearing – bouncing off the posts as it rolls down the slope to the exit slots.
Now imagine the situation with the posts vibrating back and forth across the path of the descending ball . That might be an interesting handicap in the game of pinball ! In any case , increasing scattering of the conduction electrons at higher temperatures effectively lowers their mobility and the conductivity of the material declines as it is heated . The same process occurs in pseudometals , but is outweighed by the increased production of conduction electrons by thermal promotion and tunneling . Even at high temperatures , though , true metals are still generally good electrical conductors , as we know is the case with molten metals up to their boiling points . At the lower end of the temperature scale , approaching absolute zero , the conductivities of true metals generally soar up into the millions of reciprocal ohm-centimeters . And as we know , twenty-nine of the approximately seventy elementary metals become superconducting when cooled to near absolute zero (see Table 3.1 , p. 60 , in ref. 17 , page 393) .

One common orbital feature of all seventy of these elementary metals is the presence in them of valence electrons in s – and sometimes p – native AOs ; hence they are able to have a partially-filled s-p XO conduction system to function as their metallic bond . Palladium is an odd exception , having the $4d^{10} 5s^{0}$ outer shell electron configuration , but there is undoubtedly leakage from the 4d level to the 5s sigma XO , thus permitting it to behave like a true metal . This process would resemble the well-known leakage of sigma XO valence electrons into overlapping pi XOs in the 2A (alkaline earth) and 2B (zinc) families of elements , resulting in their metallic bond and properties .

We are thus able to correlate the two general shapes of the conductivitytemperature graphs of true metals and pseudometals with Krebs's extended theorem . This provides us with a simple picture of how the use of atomic orbitals by the atoms in a metallic solid , to form their crystal orbitals (their metallic bonds) , will profoundly influence their electronic properties , especially that of electrical conductivity . Incidentally, I didn't coin the term "crystal orbital" . It has been used for some time by authors such as P.A. Cox (ref. 18 , page 393) and R. Hoffmann (ref. 19 , page 393) to describe molecular orbitals extended across the physical dimensions of a crystal , as part of the expression , "crystal orbital overlap population" (COOP , of free electrons in a metallic bond) . As you have noticed above, I often abbreviate "crystal orbital" as XO (not as CO, the chemical formula for carbon monoxide; the "X" in XO comes from "Xal", shorthand for "crystal").

Apparently Krebs's ideas about orbital nodes and superconductivity were more or less disregarded at the time of their publication in the mid-1970s, and have been completely ignored since then . I think this is because of the all-pervasive influence of the band theory and related physics concepts in the study and development of solid state science . For example, the Fermi surface and Brillouin zones are generally used to describe the movement of the free electrons through a lattice of atoms in metals under an applied potential difference . Brillouin zones are a three-dimensional plot of electron energies in "wave number (\mathbf{k}) space", and the Fermi surface is a threedimensional representation of the Fermi level of the free electrons in a metallic bond across several Brillouin zones in a metal lattice . These abstract concepts have been successfully applied to many practical metallic solids , for example the 1B coinage metals . There seemed to be little or no interest in , and use of , orbitals by metal physicists .

Sketches of the Fermi surfaces of several common metals such as gold, copper, and lead, can be found in Moore's textbook, <u>Seven Solid States</u>, and in Mackintosh's article from <u>Scientific American</u>, "The Fermi Surface of Metals", both of which are listed in ref. 14, page 392. They have rather bizarre shapes, those for copper and gold resembling spheres interconnected by tubes, and the one for lead looking like a plumber's maze of pipes and tunnels (Note 3, page 376). The Brillouin zones and Fermi surfaces represent, in effect, the volumes of interatomic space in which the free electrons are permitted to flow through the lattice in an electric field. As such, they are as good a representation of the metallic bond in a solid as we are ever likely to have. The computation of even relatively simple molecular orbitals is apparently a formidable task, and to do so for a crystal orbital in a metal would be for all intents and purposes impossible.

That being said, I would still like to use orbitals, and in particular the idea of the crystal orbital, as a **working hypothesis** in the study of metallic solids and superconductors that follows. Although Moore, for one, claims

that Fermi surfaces are a useful tool for chemists to use in their research, I must admit that for me they are mysterious and alien entities, and I prefer to work with the more familiar and commonplace orbitals to form mental pictures of the compounds and crystal systems being examined.

I will be particularly interested in looking at all, or at least the most prominent, of the chemical bonds in a given material, as well as its metallic bond. This is really a prerequisite to locating the metallic bond in the material, since, as we will see in the case studies later on, the low energy ionic and covalent bonds form first, and the metallic bond, if any, is made up of "leftover" valence electrons in higher energy, and physically outermost, atomic orbitals which overlap to form the crystal orbital. The metallic bond is a sort of "afterthought" by Nature, and is somewhat opportunistic in the sense of forming only when a suitable opportunity presents itself. Formation of the lower energy, much stronger covalent and ionic bonds will always take preference over the formation of the higher energy, weaker metallic bond. We aren't at all surprised at the relative scarcity of metallic solids in the natural world : the noble metals (in the redox sense : copper, silver, gold, the platinum group metals) can occur in the native uncombined state such as in placer deposits, and a few pseudometals such as magnetite and certain heavy metal chalcogenides come to mind.

By the same token, rational syntheses of metallic solids haven't been formally developed into standardized repertoires, either, such as we now have extensively for organic synthesis, and to a somewhat lesser extent, in inorganic chemistry. The design, and installation into a given substrate, of a metallic bond is first of all a function of the general nature of the substrate involved : molecular, polymeric, or nonmolecular, as was mentioned earlier on page 9. The synthetic technique will quite naturally have to be appropriate for each general type of desired material. For example, if we are trying to design a new type of metallic polymer, our synthesis route will have to be based on one or other of the known methods of polymer formation, modified somehow to incorporate a metallic bond into it. I will suggest general approaches to accomplish this objective as I bring forward proposals for the synthesis of new metallic solids as the narrative proceeds.

A Chemical Classification of Metallic Solids

Although we can classify metallic solids several ways, such as by molecular structure (molecular, polymeric, and nonmolecular) or by the orbitals used in the metallic bond XO (true metal, pseudometal), a third and probably more practical method – for the chemist, at least – is by their chemistry. The chemistry of metallic solids is very important, in particular, for superconductors, with respect to their transition temperatures. In this chemical classification approach, metallic solids (and superconductors) are divided into four groups whose terminology I have borrowed from an earlier classification of mixed-valent compounds devised in 1967 by M.B. Robin and P. Day (ref. 20, page 393) : class II, homovalent and mixed-valent, and class IIIB, also homovalent and mixed-valent.

Robin and Day's review is one of the earliest and most comprehensive, in terms of both theory and descriptive chemistry, of the many reports in the literature on mixed-valent compounds. They classified these materials into four distinctive, separate groups :

<u>Class I</u> compounds have a single metal element component , in an ionic or covalent form , with two well-defined , non-interacting valence states . An example is lead (II,IV) oxide , Pb_3O_4 [red lead , minium] , whose crystal structure is shown at the top of the next page in Figure 4 . The small red spheres represent lead (IV) atoms ; they are octahedrally coordinated by oxygen atoms (green spheres) . The larger aqua spheres represent lead (II) atoms , which are tetrahedrally coordinated by the oxygens (the fourth position is occupied by the $6s^2$ "inert pair" on the lead atoms , rather like the lone pair of electrons on the nitrogen atom in the ammonia molecule) . There is essentially no interaction between the lead (II) and lead (IV) atoms in this compound , which is bonded entirely by covalent bonds .

Robin and Day's classification scheme really covers only the metal atom components (cations, if ionic) in mixed-valent compounds, but later on I will propose several new metallic solids based on mixed-valent anions.



Figure 5 : The crystal structure of lead (II,IV) oxide , Pb_3O_4 [red lead , minium] . Aqua spheres : lead (II) ; red spheres : lead (IV) ; green spheres : oxygen atoms . Covalent bonds are represented in all of my crystal structures by black lines . Not shown in the sketch are the "inert pairs" of $6s^2$ electrons on the lead (II) atoms , which occupy the fourth position of the tetrahedral coordination to them and cause the open area around the lead (II) atoms .

From my background training as an organic chemist a long time ago, I prefer the "ball-and-stick" representation of crystal structures as you see above and throughout this report. In fact, I find the other two common portrayals of crystal structures, the close-packed spheres and the polygon illustrations, rather difficult to visualize (in the first instance) and mentally confusing (in the second instance), so I don't use them in this work. The close-packed spheres drawing is probably the nearest representation to the actual situation in the crystalline solids with their closely packed atoms, but nevertheless I prefer, and use here, the "exploded" view of the ball-and-stick representation, with the covalent bonds clearly showing the atomic coordinations. In fact, the M3D "working models" I built with the Molecules 3D software, from which these "frozen" JPEG pictures were made, are even more versatile in that you can twirl them about and move

them up and down to see the three-dimensional nature of these crystals in a simple yet very revealing manner, and they are a lot of fun to manipulate, as well. I urge any reader with suitable M3D software to copy the M3D files I have provided on my own web site, open them in the M3D program, and then study and manipulate them in three dimensions in their viewer, in conjunction with reading this text.

The Molecules 3D software is offered for direct purchase by download or on a CD-ROM, or you can download the fully enabled "web edition" (version 2.5) for a free trial period before purchase (or not). For further details, please consult the supplier, Molecular Arts Corporation, Anaheim Hills, California, U.S.A., at <u>http://www.molecules.com/index.shtml</u>.

I know of three other impressive software programs for drawing crystal structures, but I think they are really intended for "advanced" students or teachers of crystallography and I considered them, first, too complex for my use here, and second, far more expensive than the moderately-priced Molecules 3D program. Anyway, they are :

From Australia, Crystal Studio version 4.0, by the CrystalSoft Corporation at <u>http://www.crystalsoftcorp.com/CrystalStudio/index.html</u>;

From Germany, Crystal Impact, at http://www.crystalimpact.com/; and,

From Norway, CrystalDesigner, at <u>http://www.crystaldesigner.no/</u>. Note that this last software program can be run only on the Macintosh platform. They apparently don't offer a Windows version, unfortunately.

The crystal structure drawings I present in this report are intended to be artwork only, and **not** correctly scaled diagrams. One significant shortcoming of the M3D program is that all the metal element atoms, which are that aqua color you see above in the red lead sketch, are of a uniform size. Of course, we know that in reality both the zerovalent metal atoms and their cations have a wide range of diameters, so I have "improvised" and have tried to use different-sized spheres for different metal atoms, even though those spheres have been "tagged" for use as quite different elements. For example, the lithium and the cesium atoms and cations are all represented by the same aqua sphere, so I might use the small blue sphere for nitrogen to represent lithium, and the larger violet sphere (normally iodine) to represent cesium in my sketches. In a few rare cases I have actually used the correctly tagged spheres for the elements they are supposed to stand for in the crystal structures.

A final point concerning the M3D models : while it is possible to set the bond lengths and angles quite closely with the M3D program , I generally use the "standard" (default) settings provided with the builder palette tools . For example , the octahedral coordination has uniform bond angles of 90° , while the tetrahedral coordination has angles of 109°28' , and so on . As the structures are "exploded" for easy viewing , I usually leave the bond lengths at their default settings unless the crystal structures in the literature I refer to show a particularly long or short bond for that structure . In reality , though , most crystal structures have bond angles and lengths differing appreciably from these "ideal" values . So I would ask the reader not to take the models literally ; they are **artwork** only !

The crystal structure of red lead in Figure 4 above was based on Fig. 161, p. 477 of Wells's classic textbook, <u>Structural Inorganic Chemistry</u> (ref. 21, page 394).

A second interesting Robin-Day Class I mixed-valent compound is gallium (II) chloride , $GaCl_2$, which really has two different valence forms in its structure , the eight-coordinated Ga (I) and the tetrahedrally-coordinated Ga (III) ; the correct formula for the compound would be $Ga(I)Ga(III)Cl_4$. The ball-and-stick model for this compound is shown in Figure 5 near the top of the next page . It was based on Fig. 1 , p.16 , from the review of mixed-valent compounds by Markwell (cited in ref. 20 , page 393) ; that sketch in turn seems to have been copied from Robin and Day's comprehensive review listed in ref. 20 (their fig. 40 , p. 367) .

The preparation of gallium (II) chloride has been detailed in <u>Inorganic</u> <u>Syntheses</u>; it was described there as a white, crystalline solid, with a rather low melting point of 170.5 °C (ref. 22, page 394). These properties suggest that there is no electronic communication between the two different forms of gallium in the compound , and that covalent bonding is predominant in it .



Figure 6 : "Gallium (II) chloride" ; aqua sphere , Ga (I) ; blue sphere , Ga(III) ; green spheres , chlorine atoms . The chlorines coordinating Ga (I) come from surrounding $[Ga(III)Cl_4]^{1-}$ anions .

<u>Robin-Day Class II mixed-valent compounds</u> are somewhat similar to those of Class I, except that now there is an electronic interaction, or communication, between the two metal atom components in formally two different valence states. In reality, this interaction causes the valence states to become "blended" into an overall average valence state. The blended valence can have either an integral (even, whole number) or non-integral (fractional) value.

We also notice that in Class II compounds the coordination about the metal atom components with the two different valences usually tends to be either identical or closely related ; this is the basis of Verwey's Rule , which loosely stated , says that within mixed-valent compounds , the metal atom components must be in crystallographically equivalent sites in order for any valence electron exchange to occur . We will see later with the cuprate

superconductors that this is generally, but not absolutely true. The more general condition of Verwey's Rule is that the native orbitals used by the interacting valence electrons must be able to overlap sufficiently for a metallic bond XO to form; if that occurs, then an electron exchange between the two valences can occur, and the material will be a Class II compound. If the metal atom components with the two valences have an identical coordination by the non-metal components, then their native orbitals used for the XO probably will overlap well, but if they are significantly different, then their orbitals will be quite different, too, and they probably won't overlap. A good example of this is the octahedral and tetrahedral coordinations, which have a completely different effect on the crystal field (CF) splitting of the energy levels of d native orbitals. The wildly different d AOs in transition metal compounds with these two particular coordinations cannot "mesh" properly, and so they are unsuitable for use together in Class II compounds.

A famous example of this tetrahedral-octahedral mismatch is provided by the compound (and naturally-occurring mineral) magnetite , iron (II,III) oxide , Fe₃O₄ [also called "ferrous ferrite" , Fe²⁺(Fe³⁺O₂)₂] :



Figure 7 : The spinel structure for AB_2X_4 compounds . The model can illustrate the two types of spinel compounds , the "normal" and the "inverse" varieties ; for example , of the mineral spinel itself (MgAl₂O₄ , normal) , and for magnetite (inverse) :

Spinels							
	<u>Normal</u> , AB ₂ X ₄			$\underline{Inverse}$, $B_{tet}A_{oct}B_{oct}X_4$			
	eg. spinel , MgAl ₂ O ₄			eg. magnetite,Fe ₃ O ₄			
\bigcirc	А	Mg ²⁺	(tetrahedral)	Fe ³⁺	(tetrahedral)		
	в	Al³⁺	(octahedral)	Fe ²⁺ , Fe ³	+ (octahedral)		
	Х	O ²⁻		O ²⁻			

My M3D model of spinel was derived from the drawing in Fig. 130, p. 207 in Müller's textbook, <u>Inorganic Structural Chemistry</u> (ref. 23, page 394); this polyhedra representation was the clearest picture of spinel I could find.

The spinel structure is one of the more difficult ones to visualize (for me) and to assemble the structure for . It looks somewhat "mixed-up", but there is indeed an overall order in it . The blue spheres in Fig. 6 above form a much larger face-centered cubic structure – the common crystal form of many of the elementary metals, in close-packed structures, by the way – in which the octahedral metal atom components and their anions are packed. The reader is referred to Fig. 8.8, p. 144, in Wold and Dwight's textbook, <u>Solid State Chemistry</u> (ref. 24, page 394) for a sketch illustrating this larger scale picture of the spinel structure . In the model of the face-centered cubic (fcc) structure on the following page, the reader should imagine small cubes with alternating octahedral and tetrahedral cations packed into each octant :



Figure 8 : The face-centered cubic structure . For spinels , the blue spheres would represent tetrahedrally coordinated cations . The overall cube can be divided into eight "sub-cubes" , or octants . B_4O_4 or AO_4 cubes are placed alternately in each octant . Confused readers (or in my case , a confused writer) should refer if possible to Wold and Dwight's Fig. 8.8 , mentioned above .

The M3D modeling software is capable of making only relatively small, compact structures. When building the models onscreen, you reach a point where the program will display an error message saying, in effect, "no more atoms". I was thus unable to build the complete spinel structure within the fcc "box" shown above.

In the case of magnetite , an exchange of $3d^6$ valence electrons , formally from the iron (II) cations , can occur between the octahedrally coordinated iron (II) and (III) cations , as Verwey's Rule states . The tetrahedrally coordinated iron (III) cations are excluded from this process .

Overall, magnetite appears to behave like a pseudometal. Its ambient electrical conductivity is 100-200 ohm⁻¹cm⁻¹ and remains fairly even over a wide temperature range. However, magnetite's conductivity "crashes" at

around 120 K, and below that temperature it becomes an insulator :



Figure 9 : The electrical conductivity of magnetite versus its absolute temperature . Obviously , this isn't really a linear relationship ! The graph's data were taken from Bowen's Figure 5 , p. 299 , in ref. 25 , page 394 ; this reference also has electrical conductivity data for many other transition metal oxides . See also Cox's Fig. 6.18 , p. 189 , in ref. 18 , page 393 .

Magnetite is in the group of pseudometals called "hopping semiconductors" (Moore, <u>Seven Solid States</u>, p. 148; see also the discussion of magnetite in Cox's textbook, p. 189, in ref. 18, page 393). The temperature at which the valence electron hopping over the "base" cations becomes active, or

conversely, ceases, is called the Verwey transition, and this usually marks the point quite closely where the pseudometal's conductivity experiences a very large rise or fall.

Another compound , europium (II,III) sulfide , Eu_3S_4 – probably also an inverse spinel like magnetite – shows a similar valence electron hopping behavior , which has been monitored in a very revealing experimental study of its Mössbauer spectrum from liquid nitrogen temperature to somewhat above room temperature (ref. 26 , page 394) . The spectral curves clearly show a coalescence of the Eu (II) and Eu (III) peaks at about 250 K ; above that temperature , the two valences are "blended" so well by the hopping electrons that the europium atoms are in an observed NIOS (non-integral oxidation state) valence of 2.67+ (a total of eight positive charges divided by three europium atoms per formula) . Below 250 K , the electron hopping slows down and the "extra" electrons formally from the Eu (II) cations gradually become localized , or pinned , on them . The two separate valence states of the europium cations then become quite visible , in the form of their spectral "peaks" . We can thus instrumentally observe a Robin-Day Class II mixed-valent compound become Class I , and vice-versa .

Another well-known iron compound illustrating the characteristics of a Class II mixed-valence material is the deep blue pigment, "Prussian Blue". This compound was discovered serendipitously in 1704 by the two German tradesmen Dipple and Diesbach while experimenting in rather alchemical conditions for new dyestuffs (this story is charmingly related by the popular science storyteller and chemistry professor, Dr. Joe Schwarcz, in his book, <u>The Genie in the Bottle</u> : ref. 27, page 394). Although the chemistry of Prussian Blue and related compounds is complicated, in a nutshell it is the product of combining iron(II) cations with ferricyanide anions to produce iron(II) ferricyanide. It is also possible to carry out the "converse" synthesis with iron(III) cations and ferrocyanide anions ; this latter material was originally called "Turnbull's Blue", but has since been shown to be more or less identical to Prussian Blue.

Prussian Blue has a cage-like structure, and can act as a sort of zeolite, trapping cations and water molecules in the cubic cavities :



Figure 10 : Prussian Blue . Small red spheres : iron(III) ; medium sized green spheres : iron(II) ; aqua spheres : potassium or ammonium cations ; black and blue spheres (carbon and nitrogen atoms , respectively) are triple-bonded to form cyanide anions . Note that the carbons coordinate iron(II) atoms , while the more weakly coordinating nitrogens bond to the more electrophilic iron(III) atoms . No water molecules are shown in this model .

When Prussian Blue is prepared containing trapped cations and water molecules , it is called the "soluble" [actually , water-dispersible] form ; for a long time the trapped cations were potassiums , but it was eventually discovered that the cheaper ammonium cations could be used just as well , to produce the soft , easily ground Pigment Blue 27, with the chemical formula FeNH₄Fe(CN)₆ (ref. 28 , page 394) . When cations are absent from the cavities , the pigment , which now has the formula $Fe_4[Fe(CN)_6]_3.16 H_2O$ (ref. 29 , page 394) , is apparently harder and more difficult to grind to the desired very fine particle size .

As is generally the case for the Class II compounds, the two types of mixedvalent cations are in distinguishable crystallographic sites; in Prussian Blue the iron(II) cations are coordinated by the strongly nucleophilic carbon ends of the cyanide ligands, while the more strongly electrophilic iron(III) cations have coordinate covalent bonds to their nitrogen ends. Electron hopping between the iron(II) and iron(III) cations probably occurs via a backbonding mechanism :



Figure 11 : Backbonding in Prussian Blue . The iron cations' native 3d (xy, xz, and yz) AOs, with five and six valence shell electrons, can overlap with the antibonding MOs on the cyanide ligands, to produce a sigma MO, through which the "extra" sixth 3d electron can hop back and forth . Note the large nodes on the orbitals on both the iron atoms and the cyanides participating in this backbonding (the gray-shaded "sausage-like" sigma MOs are shown only for one Fe-CN backbond, but they can extend in three dimensions throughout the crystal of Prussian Blue).

After a fruitless search in the literature , including in <u>Chemical Abstracts</u> , I was unable to find any information on the electrical conductivity of Prussian Blue , either at room temperature or over a range of temperatures . Perhaps this has never been investigated because of the wide variability in the composition of the pigment , and the inability to define precisely a chemical and physical makeup for a "standard sample" of the material . In any case , Day mentions in a review ("Mixed Valence Chemistry and Metal Chain Compounds" , Table 2 , p. 204 , cited in ref. 20 , page 393) that in general the Class II compounds are semiconductors , with ambient conductivities in the range of 10^{-1} to 10^{-8} ohm⁻¹cm⁻¹ . Since the conduction pathway in Prussian Blue is probably the iron(II)-CN-iron(III) backbond , which is highly nodal in nature , I would predict that it would also be a rather poor pseudometal , a hopping semiconductor like magnetite and Eu₃S₄.

Robin-Day Class IIIA mixed-valent compounds, also called "metal cluster compounds", contain polyatomic metal cations surrounded by anions in the crystalline solid. The multi-metal atom cations have discernable polygonal shapes, and are undoubtedly held together by strong metal-metal covalent bonds. The metal valences are perfectly blended within each polygon, but apparently there is no electronic communication between neighboring polygons. These are little-studied materials, and relatively few examples are described in reviews. Transition metal compounds such as $[Mo_6Cl_8]^{4+}$, Nb₆Cl₁₄.8H₂O, and $[Ta_6Cl_{12}]^{2+}$ have been mentioned as being members of this obscure class of mixed-valent compounds. There are sketches of these molybdenum, niobium, and tantalum halides in several references, such as in Pauling's well-known textbook, The Nature of the Chemical Bond (cited in ref. 14, page 392; on p. 440 of the third edition and on the front cover of the Dover softcover re-issue of this book) ; in Robin and Day's original 1967 review (Fig. 23, p. 323 in ref. 20, page 393); and in a popular review article Day wrote in French for the magazine La Recherche (cited in ref. 20, page 393; Figure 3, p. 307). We can readily see the outline of the metal atoms comprising an octahedron in these Mo, Nb, and Ta compounds. The interesting metallic solid niobium monoxide has a similar sort of crystal structure; refer to Figure 22 on page 126 below. However, NbO is an excellent electrical conductor (and superconductor, near absolute zero), so it obviously cannot be included with the Class IIIA compounds, and in any case its niobium atoms are homovalent, not mixed-valent.

Day, in his <u>La Recherche</u> article (table, p. 309), describes the Class IIIA compounds as having a "coloration forte": they are strongly, or deeply colored, and are also said to be either electrically insulating or semiconducting materials.

<u>Robin-Day Class IIIB mixed-valent compounds</u> have a metallic bond directly between the metal atom components in the crystal ; that is , the metallic bond doesn't include any intervening non-metal atoms or anions , unlike the Class II compounds . The IIIB materials have many varied and unusual crystal structures as we will see in several examples later on , but in all cases the spectator anions or non-metal covalent linking atoms are "off to the side" and don't contribute valence electrons to the metallic bond . We have already met the well-known Class IIIB mixed-valent compound, KCP, on page 25 above. Crystals of KCP consist of stacks of planar $Pt(CN)_4$ "poker chips" with a Pt-Pt metallic bond passing vertically through the stacks like an axle joining up the hubs of wheels. The cyanides, bromides, potassiums, and water molecules are all excluded from the metallic bond (see Figure 16 on page 89) in K₂Pt(CN)₄Br_{0.3}. 3H₂O.

In the unusual mercury compound with the intriguing name, "Alchemist's Gold", and with the odd formula of $Hg_{2.86}AsF_6$ (or maybe Hg_3AsF_6 , depending on which paper you read), the metallic bond passes along chains of mercury atoms, holding them together in the crystal as polycations. The hexafluoroarsenate spectator anions are off to the side of the mercury chains (see Figure 20 on page 106).

The interesting compound silver subfluoride , Ag_2F , is composed of sandwich-like layers, silver-fluoride-silver....silver-fluoride-silver, and so on (Figure 21, page 109). In this case the metallic bond in the material is in the silver layers only, and ignores the fluorine linking anions.

The Class IIIB mixed-valent compounds are often called "synthetic metals" or "synmets", or "molecular metals", although this latter term is usually reserved for those synthetic metals in which the building blocks are organic molecules . Like the metallurgical (elementary) metals , they all possess a metallic luster and color (KCP is coppery , Alchemist's Gold is golden , silver subfluoride is brassy with a greenish tinge , and so on) . And , like the familiar metals , they are all excellent electrical conductors , and some are superconductors , too (but at extremely low temperatures , close to absolute zero) . Like the elementary metals and metalloids , the Class IIIB compounds are either true metals (Alchemist's Gold , silver subfluoride) or pseudometals (KCP) .

The synthetic metals were all originally discovered in a serendipitous manner, though once their chemistry was studied and understood the inevitable analogues often followed. For example, partially oxidized coordinate covalent platinum stack compounds were first prepared in 1846, but their chemistry and crystallography weren't fully elucidated until 1968 or so when a series of analogues and variants were synthesized by K. Krogmann (ref. 30, page 394), after whom these compounds are now named. I hope that this narrative will offer some insights into the chemistry of the metallic bond in the Class IIIB compounds, and thus facilitate the rational synthesis of new synthetic metals.

<u>Summarizing</u> the Robin-Day classes of mixed-valent compounds , the following Table 2 lists their most important physical properties :

Table 2 : Physical Properties of Mixed-Valent Compounds								
<u>Class</u>	<u>Optical</u>	<u>Electrical</u>	<u>Magnetic</u>	<u>Spectra</u>				
I	colorless to	insulator	diamagnetic ,	constituent				
	medium colors	s	paramagnetic	atoms				
II	deep blue ,	semiconductor ,	ferro- , anti-	constituent				
	black	poor conductor	ferromagnetic	atoms				
IIIA	intense	insulator ,	magnetically	not of consti-				
	colors	semiconductor	dilute	tuent atoms				
IIIB	metallic	excellent	Pauli	not of consti-				
	luster	conductor	paramagnetic	tuent atoms				

This Table is an adaptation of the one found in several reviews of mixedvalence chemistry, especially those written by P. Day, who with M. B. Robin first proposed the classification of mixed-valent compounds in 1967; see, for example, Day's review, "Mixed Valence Chemistry and Metal Chain Compounds", table on p. 204, cited in ref. 20, page 393.

The Eight Classes of Metallic Solids

Of the four varieties of mixed-valent compounds, only those in Classes II and IIIB will be of any interest to us. As semiconductors, conductors, and superconductors they are metallic solids, while Classes I and IIIA provide no viable candidate materials for our study.

We also know of compounds with a metallic bond – as evidenced by their significant electrical conductivity property – whose metal atom components are homovalent in nature . Several examples of these are niobium(II) oxide , NbO (page 125) , chromium(IV) oxide , CrO_2 (page 131) , and rhenium(VI) oxide , ReO₃ (page 144) , in which the metal atom components are separated by non-metal linking atoms , in these cases oxygen atoms . They would correspond to a sort of "Class II" of homovalent compounds . We can also call the elementary metals and semimetals , which are zerovalent , after all , as examples of a sort of "Class IIIB homovalent metallic solids" , in which the metallic bond involves only the metal atom components of the material . An example of a Class IIIB homovalent compound might be the remarkable material poly(sulfur nitride) [polythiazyl] , $(SN)_x$ (page 112) , which can be considered as a form of metallic sulfur ; I don't think the nitrogen linking atoms are involved with the metallic bond in $(SN)_x$.

Finally, we know that within each of these four groups of metallic solids (mixed-valent II and IIIB, homovalent II and IIIB) there are examples of both true metals and pseudometals, requiring a further subdivision. That is, there are eight distinct classes of metallic solids in all. These eight classes are discussed, with examples, in the next few pages. The first four classes are all true metals, with the inverse temperature-conductivity relationship, and as potential superconductor candidates will be of the greatest interest to us in this report. The remaining four classes of metallic solids are types of pseudometals, with the direct temperature-conductivity relationship and their semiconducting property. Of course, semiconductors are immensely important and valuable in their own right, but in this work I am aiming in the superconducting, rather than in the semiconducting direction. The four classes of true metals will therefore receive the most attention in the following pages.

<u>Class 1</u> : are true metals , homovalent , and Robin-Day Class II ; the metal atom species providing valence electrons to the metallic bond are separated by nonmetal atomic links or anions , and are in a uniform , integral valence state , including zerovalent in certain cases .

Examples :

Niobium(II) oxide , NbO ($T_c = 1.38 \text{ K}$) ; page 125 ; M3D model , page 126 . Chromium(IV) oxide , CrO₂ ; page 131 ; M3D model of rutile on page 132 . Rhenium(VI) oxide , ReO₃ ; page 144 ; M3D model on page 145 . Calcium nickel(I) nitride , CaNiN ; page 338 ; M3D model on page 339 . Copper(0) titanium sulfide , CuTi₂S₄ ; page 290 ; M3D model of a normal spinel on page 45 (key on page 46) . Tin(III) phosphide , SnP , cubic form ($T_c = 2.8 \text{ K}$) and its tetragonal form ; page 160 ; M3D models on page 161 and page 163 respectively . Thallium barium calcium copper(II) oxide , Tl₂Ba₂Ca₂Cu₃O₁₀ ($T_c = 122 \text{ K}$) ; page 240 ; M3D model on page 241 .

<u>Class 2</u> : are true metals , homovalent , and Robin-Day Class IIIB : the electronically-active metal atom species are connected directly by the metallic bond ; the nonmetal atomic links or anions are off to the side and aren't connected by the metallic bond (in some cases there aren't any nonmetal atomic links or anions in the solid) . The metal atom components of the material are all in a uniform , integral valence state , including zerovalent in some cases .

Examples :

All of the elementary metals and their alloys .

Some , but not all of the intermetallic compounds , eg. $SrGa_2$; page 170 ; M3D model on page 171 .

Magnesium diboride , MgB_2 ($T_c = 39$ K) ; page 172 ; M3D model similar to that of $SrGa_2$.

Poly(sulfur nitride) , $(SN)_x$ ($T_c = 0.26$ K) ; page 112 ; structure sketches on page 113 .

Class 3 : are true metals , mixed-valent , and are Robin-Day Class II .

Examples :

Yttrium barium copper(II,III) oxide [YBCO], $YBa_2Cu_3O_7$ ($T_c = 93$ K); page 190; M3D model on page 191.

Transition metal bronzes, eg. of molybdenum, rhenium, tungsten, etc.; page 153; M3D model of a perovskite on page 154 (A type unit cell). Some solid state chemists, eg. Cox and Rao, in their textbooks have assigned the "bronzes" to the Robin-Day Class IIIB mixed-valence compounds, presumably because of their metallic luster and high electrical conductivity. However, I prefer to place them in Class 3 of the metallic solids, which are Robin-Day Class II in nature, because the metal atom components of these materials, which provide the valence electrons for the metallic bond in them, are separated by oxygen links. That is, the oxygen linking atoms in the covalent framework of the solid are "in the middle" of the metallic bond – as is generally the case with Class II compounds – and not "off to the side", as is the situation with the synthetic metals of Class IIIB having a direct metal-metal metallic bond. That said, the oxygen links in the bronzes may participate in the metallic bond to a greater extent than in the usual dark blue or black Class II mixed-valent compounds . This will be discussed later under the topic of the bilayer metallic bond (page 148).

Class 4 : are true metals, mixed-valent, and are Robin-Day Class IIIB.

Examples :

Alchemist's Gold , $Hg_{2.86}AsF_6$ (or Hg_3AsF_6) ($T_c = 4.1$ K) ; page 105 ; M3D model on page 106 . Tricesium(0,I) oxide , Cs_3O ; page 307 ; M3D model on page 307 . Silver(0,I) subfluoride , Ag_2F ($T_c = 0.058$ K) ; page 108 ; M3D model on page 109 .

 $(TMTSF)_2ClO_4$ (T_c = 1.2 K); page 122; structure sketch on page 122.

Class 5 : are pseudometals , homovalent , and are Robin-Day Class II .

Examples : CoO, Cr_2O_3 , FeO, Fe₂O₃, MnO₂, MoO₂, and NiO. Refer to Bowen's Figure 5, p. 299, in ref. 25, page 394, in which graphs of the conductivity-temperature relationship for these, and other transition metal oxides, are presented. The compounds cited have a direct relationship and are therefore pseudometals. Their metal atom components have a simple, integral valence state appropriate to homovalent compounds, and the conductivity electrons hop between the metal atom components over oxides or oxygen links, placing these compounds in the Class II family.

Class 6 : are pseudometals, homovalent, and are Robin-Day Class IIIB.

Examples :

Silicon, germanium, and gray tin. Sodium thallide, NaTl; page 168; M3D model on page 169.

Class 7 : are pseudometals, mixed-valent, and are Robin-Day Class II.

Examples :

$$\begin{split} & \text{Europium(II,III) sulfide} , \text{Eu}_3\text{S}_4 \text{ ; page 49} \text{ .} \\ & \text{Lithium nickel(II,III) oxide} \text{ , } \text{Li}_x\text{Ni}_{1\text{-}x}\text{O} \text{ ; page 180} \text{ .} \\ & \text{Magnetite} \text{ , } \text{Fe}_3\text{O}_4 \text{ ; page 45} \text{ ; M3D model of an inverse spinel on page 45 ; } \\ & \text{key on page 46} \text{ .} \\ & \text{Prussian Blue} \text{ , } \text{FeNH}_4\text{Fe}(\text{CN})_6 \text{ [commercial , water-dispersible form] ; } \\ & \text{page 49 ; M3D model on page 50 .} \end{split}$$

Note that both Classes 5 and 7 are comprised of hopping semiconductors, the former homovalent and the latter mixed-valent in chemical makeup.

Class 8 : are pseudometals, mixed-valent, and Robin-Day Class IIIB.

Examples :

KCP , $K_2Pt(CN)_6Br_{0.3}$. 3 H_2O ; page 87 ; M3D model on page 89 . (TMTSF)₂PF₆ ; page 122 ; structure sketch on page 122 .

Note that both Classes 4 and 8 are synthetic and molecular metals, the former Class being true metals and the latter Class being pseudometals.

I believe that the reader will find this expanded classification of metallic solids useful in mentally sorting out the sometimes bewildering array of metallic materials that will be presented in the following pages. It will also help us to concentrate the search for viable new superconductor candidates, especially those with possible high transition temperatures. For example, new materials from Classes 5 to 8 inclusive, which are pseudometals, while being valuable in their own right, will be of no interest as possible novel superconductors. In Classes 1 to 4 inclusive – the true metals – we can easily predict from past experience that Classes 2 and 4, while providing researchers with the bizarre and fascinating synthetic and molecular metals, won't likely yield any high T_c materials for investigation. Yes, some of these compounds with their shininess and metallic colors are occasionally superconductors, but only very close to absolute zero. Only Classes 1 and especially 3 are predicted to be fruitful sources of new superconducting compounds with reasonably elevated transition temperatures. These two classes share a Robin-Day Class II identity, so from the outset we suspect that some sort of intervention from bridging anions or nonmetal atom links in the metallic bond of these compounds will be a definite asset in the promotion of high T_c superconductivity in them.

We'll soon launch a case-by-case study of a wide variety of metallic solids , then focus it into a closer look at a selection of modern , high T_c superconductors . The crystal and electronic structures of these compounds will be dissected so that we can try to understand the nature of the metallic bond functioning in each material . That , in turn , may give us some idea as to how and where to search for new high temperature superconductors . However , since the approach taken in this report to study the metallic bond will be an **orbital** one , we should first briefly digress to review the highlights of the application of orbitals in chemical bonds in general , and then to the metallic bond specifically .

Theories of Chemical Bonding in Solids

On page 39 I commented on the opportunistic nature of the metallic bond. That is, the strong covalent and ionic bonds form first in the crystalline solid under construction. Then, any available "leftover" valence electrons are located in the physically and energetically outer frontier orbitals. This is a direct consequence of the Aufbau principle, the gradual filling up of atomic orbitals from the lowest to the highest energy levels. It may or may not be possible for the frontier orbitals to overlap continuously in the crystal lattice to form some sort of crystal orbital (XO), which can function – together with the valence electron(s) in the XO - as the metallic bond in the solid [technically, the wave patterns of the valence electron(s) "smeared out", or delocalized, throughout the lattice are the XO]. If the frontier orbitals can't overlap continuously for some reason or other, the "extra" valence electrons will be pinned on their parent atomic kernels and the material will be an insulator. An XO periodically intersected by nodes (nodal planes or surfaces) will result in the solid being a pseudometal. If the XO is nodeless along at least one crystal axis, then the solid will be a true metal.

First, though, the skeletal structure of the crystal must be formed by overlapping together the lower energy bonding orbitals, with their valence electrons, on the reacting atoms. In this regard I subscribe to L. Pauling's "Directed Valence Bond" (usually just called "valence bond", VB) theory. This was one of the first attempts – published in 1931 (ref. 31, page 394) – to describe the covalent bond in terms of the newly emerging quantum description of the electron. Pauling took into account the electrostatic repulsion of the valence electrons in deriving the novel, unique hybrid orbitals from combinations of native atomic orbitals (AOs). As a result, the hybrid orbitals were endowed with specific spatial properties and geometric shapes. Because of this, the molecules and extended atomic lattices in solids constructed from such geometrical hybrid AOs have highly recognizable architectures in a myriad of three-dimensional structures. In organic chemistry VB hybrid AOs are so routine that they are usually overlooked in most research and discussions; one has only to think of the simple, commonplace methane molecule to appreciate this fact.

You rarely hear much of VB theory these days ; apparently it is now considered "quaint", "old-fashioned", and even obsolete . VSEPR theory (valence shell electron pair repulsion) is used to establish the molecular or lattice geometry, and molecular orbital theory (MOT) is used to describe the molecular orbital energy levels within the structure . Then , MOT is used to determine where (in which frontier orbitals) the conduction band will be located . Crystal field theory (CFT) and ligand field theory (LFT) are used , especially with the coordinate covalent compounds of the transition metals , to determine how the ligand environment of the metal cations will influence their valence electron configurations . All of these theories are described in detail in many excellent inorganic chemistry textbooks , such as Basolo and Johnson's <u>Coordination Chemistry</u> (ref. 15 , page 392) , and Cotton and Wilkinson's <u>Advanced Inorganic Chemistry</u>, <u>A Comprehensive Text</u> (John Wiley , New York , several editions) .

The reader will be interested – possibly even dismayed – to learn that I use Pauling's VB theory throughout this work . Why ? Because of its amazing simplicity (it has a complex mathematical foundation , but that theory was established long ago) , predictive power , and visual clarity . I'm not saying that VB is perfect – far from it – but modifications in its application on a case-by-case basis can be introduced to make it work better in solid state chemistry . VB was originally introduced for covalent molecules , then extended to coordinate covalent metal complexes . I don't think even Pauling envisioned it being used to describe the electronic structures of solid state lattice materials , but that's what I'll do in this report .

I don't use VSEPR theory, because it doesn't say anything about orbitals, while in VB theory the orbitals and their geometry are intimately related. We find generally that with the true metals the metallic bond is located in frontier orbitals physically covering, and at a higher energy level than, the skeleton of the crystal structure. This compares with the pseudometals, in which the metallic bond is located within the skeleton itself (recall silicon, germanium, and gray tin with their diamond crystal structures, and most of the electrical conduction occurring in their sigma covalent bonds, by the socalled "positive holes"). Thus, as far as true metals go, we must first find out what orbitals are being used in the crystal to construct its strong, low energy skeleton, then we can have some idea of where (in which frontier orbitals) the "leftover" valence electron(s) may reasonably be located. At that point, I use MOT to see if a "polymerized MO" – an XO – can form in the lattice by overlapping continuously in one, two, or three dimensions the frontier orbitals containing the extra valence electron(s).

The electronic structures and activity (including conductivity) in transition metal compounds are very complex subjects that are well beyond the scope of this review . I would refer the reader to P.A.Cox's excellent textbook on this subject , <u>Transition Metal Oxides , An Introduction to Their Electronic Structures and Properties</u> (Clarendon Press , Oxford , UK , 1995) for a comprehensive study . Even with transition metal compounds , though , VB is still useful as a "jumping off point" to assemble the skeletal structure ; then CFT , LFT , and MOT are used to modify the basic configuration if necessary and to create the metallic bond over the lattice framework . These electronic theories seem to work quite well together to provide a reasonably accurate overall picture of the metallic solid . From that we can understand its electronic functioning in a simple manner , and we might be able to make predictions as to related materials , suitability as a possible superconductor candidate , and to suggest interesting modifications to its structure .

I feel that the valence bond theory, reinforced where necessary by the crystal field and ligand field theories, and with the added molecular orbital theory for analyzing the overlap of the metallic bond orbitals, has been entirely satisfactory for the simple, nonmathematical treatment I provide here for studying metallic solids. I hope that skeptical readers will be patient with my admittedly unorthodox approach to the subject, and will feel free to substitute their own interpretations in contentious areas. Indeed, that is one of the main objectives of this work : to get solid state chemists – mainly – interested in metallic solids, to stimulate thought and discussion of them, and to arouse a new excitement and enthusiasm for their design, synthesis, study, and applications in practical fields.

Let's now take a look at how I have combined VB and MOT together to describe how the skeletal structures and metallic bonds in solids are formed.

An Overview of Valence Bond and Molecular Orbital Theories

I regard VB and MOT as complimentary , not antagonistic . Working together , and with the help of CFT/LFT in the description of transition metal compounds , they have helped us understand chemical bonding in molecules and extended atomic lattices for decades .

VB was devised by Pauling as a chemist's response to the quantum picture of the atom first proposed by Bohr. Theory and experiment (spectroscopy) had established the electron shell structure of the atom, with the four main types of electron orbitals : s, p, d, and f. These native atomic orbitals were known to have quite specific shapes; the s type were spherical, the p type were "dumbbell-shaped", the d type were in the form of a four-leaf clover [except for the $d_z 2$ AO, which again is dumbbell-shaped], and finally the f type of native AOs had rather complex shapes which can't be easily described here. Pauling's brilliant idea – and it still shines as brightly today as it did in 1931, despite skeptics and detractors – was to combine two or more native AOs, reshaping them mathematically into hybrid AOs having bonding lobes of positive symmetry, suitable for overlapping with other such hybrid AOs, thus forming a covalent bond with a pair of electrons in the molecular orbital (MO). It was well known, principally from x-ray diffraction studies, that inorganic crystals and organic molecules had welldefined three-dimensional structures . How were these structures formed with such precise, spatially directional covalent bonds? The valence bond theory thus arose, and I think that it is still one of the greatest achievements of twentieth century chemistry.

The complete VB theory is described in Pauling's original publications, for example in ref. 31 on page 394, and in his famous textbook, <u>The Nature of the Chemical Bond</u>, so I won't elaborate here on hybrid AO formation from the native atomic orbitals. Rather, I will offer a summary of many of the best-known (and some of the less familiar) hybrid AOs, presented in Table 3 on the following page. This tabulation is essentially a copy of Table 8-2, "Directional Characteristics of Some Valence Orbitals", found on p. 112 of Sanderson's inorganic chemistry textbook (ref. 32, page 395):

Table 3 : Valence Bond Hybrid Orbitals

Coordination No.	Hybrid Orbitals	<u>Geometry</u>
2	sp d _{z2} s dp	linear
	ds $d^2 p^2$	nonlinear
3	$sp^2 dp^2 d^2s d^3$	trigonal planar
	dsp	unsymmetrical plane
	p³ d²p	trigonal pyramid
4	sp³ d³s	tetrahedral
	dsp ² d ² p ²	square planar
	d²sp dp³ d³p	irregular tetrahedron
	d^4	tetragonal pyramid
5	d _{z2} sp³ d³sp	trigonal bipyramid
	$d_{x2-y2}sp^3 d^2sp^2 d^4s d^2p^3 d^4p$	tetragonal pyramid
	d ³ p ²	pentagonal plane
	d^5	pentagonal pyramid
6	d²sp³ d⁵s (<i>proposed</i>)	inner octahedral
	sp³d² sp³ds (<i>proposed</i>)	outer octahedral
	d⁴sp d⁵p	trigonal prism
	d ³ p ³	trigonal antiprism
8	d⁴sp³	dodecahedron
	d⁵p³	square antiprism
	d ⁵ sp ²	face-centered prism

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I have made several amendments to Sanderson's list, and have added two more of my own proposed hybrid orbitals, as you can see. These new hybrid AOs will have an interesting role to play in a number of molecular and crystal structures we'll examine later.

Jones has also provided a list of hybrid AOs, in Table 5.3 on p. 137 of his textbook of coordination chemistry (ref. 33, page 395). These are much the same as Sanderson's, with the addition of two hybrids which utilize f native AOs in their formation : d^3fsp^3 and d^3f^4s , both with a cubic architecture. It should be noted in this regard that compounds of the lanthanide and actinide elements usually have remarkably high coordination numbers, mostly higher than 6. For example, see the table of coordinations for lanthanide ions in Cotton and Wilkinson's textbook, Advanced Inorganic Chemistry, fourth edition, 1980, p. 986, and marvel with me at the fantastic complexity of the solid state structures of lanthanide compounds. It is interesting that those compounds of the divalent lanthanide cations have crystal structures typical of ionic compounds, such as rocksalt and fluorite, while the trivalent and tetravalent cations' compounds have the more complex structures. This suggests to me that the bonding in these latter materials is predominately covalent in nature, and that as such the lanthanide cations might well be forming, and using, hybrid AOs which include valence shell f native AOs, as Jones has stated. On the other hand, I disagree with Jones's assignment of the p^3 pyramidal hybrid AO on the nitrogen atom of the ammonia molecule ; surely not ! That would be the sp^3 hybrid, with the ammonia's lone pair of electrons in one of the nonbonding sigma lobes. Also, in another example, I have a minor quibble : in the complex cation $[(NH_3)_6Co]^{3+}$, the cobalt(III) is in a high spin state, judging from its Curie paramagnetism, and would use the outer (sp^3d^2) and not the inner (d^2sp^3) octahedral hybrid AO to bond with the ammine ligands.

You may be surprised to learn, as I was, that valence electrons located in hybrid orbitals must be energetically promoted from the ground state; the hybrids are actually in an excited state relative to the native AOs. Pauling pointed out in <u>The Nature of the Chemical Bond</u> (third edition, 1960, pp. 414-416) that a substantial hybridization energy, about 200 kcal-mol⁻¹, is required to promote carbon's native $2s^2 2p^2$ valence electrons into the sp³

tetrahedral hybrid AO . Of course , carbon uses the sp³ AO in its diamond allotrope , and in many of the vast array of organic molecules catalogued to date . Clearly , expenditure of the promotion energy to create the sp³ and other hybrid AOs is more than compensated for by formation of the carbon-carbon and carbon-X bonds . Pauling concludes ,

"There is , in fact , no reason for us not to accept configurations that involve a considerable amount of promotions of electrons" [book above , p. 415] .

The VB hybrid AOs are applicable only to covalent and coordinate covalent bonds, and not to any of the other types of chemical bonds mentioned earlier (page 24). Admittedly, it may be sometimes difficult to distinguish between, say, covalent and ionic bonding in some structures. The "test" I use when studying molecules and lattice compounds is to see if a VB hybrid might be used in constructing the skeletal framework of the material, and if there are enough valence electrons to form covalent bonds using those hybrids. For example, in sodium chloride, both the sodium cations and the chloride anions octahedrally coordinate each other, so octahedral hybrids of some sort or other might be considered for their bonding. I say "some sort or other", because sodium is a pre-transition element with no access to d orbitals or d valence electrons, and chlorine, as a post-transition element, generally doesn't use d orbitals or electrons in hybrids. Thus, the "classic" octahedral hybrid AOs, such as d^2sp^3 , would be ruled out in this case. The puzzle as to which hybrid AOs might be used in sodium chloride doesn't arise anyway, since there are no available valence shell electrons in the sodium cation to occupy any possible hybrid AOs. So I conclude that NaCl is a purely ionic compound.

How about another compound with the rocksalt structure , <u>nickel(II)</u> oxide ? In this case , the oxygens would have to form some sort of octahedral hybrid AO with six sigma bonding lobes , but it can't do this , since it has only four native AOs in its second period valence shell . Oxygen atoms , as oxide anions or as covalent oxygen links , can form three pure hybrid AOs : linear $(sp_x + p_y + p_z)$, trigonal planar $(sp^2 + p_z)$, and tetrahedral (sp^3) . It might also conceivably form a fourth combination hybrid AO , the "see-saw" shaped $sp + p^2 AO [sp is linear; p^2 is bent at a right angle]. This combination$ hybrid is rather rare; we can see it in the spinel crystal structure (page 45)where the four-coordinate oxygens aren't tetrahedral but rather have thatpeculiar "see-saw" shape.

In the case of nickel oxide, the oxygens are probably oxide anions and the compound can be confidently treated as having ionic bonding. Generally, any solid state compounds in which a second period element is involved as an anion (boride, carbide, nitride, oxide, fluoride) will have ionic bonding if the anion has a C.N. of five or greater (Table 3, page 64), and may have covalent bonding if the C.N. of the anion is two, three, or four. Of course, the physical and chemical properties of the compound may also give us a good idea of whether covalent or ionic bonding predominates in it.

Zinc oxide has the wurtzite crystal structure , in which both the zinc and oxygen atoms are tetrahedrally coordinated . We could think of the bonding in ZnO as being fully ionic , covalent , or even coordinate covalent . In the ionic case , the Zn²⁺ and O²⁻ ions are packed into the crystal in the most efficient manner consistent with their coulombic charges and crystal ionic radii . In the covalent bonding scenario , the zincs ($4s^2 4p^0$) hybridize their 4s and 4p AOs , forming tetrahedral sp³ AOs , containing the two valence electrons ($2s^2 2p^4$). The zincs and the oxygens "polymerize" together , with the tetrahedral MOs containing eight [6 + 2] combined valence electrons , two per set of overlapped sigma lobes , four each per atom .

In the coordinate covalent case , the zinc atoms are Zn^{2+} cations , the oxygens are oxide anions $[2s^2 2p^6]$, and they donate all four valence electron pairs into the empty sigma lobes on the zincs to form coordinate covalent bonds throughout the solid . It adds up to the same thing as the covalent bonding picture for zinc oxide .

We are all familiar, and comfortable, with the idea of organic polymers, the "plastics" of everyday life, and even more exotic macromolecules such as the silicones (with silicon-oxygen backbones), and the phosphonitrilic chlorides, with phosphorus-nitrogen spines. There is another, somewhat more unfamiliar concept related to this : that "purely inorganic" compounds may also , in some cases , be considered as polymers . Naturally , not all lattice compounds would fall into this category . For example , sodium chloride and nickel oxide , with their ionic bonding , would probably be excluded . Zinc oxide , though , with its covalent bonding , could reasonably be considered as a zinc-oxygen polymer . Another interesting example we can look at briefly here is lead(II) oxide , commonly called "litharge" .

Litharge is a pale yellow solid , m.p. 886 °C (the physical constants for compounds cited , such as melting and boiling points , were taken from the <u>Handbook of Chemistry and Physics</u> , the Alfa-Aesar <u>Research Chemicals</u> <u>Handbook</u> , or the Aldrich <u>Catalog Handbook of Fine Chemicals</u> , unless otherwise indicated) . Its M3D crystal structure is shown below :



Figure 12 : the crystal structure of litharge , lead(II) oxide , PbO . Large aqua spheres : Pb(II) ; smaller green spheres : covalent oxygen links . Not shown are the inert pairs of the leads' $6s^2$ valence electrons , which extend vertically above each Pb(II) atom . The structure can be extended indefinitely in the x-y plane to produce a layer of PbO that is packed together with other such layers in the crystal . This model is based on Wells's Figure 160 , p. 477 in his textbook , <u>Structural Inorganic Chemistry</u> (ref. 21 , page 394) .

Litharge is a good example of an inorganic compound in which the "inert pair effect" can be easily seen in its crystal structure . That is , a pair of valence electrons , unused in the chemical bonding in the compound , is stereochemically prominent in the structure , as revealed by an analytical technique such as x-ray diffraction . In the case of litharge , the inert pairs of electrons on the Pb(II) atoms are hinted at , although not directly revealed , of course , by the pronounced Pb-O distances in its tetragonal form :



Figure 13 : an idealized sketch of litharge , showing the extended distance between the PbO layers , with the presumed location of the leads' 6s² inert pair of valence shell electrons between the layers . This drawing was based on Fig. 2.14 , p. 107 in West's textbook , <u>Basic Solid State Chemistry</u> (ref. 34 , page 395) . A good discussion of the inert pair effect can be found in West's text , on pp. 106-107 .

The inert pair effect is typically found in compounds of the heavier elements of the 3A, 4A, and 5A families when the metal atoms are in lower valence states. Inert pairs can occur in compounds of Ga(I), In(I), Tl(I); Ge(II), Sn(II), Pb(II); and As(III), Sb(III), and Bi(III). Of course, inert pairs are well known (as lone pairs) in molecular species such as the ammonia molecule mentioned on page 65, and in the water molecule, with two lone

pairs . The important point to be made here is that the presence of inert pairs of unused valence electrons in a structure is a good diagnostic of covalent bonding in that crystal . In a material with ionic bonding , we would expect the inert pair to be spherically distributed around the metal kernel (for example , the Pb^{2+} in $PbTiO_3$). With stereochemically prominent inert pairs in a structure , however , we should immediately suspect covalent bonding , since the pairs will occur in the non-bonding lobes of a VB hybrid AO .

In litharge, for example, the lead(II) atoms have a five-fold coordination; four of the bonds extend to oxygen links, and the fifth sigma lobe contains the inert pair. I would suggest the sp³d hybrid AO is used by the lead atoms (a combination of the 6s, three 6p, and one empty 6d native AO, which are all roughly similar in energy level : Figure 4, page 35). This is the "outer" version of the "inner" $d_{x2-y2}sp^3$ tetragonal pyramid hybrid AO listed in Table 3 on page 64. The 6s² inert pair is placed in the axial sigma lobe, and the two remaining valence electrons, $6p^2$, are placed, one each, in an equatorial sigma bonding lobe of the hybrid.

The oxygens are covalent links (that is , not oxide anions) having a tetrahedral configuration , with all six oxygen valence electrons in the four sigma lobes : two singlets , and two pairs . The lead and oxygen atoms are then "polymerized" together , with eight valence electrons [2 + 6] for each PbO formula unit in four covalent Pb-O bonds , each with a bonding pair , and the leads' inert pairs sticking up from the layers .

In a later section, I'll discuss more inert pair chemistry in relation to metallic solids. For example, the inert pair can be "popped" by coordinating ligands up into frontier orbitals that may have the correct configuration to form a metallic bond, with the inert pair as the free electrons (page 286). The inert pair effect will also be seen as a contributing factor in making white tin (the familiar metal coating on "tin cans") a true metal (page 164), instead of leaving us with the much less popular gray tin allotrope, which we saw earlier is a semiconducting pseudometal. Inert pairs may also play a surprising and as yet unsuspected role in other important solid state structures, such as in the piezoelectric effect in the perovskite barium titanate (Note 10, page 386).

The idea that many lattice compounds have covalent bonds and are , in effect , "inorganic polymers" , isn't mine , but has been expounded at length in at least one chemistry textbook almost four decades ago . Sanderson discusses the "Coordinated Polymeric Model" of covalent bonding in lattice compounds in his book , <u>Inorganic Chemistry</u> (ref. 32 , page 395) , on pp. 132-135 . He concludes (p. 134) :

"From these three examples $[KCl, AgBr, and TiO_2]$, it appears that the calculation of bond energies based on the coordinated polymeric model of nonmolecular solids is simple, straightforward, and remarkably accurate".

The three principal tenets of the model are as follows :

- The crystal is composed of metal and nonmetal atoms, not ions;
- All outer electrons may be shared, and often are The nonmetal atom contributes not merely its usual bonding electrons, but all electrons in its outer shell (if the structure permits their use). All available orbitals of the metal atom become involved in the sharing.
- The valence electrons are distributed between metal and nonmetal atoms in a way as to equalize the energies of the valence orbitals (equalize electronegativities), thus imparting partial negative charge to the nonmetal and partial positive charge to the metal.

The above principles were quoted from Sanderson's textbook, p. 132.

There is nothing particularly radical or esoteric about the coordinated polymeric model of covalent bonding in lattice compounds . It is really just an extension of the picture of covalent bonding in small molecules , and it merges seamlessly with Pauling's VB hybrid orbitals . The examples of zinc oxide and litharge cited above are representative of the combination of the polymeric model and VB theory . This is the approach I'll be taking to describe the electronic structure of the solid's skeleton , based on its known crystal structure , over which will be superimposed the metallic bond . The skeleton must always be described first , since the electrons in its MOs are always at a lower energy level than those in the metallic bond . Any leftover valence electrons may then be assigned to higher energy frontier orbitals .

Molecular Orbital Theory and the Metallic Bond

Having constructed the covalently-bonded crystal skeleton using VB hybrid AOs, we proceed to the next step, placing any unused valence electrons from the metal atoms into suitable frontier orbitals at higher energy levels, and physically, above the skeletal MOs. The frontier orbitals are native AOs at the "frontier", or outer limits, of unoccupied energy levels immediately above those comprising the MOs. If there are no "leftover" valence electrons, the compound will be an insulator, or possibly a semiconducting pseudometal if the band gap is narrow enough to permit the thermal promotion of a discrete population of skeletal MO electrons (see above, page 34) into frontier orbitals. We might also convert the insulator into a metallic solid by chemical reduction, that is, adding electrons to it; these electrons will be forced into the frontier orbitals.

Most of the time the frontier orbitals will be energetically accessible to the surplus (or reductant) electrons, and they can be successfully accommodated within the crystal structure. Occasionally there are no readily available frontier orbitals for the promoted electrons at a low enough energy level. If we try to force the electrons into orbitals at an excessively high energy level, they become extremely energetic and destabilize the crystal structure, which will rearrange into one or more different structures having a lower chemical energy.

For example , it is very difficult to prepare low-valent compounds of aluminum . The two very stable , low energy forms of aluminum are Al(0) , that is , aluminum atoms in a chunk of the metal , and the Al(III) in all of the known aluminum compounds . Several experiments have shown that the intermediate valence states of aluminum , Al(I) and Al(II) , are stable only at very high temperatures , as oxides and sulfides (ref. 35 , page 395) . When such compounds are cooled to room temperature , they disproportionate into Al(0) and Al(III) : for example , a mixture of Al⁰ metal particles dispersed in Al₂O₃ . The abundance and cheapness of aluminum make it very attractive for use in new metallic solids and high temperature superconductors . It is rather discouraging to find that we can't apparently prepare the mixed-valent
compounds of aluminum which might be studied as potential superconductor candidates , for example as Class 3 metallic solids (page 57) .

One of the more important theses in this book is that it might actually be possible to synthesize quite unusual and even "impossible" compounds provided you can accommodate the metallic bond electrons in an energetically stabilizing XO, which in turn must be located in a suitably designed crystal structure. I will propose the preparation of the hypothetical lattice compound tris[aluminum(0.33+)] chloride, Al₃Cl, (page 352), in the expectation that it will be a metallic solid and might even be a superconductor with a respectable transition temperature. While I concede that it might well be an impossible compound to make, I believe that the chemical bonds in Al₃Cl – if it has the simple, compact anti-ReO₃ crystal structure – will stabilize the lattice to such an extent as to invalidate the destabilizing effect of placing the "extra" valence electrons on the aluminum atoms in frontier orbitals. That is, instead of destabilizing the structure by being located in remote frontier orbitals, the extra aluminum electrons should actually stabilize it by creating an XO in the lattice, which will act as an energetically favorable metallic bond in the solid.

The implication is , on the contrary , that the crystal structures of the low-valent oxide and sulfide compounds of aluminum , such as AlO and Al₂O , somehow prevent the formation of a stabilizing XO and metallic bond , and the surplus aluminum valence electrons are forced into very energetic frontier orbitals . That destabilizes the compounds , and they collapse into simpler , stabler materials (in this case , aluminum metal particles mixed into alumina powder) when cooled to room temperature . I'm guessing that these low-valent aluminum compounds have ionic and not covalent bonding ; this is because when aluminum bonds to oxygen it usually prefers a six-fold octahedral coordination , and to a lesser extent , a four-fold tetrahedral coordination . Thus , AlO probably would have a rocksalt structure , and Al₂O would likely have the fluorite crystal structure . In the first case , the oxides are six-coordinate , and in the latter example they would be eight-fold coordinated . Since no six- or eight-fold coordinate VB hybrid AOs can exist for oxygen , they would have to be oxide anions in an ionic crystal .

Why would that be so bad ? Well , even in crystals with ionic bonding the ligands surrounding metal cations will sterically block , and energetically destabilize , the frontier orbitals corresponding to those AOs used to form VB hybrid AOs in covalently-bonded structures . For example , in an ionic compound of aluminum , such as alumina , Al_2O_3 , there aren't any hybrid AOs on the aluminum cations . The Al^{3+} ions have a roughly octahedral coordination by the oxides , so their 3s and 3p native AOs will be blocked by the oxides (corresponding to the hybrid AO sp³d² , but aluminum has little or no access to d orbitals , and Al^{3+} is $3s^0 3p^0$).

We know from CFT/LFT that ligands, both of the simple spherical anionic and molecular varieties, when taking up positions around the electrophilic cations, physically block the unoccupied frontier orbitals around the cations when they electrostatically bond to them. This makes placing the "extra" valence electrons from the metal cations in frontier orbitals energetically quite difficult, and any electron placed in such an energetic orbital will tend to destabilize the structure, causing it to disproportionate into stabler materials. Another possible way of looking at the situation might be that the ligands occupy the destabilized orbital's physical space, preventing the formation of the electron-in-orbital in that interatomic volume. Of course, ligands are vastly larger than electrons, and will occupy correspondingly more physical space around the cation, making it even more difficult to squeeze in the "extra" valence electron somewhere.

So it doesn't really matter whether or not we're considering an ionic or a covalent structure ; the end result will be much the same . The same frontier orbitals will be "used up", either for making the VB hybrid AOs in covalent bonding , or by being energetically blocked by physically large ligands , as in the picture presented by CFT/LFT for ionic structures .

Back to the aluminum compounds : since the 3s and 3p orbitals will be blocked in ionic aluminum compounds , any metallic bond free electrons will have to be located in the 4 s-p frontier orbitals . Judging from past failures with the unstable Al(I) and Al(II) compounds , these will be energetically unsuitable to receive the extra valence electrons . Recall that the various electron shells around an atomic nucleus each have a distinct and specific radial distribution with a statistical "peak maximum" at a certain distance from the nucleus . I'm guessing here , but I suspect that the Al^{3+} cations' 4 s-p frontier orbitals are located precisely where the ligands , such as oxide anions , are clustered around it ; or more precisely , by occupying the physical space around the cation , the ligands prevent the occurrence of the free electrons-in-orbitals at that level . Thus there is no stabilizing metallic bond XO in the low-valent aluminum compounds , and they collapse into Al(0) and Al(III) when cooled to room temperature .

In my hypothetical new compound Al_3Cl , by contrast, the covalent bond should be – if all goes according to plan – the 3 sp hybrid AO on Al(I), and the metallic bond free electrons will be located in the 3p orbitals, which is normal for aluminum anyway. These are relatively low energy orbitals, and we should thus avoid forcing the extra valence electrons into any high energy frontier orbitals where they would destabilize the compound. Based on these and other related considerations, which will be discussed later, I believe that Al_3Cl might actually stand a good chance of surviving its preparation intact. It would have a most unusual metallic bond, and would be well worth studying from both the academic and technological points of view.

Molecular orbital theory (MOT) is discussed at length and in great detail in many textbooks, so I won't go into specifics here. I use an extremely simple form of the theory to construct "polymerized" MOs over the crystal skeletons; these crystal-wide MOs are the XOs that, with their valence electrons, form the metallic bonds in solids.

Consider the benzene molecule . It has a strong covalent skeleton in the form of a hexagon of carbon-carbon sigma MO bonds (with carbon-hydrogen side bonds) . A much weaker carbon-carbon pi MO is located over this skeleton , extending further out from the carbons and also at a higher energy level than it . The reactivity of benzene is readily rationalized from such an orbital structure , as well as its other chemical and physical properties . I mention the example of benzene in particular ; because of the electron resonance in the pi MO , there is a continuous "cloud" of electron probability over the skeleton , resulting in the aromaticity of benzene and related organic compounds . In one picture of the mechanism of superconductivity , the "Resonant Valence Bond" (RVB) theory , first proposed by P.W. Anderson in 1987 (for a discussion of the RVB theory , including references , see pp. 227-228 in the book <u>Superconductivity</u> by Poole , Farach , and Creswick , ref. 17 , page 393) , the electron spin pairs that are now known to be the electrical charge and energy carriers in superconductive currents are thought to resonate in the metallic bond in a manner similar to the electron pairs in the pi MO in benzene .

There are two main differences between RVB superconductivity and benzene . First , benzene is an electrical insulator , and there is no metallic bond connecting up the separate molecules . The pi MO electrons thus can't flow through a mass of the compound , even if it was frozen solid .

Second , the spin pairs in RVB superconductivity are all above the Fermi level in the metallic bond XO , so they can flow through the solid . There is a substance that has aromatic pi MO electrons like benzene , but is a lattice material : graphite . Graphite is only a modest electrical conductor (pure , undoped , virgin graphite has an ambient electrical conductivity of about 25,000 ohm⁻¹cm⁻¹) , and doesn't become superconducting , even near absolute zero . This is because its valence electrons in the continuous 2p pi XO – the metallic bond in graphite – have been "crunched" in the Fermi distribution and have been redistributed as singlets above the Fermi level . That results in graphite behaving like a "conventional" (Class 2) metallic solid (page 56) .

The examples of benzene and graphite are representative of the picture I am presenting here of the use of MOT to construct XOs in lattice compounds . It is possible to overlap the s , p , d , and presumably even f native AOs with themselves and each other in many different ways to obtain a host of MOs having every conceivable shape and geometry . Samples of some of these MOs are portrayed in most college-level inorganic chemistry textbooks . Since the great majority of these MOs are nodal in nature , they will be of little interest here . However , three types of MOs can be formed which are nodeless along at least one crystal axis , and will therefore be very useful in the formation of XOs which can function as the metallic bond in a crystal :

<u>s-s sigma</u> MOs , when extended throughout the crystal as a sigma XO , are nodeless along all three crystal axes . This is basically a shapeless "blob" of electron probability density , and is the most voluminous of the three types of XOs :



Ellis et al. (cited in ref. 14, page 392) illustrate the formation of sigma XOs in metallic solids by the continuous overlapping of native s AOs in their Figures 7.1 (p.188) and 7.3 (p. 190) of the text, <u>Teaching General</u> <u>Chemistry</u>, <u>A Materials Science Companion</u>. These figures are in support of their discussion of the band theory as it applies to bonding in metals, and generally in solids.

I recall a photograph in a High School physics textbook that showed a mechanic holding up several gauge blocks stuck together . Gauge blocks are rectilinear blocks of metal (of which type , I don't know , but probably stainless steel) , machined to be extremely smooth , flat , and polished , and of precisely established dimensions . They were stuck together , but not with glue , or magnetism , or a vacuum suction , but rather by interatomic forces ; more precisely , I believe , by a sigma XO . That is , the metallic bonds in the separate blocks of metal actually "fused together" to form a single , overall bond throughout the adhering blocks . This wasn't a strong bond , mind you ; the mechanic could pull the blocks apart again by his own strength , something utterly impossible to do to the individual blocks themselves , even with powerful machinery ; steel is a really tough material !

The same sort of thing can be observed if you have the misfortune to touch a live electrical wire . Even the slightest , light touch of a finger will instantly produce that very unpleasant numbing , tingling sensation . The electrical energy must be passing through the live electric wire (usually copper or aluminum) , through your finger and body , and into the ground . The

general theme in this study is that the electrons in matter are all in orbitals of some sort or other (an exception might be the electrons in static electricity, but I won't go into that here). Thus, the metal orbitals in the live wire must be overlapping slightly with those in the skin of your finger, to provide a pathway for the electrical current. The metal orbitals that are physically farthest out from the atomic kernels are the s AOs. The sigma XO in metallic solids must extend relatively far above the surface atoms of the metal in order for us to observe gauge blocks being stuck together, and to experience (I hope, very rarely, if ever) the unpleasant sensation of touching a live electrical wire. Sigma XOs must correspondingly be very voluminous within the interatomic spaces.

<u>Face-to-face p-p pi</u> MOs , when extended throughout the crystal as a pi XO , are nodeless along two crystal axes , but are nodal along the third axis :



In the above sketch , the white lobes are of positive symmetry , and the gray lobes are of negative symmetry . Overlapping positive with positive symmetry , or negative with negative symmetry , will produce a bond ; overlapping positive symmetry lobes with negative symmetry lobes will generate an antibond . The pi MOs and XOs are less voluminous than the corresponding sigma MOs and XOs .

Compared to the native s AOs , p AOs are somewhat closer to the nucleus , judging from plots of the probability distribution function , $r^2R(r)^2$, versus r (distance from the nucleus). These plots are shown in several inorganic chemistry textbooks , such as those by Rodgers (ref. 36 , page 395 ; his p. 238) , and by Cotton , Wilkinson , and Gaus (ref. 37 , page 395 ; their Figure

2-7, p. 43). I assume that the corresponding sigma and pi MOs and XOs will follow the same trend.

<u>Face-to-face d-d delta</u> MOs , when extended throughout the crystal as a delta \overline{XO} , are nodeless along one crystal axis , and are nodal along the other two :



As with the p-p overlapping to form a pi MO or XO, positive symmetry lobes must overlap with other positive symmetry lobes, and negative with negative, in order to form a delta MO, and by extension, a delta XO. The sketch was based on Companion's Figure 4-5, p. 42, of her nice textbook, <u>Chemical Bonding</u> (ref. 38, page 395).

Following the trend with native s and p AOs, d AOs are smaller still and closer to the nucleus than s and p AOs, so presumably this is true also for delta MOs and XOs. Bonding atoms together with delta MOs, and formation of a delta XO as the metallic bond in a solid, can be achieved only if those atoms are very closely packed, and of course, native d AO valence electrons must be available for the MO and XO. Such conditions are present in the transition metals; it is quite possible that delta MOs, and conceivably even a delta XO, might be found in some of the transition metals.

An interesting molecular solid that is thought to possess quadruple bonds (three sigma and one delta bond), is molybdenum diacetate dimer,

[Mo(OAc)₂]₂, whose M3D ball-and-stick structure is shown below :



Figure 14 : The molecular structure of copper(II) acetate dihydrate . The small red spheres are metal atoms in general , and copper in this case , or of molybdenum in the case of molybdenum acetate dimer (minus the two water molecules of hydration in the axial positions , of course) . The groupings of two black spheres represent acetate anions ; the green spheres are oxygens , which do the actual coordinating of the metal atom . The small gray spheres are hydrogen atoms on the acetates , and on the water molecules . The dashed line represents a possible weak bond between the two metal atoms in this family of compounds , four examples of which are :

<u>Metal</u>	M-M distance (cmpd.)	M-M distance (metal)
Cu	2.64 Å	2.556 Å
Mo	2.10	2.725
Cr	2.46	2.498
Rh	2.45	2.690

Data for the M-M distances in the dimeric acetate compounds were taken from Krebs's textbook, <u>Fundamentals of Inorganic Crystal Chemistry</u> (ref. 8, page 391, pp. 322-323); my M3D model was also based on his Fig. 27.1 from p. 322. The M-M distances in the parent metal elements were taken from the <u>Handbook of Chemistry and Physics</u>.

Except for the Cu-Cu distance in copper(II) acetate dihydrate , the other three M-M distances in the acetate dimers are actually shorter than in the bulk parent elementary metal , especially so in the case of molybdenum diacetate dimer . The valence shell electron configuration of Mo(0) is $4d^5 5s^1$, so that of the Mo(II) in the compound will be $4d^4$. Omitting the two axial water molecules in Figure 14 above , the molybdenum atoms are square planar coordinated by the acetates , and are expected to use the familiar dsp^2 hybrid orbital to accept a bonding pair of electrons from each of the acetates' oxygens .

At this point, we will make recourse to the CFT/LFT, which says that in different ligand geometries the d AO energy levels of coordinated transition metal atoms will be split into characteristic patterns; for example :

			x ² - y ²
energy		x ² - y ²	
xy , xz , yz	x ² - y ² , z ²	z ²	
			ху
x² - y² , z²		хy	Z ²
	xy , xz , yz		
		xz,yz	xz,yz
		4-4	
Tetrahedrai	octanedraí	tetragonal	square planar

In the above simplified sketch, the single energy level for all five d AOs of a hypothetical uncoordinated transition metal atom will lie about in the center of the drawing . Thus , for a square planar coordinated metal atom , such as the molybdenum in our dimeric acetate compound , the xz , yz , and z^2 energy levels will be stabilized , the xy AO will remain relatively unaffected , and the x^2-y^2 AO will be destabilized with respect to placing unused valence electrons in it . Of course , according to the VB approach , the x^2-y^2 AO will be removed in making the dsp² hybrid AO for use in the coordinate covalent bonding . However , CFT/LFT is helpful in locating the unused 4d⁴ valence electrons around the molybdenum kernel underneath the ligand appendages .

Since we have four 4d AOs available for these electrons (the x^2-y^2 AO has been removed for the hybrid orbital), one electron each will be placed in these orbitals, according to Hund's Rule (the maximum number of singlet electrons possible in the d AOs, for maximum energy stabilization). There will be one 4d electron in each of the xz, yz, z^2 , and xy AOs, in increasing energy level.

Looking again at Figure 14, and omitting the two axial water molecules, let's assign the x-y coordinates to the MoO_4 plane. The xy AOs will lie on that plane, and might be able to form a delta bond between the two Mo atoms :



The xz and yz AOs will be perpendicular to the MoO_4 (xy) plane, and might be able to overlap "tip-to-tip", as shown above. The z^2 AO is oriented perpendicular to the xy plane, of course, and might be able to overlap in the dimeric molecule to form the third sigma MO. Hence, $Mo(OAc)_2$ dimer is thought to have a quadruple Mo-Mo bond in its 4d AOs, one of those four bonds being the rare and unusual delta MO.

The overlapping d_z^2 AOs shown above can form a fully functional metallic bond XO, as we will see in the case study of the "molecular stack metal" KCP (page 87); however, note carefully that there are nodes periodically intersecting the sigma MOs along the chain of bonded atoms. These nodes occur around the atomic kernels of the atoms participating in the metallic bond, and they make the resultant solid a pseudometal as a result (KCP is a Class 8 metallic solid : page 58). Of the four types of bonds shown above, only the delta MO is nodeless, and that along one crystal axis only. While the delta XO is theoretically interesting in connection with this study of metallic solids and superconductors, it is probably impractical for actual implementation in the design of new candidate materials for future study. It would be a challenging task indeed to devise a new lattice compound with a metallic bond based on a delta XO !

As mentioned earlier, the s AOs are large, voluminous, and diffuse, and XOs formed from them result in rather weak metallic bonds, the weakest of all types of chemical bonds, in fact. The alkali metals are good examples of solids bonded almost entirely by sigma XOs. With the exception of lithium, they are all very soft solids, easily cut with a knife and readily extruded through dies.

The trend in the families of metallic elements is that usually the lightest member of each family (in terms of atomic weight) has the lowest density, and is the hardest, toughest, mechanically strongest, and the highest melting of the series. These properties gradually change with increasing atomic weight to softer, weaker, and less refractory metals. In orbital terms this observation might be rationalized by noting that <u>first</u>, the s AOs with the valence electrons that form the solid's metallic bond become larger with the increasing atomic period, and the electron probability density in them

steadily thins, resulting in a weakening metallic bond.

<u>Second</u>, p AO overlap becomes effective only with very short atomic distances, so the p-p pi XO bond strength in the families of metals weakens rapidly as the atomic radii increase in the series. This is why lithium metal is relatively hard compared to the heavier alkali metals; it must have the strongest of their pi XOs. Similarly for beryllium: it is a remarkably tough, refractory metal, especially when compared to the heavier elements in the alkaline earth family.

This p-p pi bonding is also striking when the alkali metals are compared to their alkaline earth neighbors . In the former elements , there is relatively little leakage from the s AOs into the corresponding p AOs , so there is relatively little pi bonding in them , even in lithium . In the latter elements , there is substantial leakage , or overlapping , of valence electron probability density from the filled s AOs into the empty p AOs . The resulting additional pi bonding is usually cited as the main reason why the alkaline earth metals are harder , tougher , and higher melting than the alkali metals .

This trend is also noticeable in the melting points of the 2B metals : zinc (m.p. 420 °C), cadmium (321 °C), and mercury (-39 °C). The increasingly diffuse outer s AOs containing the two valence electrons in these elements is likely one contributing factor in the observed trend of their decreasing melting points. More striking, though, might be the rapidly declining p-p pi bonding in these three solids with increasing atomic weight. Mercury in particular shows a strong preference for sigma chemistry. For example, the mercury (I) ["mercurous"] cation , $[Hg_2]^{2+}$, is a diatomic molecule with a strong $6s^{1}-6s^{1}$ covalent bond, rather like a bloated hydrogen atom. Mercury(0) atoms seem content, like helium, to keep their two valence shell electrons in an s orbital, with only a very minor leakage into the 6p orbitals. Mercury barely manages to be a metallic material (its electrical conductivity is fairly low : 10,406 ohm⁻¹cm⁻¹ at 298 K). It boils away at a remarkably low 357 °C into a colorless gas, which probably is more representative of its true nature – again like helium – than the familiar dense liquid "quicksilver".

Conventional thinking on pi bonds suggests that – at least for molecular compounds and solids – they are common to a few non-metal elements of the second period (B, C, N, O), and possibly to a few heavier elements such as silicon, sulfur and phosphorus. In the latter cases, d-p secondary bonds are also thought possible in certain molecular systems (Rodgers, ref. 36, page 395, his Figure 15.4 of $p\pi$ -d π bonding in trisilylamine, p. 386). Apparently little consideration has been given to the thought that p-p pi bonding may occur to any significant extent in the solid state compounds of heavier elements. Personally, I believe p-p pi bonding may be quite significant throughout the chemistry of many of the elements, regardless of their atomic weight; this will be especially true in the cases of lattice compounds, and in those compounds of metallic elements with the "light" nonmetal elements of the second period : B, C, N, and O, whose 2p orbitals may be quite active in p-p pi bonding. In fact, I anticipate p-p pi bonding as playing an important and possibly even pivotal role in high temperature superconductivity, as will be discussed later.

Band theory has been important in emphasizing the emerging importance of pi bonding in the elements and compounds . We have seen that band theory has been used to explain why, for example, the 2A (alkaline earth) and 2B (zinc) families of elements are metallic in nature ; this would be difficult to rationalize without having p orbitals to accept valence electron leakage from the neighboring s AOs . Similarly, as discussed above, the physical properties of the 2A and 2B families of elements can be at least partially attributed to the presence in them of p-p pi bonds (and probably p-p sigma bonds as well).

For a while I was wondering if I was alone in theorizing the existence of pi bonding in compounds of heavier elements, so I was somewhat relieved to discover an interesting paper by Hoffmann and co-workers concerning their theoretical calculations, based on the COOP [crystal orbital overlap population] approach – a simplified form of MOT applied to threedimensional crystal structures – for the solid-state material YCoC, which had been prepared earlier by a German research team specializing in carbides. Hoffmann and his students apparently also subscribe to the "coordinated polymeric model" (page 71) of covalent bonding in lattice compounds , judging from the title of their paper : "YCoC : A Simple Organometallic Polymer in the Solid State with Strong Co-C π Bonding" (ref. 39 , page 396) . They commented , "There is substantial π bonding in these [Co-C] chains" (p. 6602) . This is comforting support for a proposal that I'll bring forward later , in which such shishkebab compounds (in which there are long parallel chains of "polymerized" MX metal-nonmetal atoms , with cations nested in between the chains) might be designed into high temperature superconductors . The metallic bond in these compounds , in which the superconductivity occurs , would theoretically be a pi XO above and along the MX chains (page 335) .

In any event , I hope to reveal more of the "secret life of pi bonds" as this report unfolds , and let the reader judge for himself . Of the three types of nodeless XOs that might be used by true metals , and therefore by superconductors , the pi XO seems to be the best candidate for application in high temperature superconductors . Delta XOs , while undoubtedly present in the transition metal elements , seem too exotic for inclusion in any new metallic solid designed and synthesized by conventional techniques . Sigma XOs , universally present in the metallurgical metals and their alloys , may be too large and diffuse for high T_c applications , and their omnidirectional geometry may actually inhibit the antiparallel alignment of the free electron spins required for the formation of Cooper pairs . Only the pi XOs may be optimal as the pathway for high temperature superconductivity . Their smaller , more compact shapes , and rectilinear geometry may prove to be just what we need as the best sort of metallic bond for any sort of superconductor candidate compound we can devise in the following pages .

Having discussed in a general sort of way the basic theories underpinning the bonding pictures I use in discussing the crystal and electronic structures of solid state lattice compounds in general, and metallic solids specifically, we can now turn to a brief look at a number of fascinating and informative chemical systems, and compounds, that contain metallic bonds. I have chosen each case study for its value in reviewing the concepts outlined above, and for revealing yet more interesting facets of the remarkably complex nature of the metallic bond. This review of a number of metallic solids will prepare us for the next challenging topic, the superconductors. Several Interesting Metallic Solids

<u>KCP</u>, $K_2Pt(CN)_4Br_{0.3}$. $3H_2O$

Partially oxidized coordination compounds of platinum(II) have been known since 1842-6, when the German chemist W. Knop (with G. Schneidermann) reported the preparation of highly colored platinum complexes . The first detailed investigation of the mixed-valent platinites , as their oxalate complexes , was carried out by the great Swiss researcher , Alfred Werner (sometimes called the "father of coordination chemistry") , in 1896 . He apparently was intrigued by their very dark solutions and metallic colors – usually coppery – and metallic luster as crystalline products . A more comprehensive study of a series of mixed-valent platinite complexes , including KCP , was undertaken in the late 1960s by another German researcher , K. Krogmann . He was able to determine the crystal structure of this general class of compounds , showing that they were composed of tall stacks of molecules , rather like wheels on an axle (ref. 30 , page 394) . The mixed-valent platinum(II) stack compounds are now often referred to as "Krogmann salts" in honor of the scientist who first unveiled their structure .

KCP is a crystalline material with a reddish, coppery color and a noticeable metallic luster. It can be prepared by the electrochemical oxidation of the $[Pt(CN)_4]^{2-}$ anion at the anode, a useful procedure ("electrocrystallization") for synthesizing the long, slender needles of product for subsequent electrical conductivity measurements; and it can also be made in a straightforward manner by first preparing a quantity of the corresponding platinum(IV) salt, $K_2Pt(CN)_4Br_2 - by$ oxidizing $K_2Pt(CN)_4$ with Br_2 in water solution – then mixing a quantity of this intermediate with more unoxidized $K_2Pt(CN)_4$, again in water (ref. 40, page 396).

I find this latter procedure interesting from the theoretical point of view, that in the dibromo intermediate, the platinum(IV) atoms are octahedrally coordinated by the four cyanides equatorially, and by the two bromides axially (Figure 15, next page); but when the mixed-valent stack compound crystallizes from solution, the metallic bond is strong enough to cause a displacement of the two bromide anions outside the stacks :



Figure 15 : The platinate(IV) intermediate , $K_2Pt(CN)_4Br_2$, in the synthesis of KCP by the aqueous addition method of Pt(II) and Pt(IV) salts . The aqua sphere is Pt(IV) ; the brown spheres are bromides ; the combination of gray (carbon) and blue (nitrogen) spheres are cyanide anions .

In KCP, the $Pt(CN)_4$ "poker chips" – as they are sometimes referred to – are stacked up to form vertical columns in the elongated crystals, the columns being aligned parallel to each other, with potassiums, bromides, and water molecules bonding the stacks together side-by-side. A metallic bond runs the length of the columns, joining together the platinum atoms like an axle running through the hubs of wheels (Figure 16, next page). To minimize steric repulsion between the equatorial cyanide ligands, they are rotated by 45° with respect to cyanides above and below them.

In the process of forming KCP crystals from a mixture of Pt(II) and Pt(IV) salts in a roughly 5:1 ratio, the resulting overall platinum oxidation state is averaged to 2.30+; this non-integral oxidation state (NIOS) is typical of Robin-Day Class IIIB mixed-valent compounds (page 52).



Figure 16 : The crystal structure of KCP (and generally, of related platinum stack compounds). Aqua spheres : Pt(2.30+); gray spheres are carbon, which with the blue nitrogens, form the cyanide ligands. The yellow spray paint connecting the platinums is the metallic bond – the $5d_z^2$ sigma XO – in KCP. For the sake of simplicity the interstack potassium cations, bromide anions, and water molecules of hydration have been omitted. Of course, the stacks of $Pt(CN)_4$ units are extended indefinitely in both vertical directions. For example, see Cox's Fig. 6.1(a), p. 167 in ref. 18, page 393.

I have placed KCP in Class 8 (page 58) of the metallic solids ; it has a direct temperature-conductivity relationship (Figure 17, next page), it has NIOS (mixed-valent) platinums, and it is a Robin-Day Class IIIB mixed-valent compound, meaning it has a direct metal-metal metallic bond excluding the spectator anions. KCP is one of the best known of the "synthetic metals" (also sometimes referred to as "synmets") or molecular metals. I prefer to use the former term for those metallic solids having metal atom cores complexed by ligands, and to reserve the latter term for compounds based

on nonmetal molecules, especially organic molecules. We could also reserve a third term, macromolecular (or polymeric) metals, for those metallic solids based on long chains of nonmetal atoms, both inorganic and organic in nature.

The ambient electrical conductivity of KCP is about 830 ohm⁻¹cm⁻¹, and it steadily declines as the material is cooled down toward absolute zero :



Figure 17 : Graph of the electrical conductivity of KCP versus its absolute temperature , showing their direct relationship . Note the logarithmic scale for the conductivity ; below about 60 K the conductivity of KCP crashes ! The data for this graph were taken from Zeller and Beck's Fig. 3 , p. 80 in ref. 41 (page 396) .

As can be readily imagined, KCP is anisotropic with respect to several of its physical properties. The electrical conductivity is about four orders of magnitude less when measured across the elongated crystals (that is, across their minor axes), compared to along the major axis of a needle-like pure crystal (see the Zeller and Beck reference 41, above). The light reflectance from the crystals is also a function of the viewing angle through an oriented polarized filter : metallic luster is observed when KCP is observed through the filter in one orientation, but not when the filter is rotated through 90°.

As mentioned on page 25, all five types of chemical bonds can be found in KCP, but the two most important ones in our case study are the coordinate covalent and the metallic bonds. The former type are used for the strong, low energy skeleton of the component molecules, while the metallic bond is really just an opportunistic "add-on" to the structure that connects the platinum atoms together.

Treating the compound in the VB manner , the core platinum(II) atoms have the 5d⁸ electronic configuration . They are square planar coordinated by the cyanide ligands , and so would use the dsp² hybrid AO to bond with them . The platinums' $5d_x^{2}{}_{-y}^{2}$ AOs have been taken for the hybrid AO , and the other four 5d native AOs on the platinums , each with a localized spin pair of electrons , have the energy level dispositions shown in the sketch at the bottom of page 81 : xz/yx , z² , then xy . Note that there is a relatively narrow energy gap separating the z² and xy AOs .

In unoxidized $K_2Pt(CN)_4$, there are no unpaired 5d AO electrons, and when some of the platinums – about one sixth of them, stoichiometrically – are oxidized by the bromine to platinum(IV), their electronic configuration changes to $5d_{xy}^2 \ 5d_{xz}^2 \ 5d_{yz}^2$, with their new octahedral coordination. When the mixture of Pt(II) and Pt(IV) salts crystallize from the water solution, the Pt(CN)₄ "poker chips" can approach each other closely and stack up into the columnar structure of KCP. The metallic bond spontaneously forms – at ambient temperature – and displaces the bromide anions from the Pt(IV) intermediate, $K_2Pt(CN)_4Br_2$.

The $5d_{xy}$ AO is fairly "flat", lying in the Pt-CN plane , while the $5d_z^2$ AO is

stereochemically quite prominent , sticking up well above the Pt-CN plane . As the Pt(CN)₄ units begin to stack up , it is the "tall" $5d_z^2$ AOs that interact with each other first , overlapping their positive symmetry sigma lobes continuously along the chain of platinum atoms (see the sketch at the bottom of page 82) . There is , by contrast , relatively little overlap of the $5d_{xy}$ AOs in adjoining platinums in the stacks :



Figure 18 : Overlapping of the platinum atoms' 5d native AOs, with their contained electrons, in the stacks of $Pt(CN)_4$ units in KCP. The $5d_z^2$ AOs are most stereochemically prominent above the Pt-CN plane, so they overlap most strongly to produce the metallic bond in the compound. This sketch was adapted from Miller and Epstein's Fig. 26, on p. 53 of their excellent review of synthetic and molecular metals (ref. 42, page 396).

The unoxidized K₂Pt(CN)₄ starting material provides Pt(II) with $5d_z^2$ AOs with two electrons, and the oxidized K₂Pt(CN)₄Br₂ provides Pt(IV) with similar AOs but without any electrons; or, if you prefer, two holes. Thus, in the continuous chain of overlapping $5d_z^2$ AOs, there are occasional vacancies. Since KCP is a Robin-Day Class IIIB mixed-valent compound,

the electrons in the $5d_z^2$ AOs , now forming a continuous sigma XO along the stacks , can hop back and forth into and out of these vacancies .

We can look at the XO in two ways : first , it can resemble the example of silicon discussed above on page 34 , except that with KCP the holes are produced in the XO chemically , by partial oxidation , rather than by thermal excitation , as with silicon . As the following sketch of the d_z^2 AO shows , there is definitely a node , located at the platinum atom's kernel , separating the two positive lobes of electron probability density :



This illustration was based on Figure 4.3 on p. 60 of Rodgers' textbook (ref. 36, page 395), which clearly shows the node at the atomic kernel.

Note that the $d_z^2 AO$ is actually somewhat like a hybrid orbital, being a linear combination of two more basic ("dependent") orbitals, the $d_z^2 d_{-x}^2$ and the $d_z^2 d_{-y}^2$. It thus has two rather voluminous sigma type lobes, of positive symmetry, that can overlap directly with other such positive lobes to form sigma MOs. Each of these new MOs in the chain will contain an electron pair, except at the platinum(IV) kernels, whose $5d_z^2 AOs$ are empty. These occasional empty MOs, acting as "holes" in the XO, permit the physical

flow of the 5d electrons, as particles, along the chain, which thereby acts as an electrical conductor. However, the periodic nodes at the platinum kernels will still impose an obstruction to the passage of the free electrons, and will make KCP a pseudometal. Since platinum is a heavy element, we would expect very narrow nodes – band gaps, in conventional terminology – at the platinum atoms, as is the general trend we looked at in Table 1 (page 35). KCP should therefore have a respectable ambient electrical conductivity, and it does, to a certain extent (but not as high as gray tin, for example).

The second way of looking at the XO in KCP is to regard the $Pt(CN)_4$ molecular units as "stepping stones" in a brook around which the free electrons flow like water under an applied potential difference (p.d.) across the ends of the crystal. The platinum atoms in these "stepping stones" would be uniformly in the tetravalent oxidation state, and all the electrons in the $5d_z^2$ AOs would be "crunched" in the Fermi distribution.

When KCP is cooled down toward absolute zero , it is found by x-ray diffraction that the Pt-Pt bond lengths begin to distort , that is , lengthen and shorten , in step with its declining electrical conductivity . This physical phenomenon is called Peierls distortion , after the British solid state physicist , Sir Rudolph E. Peierls , who first predicted such a distortion in one-dimensional electrical conductors ("Peierls's Theorem" , 1955) . The declining conductivity in KCP with falling temperature is usually attributed to Peierls distortion in the chains . However , the cause of the physical distortion and plummeting conductivity is the presence of the nodes at the platinum kernels ; Peierls distortion and its related physical changes are the effects , induced in the solid by deeply chilling it .

As KCP is cooled down, fewer and fewer of its sigma XO electrons have enough energy to cross the nodes – either by hopping or tunneling – as more and more of them fall below the Fermi level. With declining temperature the sigma XO looks more and more like a series of separate covalent MOs, containing localized valence electrons. As these formerly "free" electrons settle down onto their nearby platinum kernels, those platinums become recognizable as individual Pt(II) and Pt(IV) species, which have longer and shorter bond lengths to each other and the cyanide ligands . This is a random process , with a scattering of short and long bond lengths in the crystal . The metallic bond , with its associated electrical conductivity , gradually fades away in KCP , as it is cooled down and the mobile electrons in the XO become localized around their platinum kernels .

As KCP is warmed up , the reverse process occurs . More and more Pt(II) valence electrons rise above the Fermi level in the XO and can cross the nodes . These electrons become "blended" to form the NIOS valence of 2.30+ at higher temperatures as the individual Pt(II) and Pt(IV) cations lose their separate identities and become , in effect , Pt(IV) centers surrounded by a stream of mobile free electrons . The metallic bond is gradually restored to full functioning as the temperature of the solid rises , and its electrical conductivity rises accordingly .

These electronic processes in KCP with warming and cooling nicely illustrate the chemical phenomena of disproportionation and reproportionation . The former process occurs in a compound whose metal cations , having a uniform valence state , separate out into two different valences , one higher and the other lower than the original uniform valence . Usually when this happens the anion coordinations about the metal cations with the two different valences are different , also , leading to a change in the crystal structure of the compound whose cations are undergoing disproportionation . That's what happens with KCP , when it is cooled down toward absolute zero .

Reproportionation occurs when two different valence states of a metal cation (and sometimes, as we will see, a zerovalent metal atom) are "blended" together to form a single uniform valence state in the compound. This may happen internally, in a single compound (as with KCP), or externally, when two separate materials are reacted together to form a third, unique compound with the single "blended" valence state.

Reproportionation is an invaluable technique in the preparative chemistry of metallic solids . This is because compounds with "normal" valence state metal cations are often rather ordinary , electronically inactive insulators ,

while those with "abnormal" valence states , particularly NIOS valences (page 88) , have the "extra" valence electrons that are located in atomic orbitals capable of forming XOs , and metallic bonds , in the solids . The technique of reproportionation can be used to prepare the mixed-valence compounds of Classes 3 , 4 , 7 , and 8 (page 57) , and even some of the other unusual metallic solids with homovalent metal atoms , such as niobium(II) oxide , NbO .

In KCP we see the metallic bond appearing and strengthening with warming of the solid , as the individual Pt(II) and Pt(IV) valences are reproportioned into the uniform Pt(2.30+) NIOS valence . Cooling of the crystals induces in them disproportionation of Pt(2.30+) back into Pt(II) and Pt(IV), and as that occurs , the metallic bond shrinks and vanishes . The physical effect of Peierls distortion is thus intimately linked with the chemical effect of disproportionation .

It was originally thought – as expressed in Peierls's Theorem – that onedimensional metallic bonds (or bands) were inherently unstable, and underwent distortion into localized covalent bonds spontaneously. It is now recognized that Peierls distortion can readily occur in two and three dimensions in a crystal structure. For example, in his excellent textbook, <u>Inorganic Structural Chemistry</u> (ref. 23, page 394, his pp. 100-101), Müller discusses the crystal structures of several elements such as As, Sb, Bi, Se, and Te in terms of a three-dimensional Peierls distortion having occurred in a more symmetrical idealized form (the α -polonium structure) to produce the actual known structure of these elements in their solid state form.

The reader has undoubtedly heard the saying , "Nature abhors a vacuum"; to this we can certainly add , "Nature also abhors a metallic bond" ! Of course , Nature can do little to avoid a metallic bond in the metallurgical elements , that is , those with the simple atomic packings (bcc , hcp , and ccp/fcc) . In the other elements , and in the vast profusion of chemical compounds , though , Nature indeed strives mightily to avoid having a metallic bond in them . The result is a pronounced preference for covalent and ionic bonding in these substances . Let's take a very simple example , that of hydrogen , to illustrate this point .

Hydrogen, in its gaseous, liquid, and solid forms is preeminently a covalent, molecular compound. In 1935, E. Wigner (later more famous as a nuclear physicist) predicted that hydrogen, if compressed sufficiently, would become a metallic solid. His suggestion prompted considerable research into the ultrahigh pressure properties of hydrogen and other elements and compounds, but the enormous pressures required to force hydrogen into a metallic state eluded researchers for six decades.

However, in 1996 a team of physicists at the Lawrence Livermore National Laboratory in California, using a "shock wave" technique, inarguably produced the first (if tiny) sample of metallic hydrogen in their experimental setup (ref. 43, page 396). The sample was ephemeral in nature, and was synthesized from liquid hydrogen at 20 K under rather extreme conditions, 1.4 megabars pressure and 3000 K temperature, but it existed long enough to measure its electrical conductivity, which was 2000 ohm⁻¹cm⁻¹. This was comparable to the conductivity of rubidium and cesium under similar conditions.

The team leader , William J. Nellis , has written a very clear , concise report on their research with metallic hydrogen , which can be found online on his web site , at <u>http://www-phys.llnl.gov/H_Div/GG/Nellis.html</u> ; his report is titled , "Jumpin' Jupiter ! Metallic Hydrogen" . The Jupiter reference recalls the planetary science theory that the core of the planet Jupiter (and probably those of the other outer "gas giant" planets , Saturn , Uranus , and Neptune) is thought to be composed of very hot , supercompressed metallic hydrogen . The powerful magnetic fields around Jupiter might arise from this metallic core . In any case , I congratulate Dr. Nellis for his excellent presentation , clearly explaining the phenomenon of metallic hydrogen , and his research with it . His article is at the academic level of those published in , say , <u>Scientific American</u> and <u>American Scientist</u> magazines , and is fairly comprehensible to even a physics-deficient person like me . I wish other scientists would present their research work to the public , and to the world , in such a well-written and accessible style !

Near the end of Dr. Nellis's article, he mentions that, "Metallic solid hydrogen has been predicted to be a room-temperature superconductor"

I find this prediction rather surprising . Intuitively I would place hydrogen as an element , at least its solid , metallic allotrope , in the alkali metal family (group 1A) . As is well known , none of the alkali metals exhibits any sign of superconductivity , not even close to absolute zero . Why then should metallic hydrogen be superconducting under cryogenic conditions , let alone at room temperature ? I haven't read the original papers in this area , so I can't quantitatively justify my intuitive feelings in this matter ; let's say that for the time being , at least , I remain unconvinced by predictions of superconductivity for metallic hydrogen under any conditions .

Metallic hydrogen would seem to be an extremely unstable "pre-Peierls distortion" material . Suppose it was possible to isolate a small sample of it under ambient conditions for the briefest moment ; a three-dimensional Peierls distortion would instantly occur in the solid , with disproportionation of the free electrons in the 1s sigma XO into $1s^2$ sigma MOs . That is , the metallic solid would – literally ! – explode into diatomic hydrogen molecules as the metallic bond valence electrons "settle down" into the molecular covalent bonds .

Under ambient conditions, then, molecular hydrogen is vastly more thermodynamically stable than the metallic form, and there appears to be little if any kinetic barrier to the transformation of the metallic phase to one of the molecular phases. Compare this to the familiar diamond/graphite interconversion processes : diamond is thermodynamically less stable than graphite, but is kinetically inhibited from converting spontaneously to it under ambient conditions. Diamond can thus be considered as a metastable material, albeit an extraordinarily stable one under most conditions.

These sorts of considerations are important in the study of metallic solids, as the researcher wishing to prepare new candidate materials may be faced with the problem of the disproportionation of the desired new single metallic phase into two or more semi- or nonconducting phases. I think that metallic compounds should all be considered as metastable, a philosophy in accord with that of A.W. Sleight, who has commented on the subject in several papers (for example, see ref. 4, page 390). Chemists aiming to synthesize new metallic compounds should therefore give careful consideration to the

selection of a suitable crystal structure in which the free electrons of the metallic bond XO will exist in a stable configuration. This might be very much a trial-and error process, at least in early stages of the investigation.

I mentioned above on pages 55-58, for example, the fruitless attempts to prepare low-valent oxides and sulfides of aluminum, and how the novel hypothetical compound Al₃Cl might be both metallic and superconducting. Other examples comprise the Robin-Day Class I mixed-valent compounds in general. Gallium(I,III) chloride, with the empirical formula of GaCl₂, which was mentioned on pages 26-27, is a colorless insulating solid. Might it be possible to force the Ga(I) component – which has a 4s² inert pair of valence electrons – to reproportionate with the Ga(III) component (4s⁰) into "genuine" Ga(II), which is 4s¹ electronically? The crystal structure of the resulting "genuine" GaCl₂ might then resemble something like [I'm guessing here] the 8:4:4 fluorite structure :



Figure 19 : The crystal structure of fluorite , MX_2 . The mineral fluorite is calcium fluoride , CaF_2 (small red spheres represent calcium cations with an eight-fold square prism coordination ; the large green spheres represent fluoride anions with a four-fold tetrahedral coordination).

Quite possibly it is this high degree of coordination of the hypothetical Ga(II) cation that destabilizes the $4s^1$ free electrons in the crystal lattice, and so prevents the formation of GaCl₂ with a fluorite structure. Of all possible crystal structures for "GaCl₂", it would seem that only the Class I compound's atomic arrangement is thermodynamically stable enough to exist under ambient conditions.

In general , then , reproportionation can be considered as an invaluable preparative technique in the synthesis of new metallic compounds , provided the crystal container for the metallic bond is able to stabilize it . On the other hand , disproportionation must be regarded as being hostile to the formation of a stable metallic bond in a crystal structure , resulting in the localization of the free valence electrons on atomic kernels , and the production of semior nonconducting solids . A stabilizing crystal structure is thus a prerequisite for a stable metallic bond in the solid , and for the avoidance of disproportionation in it . Also , as we have seen with KCP , metallic compounds with nodal XOs will likely exhibit "reversible metallic bonds" ; that is , reproportionation and disproportionation will occur with a rise and fall , respectively , in the temperature of the material . Such reversibility will be avoided in those metallic bonds comprised of nodeless crystal orbitals .

To conclude this discussion of the many interesting aspects of KCP, I should note that many analogues and variations of the partially oxidized platinites have been synthesized by researchers worldwide. For example, there is a nice colored photograph of the compound $K_{1.75}Pt(CN)_{4.}1.5 H_2O$ in Epstein and Miller's review article of linear chain metallic compounds in <u>Scientific American</u> magazine (ref. 44, page 396), showing it as a cluster of brass-colored needles growing on the anode in an electrocrystallization cell. In this case the partial oxidation of the [Pt(CN)_4]²⁻ anions was accomplished by removing some spectator potassium cations from the reaction mixture.

When the potassium cations are removed from the system , an equal number of electrons must also be simultaneously removed in order to maintain the electrical neutrality of the system . The anode is the "oxidizing agent" in this particular electrocrystallization reaction , removing electrons from the TCP anions , converting some of them , in effect , into $[Pt(CN)_4]^0$ units . These latter zerovalent molecules form the base of the stack "poker chips" , with the unoxidized $[Pt(CN)_4]^2$ providing the free electrons forming the $5d_z^2$ sigma XO . The electrical neutrality of the $[Pt(CN)_4]^0$ base molecules allows them to stack closely together and so form relatively strong Pt-Pt bonds .

If this simple picture is correct, then it suggests that cognate stack compounds might be prepared using similar sorts of readily oxidizable anionic metal complexes. The anions would be oxidized on the anode surface to a formally zerovalent coordinate covalent molecule, which would then stack tightly with other such units blended in with the original, unoxidized anions. For example, how about using the lighter analogues of platinum, nickel and palladium, as their potassium tetracyano complexes, which are commercially available as the hydrated salts ?

At this point, redox chemistry must be referred to . The standard oxidation potentials for Ni(II), Pd(II), and Pt(II) are as follows (a more extensive Table of Oxidizers can be found on page 251 below) :

Ni(II) – e ⁻		Ni(III) ; $E^0 = -1.17 V$;
$Pd(II) - 2e^{-1}$		$Pd(IV)$; $E^0 = -1.288 V (Cl^{-} solution)$;
$Pt(II) - 2e^{-1}$	×	$Pt(IV)$; $E^0 = -0.68 V$ (Cl ⁻ solution).

The negative values of the oxidation potentials , E^0 , indicates that the divalent form of the elements concerned are of low energy , and that energy is required to oxidize them into their higher energy , higher-valent forms . We see that while it relatively easy to oxidize platinum to its higher valent form , it is much harder to do so for nickel and palladium . In fact , Ni(III) and Pd(IV) are fairly strong oxidizers . We might well find that any attempt to anodically oxidize $[Ni(CN)_4]^2$ and $[Pd(CN)_4]^2$ will in practice merely destroy them , or cause unwanted side-reactions with the solvent .

Another concern with the lighter analogues , nickel and palladium , is that their $3d_z^2$ and $4d_z^2$ AOs , respectively , may be physically too small to provide sufficient overlap for the formation of the required strong metalmetal bonds in the stacks . Nevertheless , there are several interesting systems that might be investigated with respect to possibly forming stack compounds with a metallic bond . Williams and Schultz (ref. 45 , page 396) in their Table 1 , p. 339 of the book <u>Molecular Metals</u> , provide examples of "Metals with Accessible d⁸ Electron Configurations" ; the 3d⁸ series are : Fe(0) , Co(I) , Ni(II) , and Cu(III) . We have already looked at Ni(II) and have found that the corresponding Ni(III) was too strong an oxidizer to be supported by coordinate covalent ligands (probably) . Trivalent copper is even worse ; it is the most powerful metal-based oxidizer known , with $E^0 = -2.4 \text{ V}$, and so is completely impractical for use in this application .

Zerovalent iron and univalent cobalt , however , are both chemically reducing in nature , and so might be amenable to anodic oxidation in an electrocrystallization cell . The chemical source of Fe(0) might be the oily orange liquid , pentacarbonyl iron(0) , Fe(CO)₅ , b.p. 103 °C . This is known to be a fluxional compound , with its molecular structure oscillating back and forth very rapidly from a square pyramid (iron atoms having a $d_x^2 g^2 g^3$ VB hybrid AO) to a trigonal bipyramid ($d_z^2 gp^3$) coordination ; refer to Rodgers' textbook , pp. 45-47 , ref. 36 , page 395 . That is , we can assume that the two valence electrons , $3d^{7,8}$, are very labile and also rapidly oscillate between the $x^2 g^2$ and $z^2 AOs$, being displaced by the fifth carbon monoxide ligand .

The question is , can the fifth CO ligand be entirely displaced in the electrocrystallization process , leaving a square planar assembly of $Fe(CO)_4$ molecular units neatly stacked up , with Fe-Fe bonds , forming nice shiny acicular crystals on the anode ? The reason that $Fe(CO)_5$ has that annoying fifth CO ligand , by the way , instead of the more convenient four CO ligands in a square planar configuration – which it **could** , but doesn't have – is that the iron atom has a total of twenty-six electrons in its shells , and by gaining ten more [two each from five CO ligands] , it will attain the blissful nirvana of krypton's inertness , with thirty-six electrons in all .

On a practical note, iron pentacarbonyl is a neutral molecule and not an anion, so it wouldn't be electrostatically drawn to the anode like anions are. Instead, we would hope that simply the physical impact on the anode of the carbonyl molecules, bouncing around in solution, would cause them to be oxidized on its surface. In this picture, warming the reaction solution, and rapidly stirring the anolyte, might be helpful in pushing the reaction forward and promoting the growth of metallic needles of product on the anode.

Another neat trick that has been used in the crystallization of acicular solids from solution was described by Sugihara and Newman (ref. 46, page 396). In their technique, a surfactant, specifically a detergent, was added to the reaction solution in very low concentrations. This surface-active agent tended to adsorb on the sides of the growing crystals, inhibiting their growth outward, but not on their ends, permitting length-wise growth, that is, elongation of the crystal. Apparently such "crystal habit modifiers" are well known, and can have striking effects in altering the growth patterns of solids crystallizing from solution. It might be possible to incorporate low concentrations of organic-soluble detergents in the anolyte with the iron pentacarbonyl reactant, to try to promote the growth of long, thin needles of stack compound, which are greatly sought-after, essential even, for electrical conductivity measurements on the material.

One worrisome problem with iron pentacarbonyl is that some of its neutral molecules will be oxidized at the anode to $[Fe(CO)_4]^{1+}$, which will be accompanied by an inert spectator anion from the reaction solution, such as BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , etc. (this assumes that the fifth CO ligand has indeed been displaced from the pentacarbonyl molecule). We hope that these cations will co-crystallize with neutral square planar Fe(CO)₄ units to form the molecular stack compound. Note carefully, though, that this time it will be the cation, $[Fe(CO)_4]^{1+}$ that will be the base stack unit. Since the positively charged units will tend to electrostatically repel one another, the Fe-Fe separation may be too great to permit strong enough metal-metal bonds to form. There is also the smaller $3d_z^2$ AO in iron to contend with as well, compared to the larger $5d_z^2$ AOs in KCP.

I wonder if it would be possible to react equimolar quantities of iron pentacarbonyl and cyanide anion, the latter in the form of a salt that is soluble in organic media (possibly the lithium or tetraethylammonium salt), which would form the desired anionic substrate :

 $Fe(CO)_5 + Li^+CN^- \longrightarrow Li^+ [Fe(CO)_4CN]^- + CO(g);$

This latter intermediate salt would be subjected to electrocrystallization in the anolyte of an electrolysis cell , with (say) LiPF₆ as an electrolyte , and using a highly polar , inert solvent such as propylene carbonate as the reaction medium . This time , the cyano-carbonyl anion would be drawn to the anode , some of it being oxidized to the "zerovalent" molecule , $[Fe(CO)_4CN]^0$. Assuming that formation of the $3d_z^2$ sigma XO Fe-Fe metallic bond is forceful enough to displace another carbon monoxide molecule – recall that such a ligand displacement occurred with the platinate intermediate $K_2Pt(CN)_4Br_2$ [page 88] – the blend of the two types of precursor molecules , $[Fe(CO)_3CN]^{0,-1}$, should produce the desired stack compound with the Fe-Fe metallic bond having the empirical formula , $(Li^+)_x$ [Fe(CO)₃CN]^{x-} , where x is a mole fraction between zero and unity . This time , the base of the stack molecules is zerovalent , which should permit their close approach to each other and hopefully create a strong Fe-Fe metallic bond .

The molecule $[Fe(CO)_3CN]^0$ would actually be a neutral free radical , with the singlet $3d^7$ electron localized in the $3d_z^2$ AO . In the corresponding anion this AO would be occupied by a spin pair of electrons , $3d^{7,8}$. Continuous overlapping of the $3d_z^2$ AOs in the stack compound should thus produce a partially occupied sigma XO in the molecular chains , which could act as their metallic bond . I assume that the $3d_z^2$ AOs are voluminous enough to overlap successfully in this hypothetical iron-based synthetic metal .

If the above experiments were successful with iron pentacarbonyl, would it be possible to synthesize a comparable stack compound from **tetracarbonyl nickel(0)**, Ni(CO)₄? This is a volatile (b.p. 43 °C), very toxic liquid reagent – I would be loathe to recommend it to researchers because of its hazardous nature – that is commercially available, and indeed has found

many uses in research and industry . The nickel(0) in this compound is $3d^{10}$ electronically, and uses the (4)sp³ VB hybrid AO, with a tetrahedral coordination of the CO ligands about the nickel atom. It might well be possible to oxidize nickel tetracarbonyl anodically, removing the 3d¹⁰ electron from one of the protruding $3d_{xy,xz,yz}$ AOs , which are of higher energy level than the x^2-y^2 and z^2 AOs in a tetrahedral coordination environment. However, the resulting cationic molecule still wouldn't be able to form the square planar structure required for stacking, because the $3d_{x}^{2} g^{2}$ AO contains a spin pair of inner valence electrons. That is, the square planar hybrid AO, $d_{x}^{2} g^{2} g^{2}$, couldn't form with either nickel tetracarbonyl or its oxidized cation . I doubt that the tetrahedral base cations and parent molecules would be able to stack together to form the required molecular chains. The same considerations would apply to any anionic derivative of nickel tetracarbonyl, ruling out that approach as well. In all cases the nickel atoms' 3d¹⁰ electronic configuration results in the occupancy of their $3d_{x-y}^{2-2}$ AOs by a pair of electrons. Thus blocked, no square planar hybrid AO can form, so no stack compound can be prepared from nickel(0) precursors having a square planar coordination by four ligands. However, if a CO ligand could be displaced from Ni(CO)₄, a stack compound might be electrocrystallized from the sp^2 trigonal planar Ni(CO)₃ molecules . See Note 11, page 389.

KCP, its analogs, and related hypothetical stack compounds have been highly educational in our study of the metallic bond in solids. We'll now look at a couple of synthetic metals in which the metallic bond is more three-dimensional in nature than the highly anisotropic one in KCP.

Alchemist's Gold, Hg₃AsF₆

Calomel has been known since the time of the medieval alchemists . It has the formula Hg_2Cl_2 , and is a white , water-insoluble solid . The mercury atoms in calomel are bonded together in pairs by a simple Hg-Hg covalent bond to form mercurous cations , $[Hg_2]^{2+}$. This 6s² sigma bond somewhat resembles a bloated 1s² sigma bond in the hydrogen molecule . Calomel is

an example of a simple compound whose metal atoms are bonded with a metal-metal covalent bond.

A mercury-based synthetic metal with a metallic bond has been prepared and characterized . This was the remarkable compound poetically called "Alchemist's Gold" by its discoverers . In 1974 R.J. Gillespie and coworkers described their preparation of Alchemist's Gold by the partial oxidation of mercury with AsF_5 in liquid sulfur dioxide (an inert , nonaqueous solvent) . The reaction product was described by them (ref. 47 , page 397) as a "golden , crystalline mass" , and the gleeful chemists , with tongue in cheek , pretended that they had transmuted the base metal , mercury , into the noble metal gold , which of course was long an elusive goal of the alchemists .

Crystallographic analysis revealed that Alchemist's Gold was constructed with long linear chains of mercury atoms, overlaid in alternating parallel layers, the AsF_6 spectator anions nesting in between the mercury layers:



Figure 20 : Alchemist's Gold . The aqua spheres are mercury atoms , and the small red spheres are arsenic atoms , which are combined with the green spheres (fluorine) to form the octahedral AsF_6 anions . This M3D model

was based on Fig. 3, p. 648, ref. 47, page 397 (A.J. Schultz et al.).

The empirical formula of Alchemist's Gold has been given as $Hg_{2.86}AsF_6$ by its discoverers (Brown et al. in ref. 47), or more simply as Hg_3AsF_6 (Schultz et al., also cited in ref. 47). Assuming the latter composition for the sake of simplicity, we see that it is a Robin-Day Class IIIB mixed-valent compound with a NIOS valence state for the mercury atoms of 0.33^+ , and with a direct Hg-Hg metallic bond.

The ambient electrical conductivity of Alchemist's Gold , 8000 ohm⁻¹cm⁻¹ , is somewhat less than that of the parent elementary mercury (10,400 ohm⁻¹cm⁻¹) , but it rises to about ten million ohm⁻¹cm⁻¹ at 4.2 K . Then , like mercury , it becomes superconducting at 4.1 K . The Hg-Hg bond lengths in the compound are 2.64 Å (versus 3.005 Å in frozen mercury and 2.50 Å in the mercurous cation) , and the Hg-Hg interchain distance is 3.24 Å . It has been suggested that the electrical conductivity in the material is really three dimensional in nature , and not one dimensional , as implied by the chain structure . Alchemist's Gold is thereby able to avoid the fate of Peierls distortion . As we have seen with KCP , this argument is misleading , since Peierls distortion may occur in linear chain (and maybe other) structures with nodal metallic bond XOs – pseudometals – but never in materials with nodeless XOs , whatever the dimensionality of their metallic bonds .

Clearly, Alchemist's Gold is a true metal, and as a Robin-Day Class IIIB mixed-valent compound it is placed in Class 4 (page 57) of the metallic solids. The base of the metal atom chains consists of mercury(I) cations, which are 5d¹⁰ 6s¹ electronically. The linear structure of the chains hints at a possible underlying covalent bond network in them, and the true metal nature of the material implies it has a nodeless XO as the metallic bond. We know that mercury has a pronounced s orbital type of chemistry; this was alluded to earlier on page 84. We also know that mercury shows a distinct preference for a linear type of coordination by ligands. The 5d and 6s-p energy levels overlap in the heavy elements such as mercury (Figure 4, page 35), and the linear dp hybrid orbital, from the combination of the

 $5d_z^2$ and $6p_z$ native orbitals , might form the Hg-Hg covalent bonds along the chains :



The 6s orbitals $(6s^2 \text{ for Hg}^0, \text{ and } 6s^1 \text{ for Hg}^{1+})$ then overlap continuously along the chains to form a nodeless sigma XO over them, incompletely filled with valence electrons, which is the metallic bond in the compound.

Alchemist's Gold has been observed to disproportionate to Hg^0 and $Hg(AsF_6)_2$ around 4.1 K, at which point the mercury component becomes superconducting. This disproportionation may be the result of purely mechanical causes, perhaps by stress forces acting on the mercury chains as the extreme cold causes them to shrink around the AsF_6^- anions. The lattice then rearranges into entirely new phases in which the stress has been either reduced or eliminated altogether.

Silver Subfluoride , Ag_2F

Another example of a synthetic metal is silver subfluoride , Ag_2F , which seems to have been first prepared electrolytically by a German chemist , A. Hettich , in 1928 (ref. 48 , page 397) . It can also be synthesized even more simply by a direct combination of Ag^0 and AgF; reproportionation of Ag(0)and Ag(1+) yields the NIOS valence of 0.5+ for silver in the compound .

Silver subfluoride has been described as a very hard, crystalline material, brass-colored with a greenish cast and a metallic luster. Its ambient electrical conductivity is 42,000 ohm⁻¹cm⁻¹ (that of pure silver, by comparison, is 618,430 ohm⁻¹cm⁻¹ at 298 K, the highest of any of the metallurgical metals). It becomes superconducting at 0.058 K.
Silver subfluoride was found to have the anti-cadmium iodide crystal structure :



Figure 21 : The M3D crystal structure of silver subfluoride . The aqua spheres are silver(0.5+) cations , and the smaller green spheres are fluoride anions . These Ag-F-Ag layers extend indefinitely in the horizontal plane , and are stacked up in layers in the vertical direction . This structure was based on that shown in Fig. 1.31 , p. 27 of Smart and Moore's nice solid state chemistry textbook (ref. 49 , page 397) .

The silver atoms in the compound are separated by a distance of 2.86 Å, comparable to the Ag-Ag length of 2.89 Å in elementary silver . Although it seems as though there is a distinct layering of the Ag-F-Ag "sandwiches" in the crystal, silver subfluoride isn't at all flaky like graphite. Rather, it has been described as being very hard, and was found to be quite difficult to grind to a powder in a mortar with a pestle.

We can see in the M3D structure above that the fluorides are octahedrally coordinated by the silver atoms , and that the silver atoms have a trigonal pyramid coordination to the fluorides . The fluoride anions , with their $2s^2 2p^6$ configuration , probably can't form a proper octahedral VB hybrid AO (with the same argument used in the case of the oxide anion earlier on page 66 above) , so the underlying skeletal bonding must be ionic in nature . In the case of the silver atoms , their trigonal pyramid coordination results in them having a "p³ equivalent VB hybrid AO" ; that is , their $5p_{x,y,z}$ AOs are

energetically destabilized by the fluorides , and are "knocked out of action" by them . The $5s^1$ and $5s^0$ AOs on the (formally) Ag(0) and Ag(1+) atoms , respectively , can overlap continuously over the layers of silver atoms to form the nodeless 5s sigma XO that is likely the metallic bond in silver subfluoride . The material is thus a Robin-Day Class IIIB mixed-valent compound , and being a true metal has been placed in Class 4 of the metallic solids categories .

While silver subfluoride itself is of limited interest, it does give us an intriguing idea about how possibly to prepare a new type of layered metallic solid. We note that the 5p AOs in the silver atoms are "used up" by coordination to the fluorides, although in this case no coordinate covalent bonds are formed; the skeletal bonding is ionic in nature. However, in the "inverse" type of crystal structure, the cadmium iodide and related types of structures, anions are in the place of the silvers.

For example, in cadmium iodide we can picture the cadmium cations, which can likely form empty octahedral VB hybrid AOs (sp^3d^2) , receiving charge in coordinate covalent bonding from the iodides' anions, whose $5p^6$ orbitals are hybridized together to form the trigonal pyramid p^3 AOs. Those electrons won't be available to external oxidizers. However, the iodides' $5s^2$ electrons aren't used in any bonding, and in their voluminous spherical orbitals should be readily accessible to oxidizers.

We might try to very gently oxidize cadmium iodide , using a suitable oneelectron oxidizer , depositing an inert anion in between the iodide layers . Such an oxidizer might be one or other of the commercially available salts of the nitrosonium cation , NO⁺ (with inert spectator anions such as BF₄⁻, PF₆⁻, AsF₆⁻, or SbF₆⁻). Nitrosonium cation is a fairly powerful oxidizer , having a standard reduction potential of $E^0 = 1.45$ V at STP (the standard oxidation potential of iodide is -0.5355 V). A gentle , low temperature , one-electron oxidation of iodide is preferred , so as not to eject molecular iodine from the crystal structure . That is , we would want to convert some of the I⁻ to I⁰ , but leave the layered structure intact . The inert spectator anion would be lodged in between the iodine layers ; a homely analogy would be putting out the trash in garbage cans in the alleyway behind the house . A typical example of this reaction would proceed – we hope, with fingers crossed – as follows (with tetrafluoborate as a spectator anion) :

 $CdI_2 + x NO^+BF_4^- \longrightarrow Cd(I^0)_x(I^{1-})_{2-x}(BF_4^-)_x + x NO(g).$

Here "x" represents a mole fraction taken experimentally between zero and two, although in practice it would likely be rather low; I'm guessing not greater than 0.25, since at higher values we would likely just be carrying out a sort of metathesis reaction:

 $CdI_2 + 2 NO^+BF_4^- \longrightarrow Cd(BF_4)_2 + I_2 + 2 NO(g).$

An inert reaction solvent would be invaluable for this reaction, but given the powerful oxidation potential of the nitrosonium cation, it would have to be investigated very cautiously and at ambient temperature or lower. One highly effective solvent that could be examined in this context is propylene carbonate (PC), which has a remarkably high dielectric constant and dipole moment, and is known to be capable of dissolving even inorganic salts to a certain extent. PC has found some use as a reaction solvent in electrochemistry research (ref. 50, page 397).

Another family of layered materials that might be examined as potential substrates for new metallic solids are the flaky transition metal dichalcogenides . The relatively inexpensive industrial lubricant molybdenum disulfide , MoS_2 , which physically resembles graphite somewhat , comes to mind immediately . So does the related material titanium disulfide , TiS_2 , which has been much investigated in the past decade or so for its ability to intercalate metal atoms such as lithium and molecular species such as pyridine . These dichalcogenides – mostly disulfides – have a crystal structure which is either that of cadmium iodide , or closely related to it . As such , the sulfide anions' $3p^6$ electrons are expected to be engaged in coordinate covalent bonding to the metal atoms , leaving their exposed $3s^2$ electrons ready for potential oxidation .

These CdI_2 and related layered structures are interesting from the theoretical point of view of creating a metallic bond in the anion , rather than in the

cation layer of the solid . These are like Robin-Day mixed-valent compounds , but with the mixed valency derived from zerovalent and polyvalent anions . We start with a fully occupied sigma XO , then we chemically create vacancies in it so as to permit electron flow in the XO . What effect , if any , would that have on the properties , such as electrical conductivity , of the partially oxidized substrate ? Would one-electron oxidation of the iodide or sulfide anions result only in ejection of iodine or sulfur , respectively , from the substrate ? It should be possible for the nitrosonium salt oxidizer to penetrate the flaky layers of the dichalcogenide substrates , but would it be able to pry apart the iodide layers in CdI₂ , for example ?

Poly(sulfur nitride) [PSN, poly(thiazyl), (SN)_x]

That the metallic bond is a very general sort of chemical bond, appearing in a wide variety of different materials, is illustrated by the macromolecular, or polymeric compound poly(sulfur nitride), $(SN)_x$, also known as poly(thiazyl). It will be convenient to abbreviate its name to PSN.

Poly(sulfur nitride) was discovered serendipitously in 1910 by the English chemist F.P. Burt, who was attempting to vacuum sublime, and so purify, a sample of the rather unstable compound tetrasulfur tetranitride, S_4N_4 . PSN consists of elongated crystals with a golden color and metallic luster when viewed from above, or dark blue when the ends of the crystals are observed. They are somewhat soft and malleable, and can be rolled into thin sheets. When left out exposed to the air and humidity, PSN crystals tarnish and become dull like conventional base metals. The ambient electrical conductivity of very pure, well-formed PSN crystals is about 4000 ohm⁻¹cm⁻¹, and the compound becomes superconducting at 0.26 K. PSN can react with one-electron oxidizers such as bromine to form black "salts" that are also highly conductive (ref. 51, page 398).

X-ray diffraction studies showed that the crystal structure of PSN consists

of long chains of alternating sulfur and nitrogen atoms in a crenellated , or "all-Z" pattern :



Note that in this "organic chemistry" representation of $(SN)_x$, the sulfur atoms are formally shown as alternating sulfur(II) [sulfide] and sulfur(IV) [sulfurane] species . In practice , however , pi electron resonance occurs spontaneously in the chains , so that a pattern of alternating pi bonds is established along them . When this happens , the "sixth" valence electron on the sulfur atoms is forced out of its $3p^6$ orbital , and up into a higher energy level frontier orbital :



In this scheme, the sulfur and nitrogen atoms have the same sort of VB hybrid AO, namely trigonal planar sp² (as the nitrogen atom in the pyridine molecule has, for example). This hybrid AO will normally be able to hold five valence electrons ($\sigma_a^{\ 1} \sigma_b^{\ 1} \sigma_{lp}^{\ 2} \pi^1$) per atom, which is fine for the nitrogens, but not so good for the sulfurs, which of course have six valence electrons. Where can the "sixth" sulfur electron go when it is forced out of the sp² structure ?

I believe , without being able to present any sort of mathematical proof , that the sulfur $3p^6$ "extra" , or "leftover" electron is promoted up , energetically speaking , into the 4 s-p AOs (mostly the 4s AO , probably) . MacDiarmid et al. (cited in ref. 51 , page 398) have proposed that the extra electrons go into the 3p pi* ABMO above the S-N monomeric units , by analogy with the extra electron (from the oxygen atom) in the nitric oxide molecule , NO .

A sketch of a pi* ABMO (also shown on page 51) clearly reveals the nodal nature of this orbital :



If this sort of orbital was used to bond PSN, it would have to be a pseudometal, according to Krebs's Theorem (page 30). It is actually a true metal, and a superconductor, albeit close to absolute zero. Therefore, we should look for a nodeless XO to function as the metallic bond in poly(sulfur nitride). Apart from the pi* ABMO, two other possibilities for the extra electron location are the 3d AOs and the 4s-p AOs. The d AOs aren't very prominent in sulfur, a post-transition element, and are an unlikely destination for the sixth electrons. That leaves the 4s-p orbitals as their probable site.

Actually, the 3p pi* ABMO and the 4s-p AOs may be at roughly the same energy level in poly(sulfur nitride), with the possibility of electron resonance between the two sites . However, the 4s-p AOs will permit the formation of a stabilizing XO (mostly 4s sigma), acting as the metallic bond in PSN, whereas location of the extra electrons in the pi* ABMO will produce a destabilizing ABXO along the polymer spine, resulting in a sort of "metallic anti-bond". Clearly, under normal circumstances, the stabilizing 4s sigma XO will be preferred to the destabilizing 3p pi* ABXO in PSN; after all, the compound exists, doesn't it? In fact, PSN is a rather unstable material. It sublimes in vacuo at about 135 °C, and explodes in air at around 240 °C (strong mechanical compression will also cause PSN to detonate). This thermal and mechanical lability might be caused by a ready transfer of valence electrons from the bonding orbitals to their corresponding antibonding orbitals (for example, 4s to 3p pi*). The underlying valence electrons in the skeletal sigma and pi bonds might also drift into antibonding orbitals as the compound is heated up. When enough electrons have been transferred to the ABMOs, the internal vibrations would overcome the stabilizing effect of the remaining chemical bonds; then the molecule would disintegrate with great force.

Possibly a similar scenario occurs in the process of the boiling of liquids . For example, mercury boils at 357 °C. In the liquid phase it could be held together by a weak 6s sigma XO metallic bond. As the liquid becomes hotter and hotter, the 6s valence electrons are promoted more and more into the 6s sigma* ABXO. The point is reached where the ABXO destabilization is stronger than the XO stabilization, and the mercury atoms fly away into vapor.

On Figure 4, page 35, we note the large gap between the 2 s-p energy levels (of the nitrogen links) and the 4s level of the sigma XO above the sulfur atoms . A free electron in the 4s XO will therefore tend to be strongly destabilized as it "passes over" the nitrogen links . As a result, it will avoid them and remain over the sulfur atoms . That is, the 4s sigma AOs will likely overlap with each other only from sulfur to sulfur atom, ignoring the nitrogen links . PSN is really a form of metallic sulfur , with electronically inert nitrogen atom linkages .

The sulfur-sulfur bond lengths in PSN are a uniform 2.76 Å (Labes , Love , and Nichols , cited in ref. 51 , page 398) . Assuming that the sulfurs' 4s AOs have a covalent radius of 1.96 Å – similar to that of the potassium atom , whose valence electron is also $4s^1$ – we can readily calculate the length of the overlap of the 4s AOs along the sulfur-sulfur axes to be 1.16 Å , or 42% of the S-S bond length . If we assume the larger value for the metallic radius of 2.35 Å (also for potassium) , then the overlap length of the 4s AOs will be

substantially greater , 1.94 Å , or 70% of the S-S bond length . Either way , there should be enough overlap of the 4s AOs over the sulfurs to produce a reasonably strong 4s sigma XO along the $(SN)_x$ polymer chains . This will be nodeless , and would be satisfactory as the metallic bond in PSN . The physical and chemical properties of PSN (softness , malleability , rapid tarnishing) outlined above on page 112 are also consistent with a 4s¹ electronic configuration for poly(sulfur nitride) . As a minor quibble , it would be more accurate to refer to PSN as poly(sulfur imide) , since the word "nitride" usually connotates the ionic N³⁻ species , which is definitely not found in PSN .

Several Molecular Metals

Charge transfer compounds have been known for a long time in organic chemistry . I recall in a college chemistry course preparing adducts of several aromatic hydrocarbons, such as napthalene and anthracene, as charge transfer compounds with electrophiles like 1,3,5-trinitrobenzene and picric acid (2,4,6-trinitrophenol). These addition products were highly colored, nicely crystalline solids with sharp melting points, suitable for identifying the unknown hydrocarbon compounds.

There apparently is some argument about how – and how much – charge is transferred from the nucleophilic hydrocarbon molecules to the electrophilic nitro compounds in these derivatives . Perhaps there is an electron resonance between the two species , with the resonance slightly favoring , and shifted toward , the electrophile . The adduct crystals are made up of long columns of molecules , with alternating A and B molecules in the stacks .

By using acceptor and donor molecules which are genuinely oxidizing and reducing, respectively, we can observe a net transfer of electrons from the reducer molecules to the oxidizer molecules, just as we see in inorganic redox ions. The "zerovalent" organic molecules in these cases will be subsequently converted into radical anions and cations, respectively, and will form crystalline stack compounds in the solid state. Some of these stack

compounds were observed to be modest electrical conductors , which was considered quite remarkable for organic substances . Of course , the reader will be comfortable by now with the concept of the universality of the metallic bond in a wide array of compounds and materials , so the discovery of a metallic bond in molecular solids should not come as too big of a surprise .

The new electrically conducting charge transfer compounds were different from the more "ordinary", familiar insulating ones. While the insulating adducts were brightly colored and had alternating molecules in their stacks, the new conductive ones had a shiny, black appearance and – as was shown by X-ray crystallography – had all similar molecules in each stack ("self" stacks); that is, there were columns of electron donors and columns of separate electron acceptors in the crystalline solids.

In 1973 the remarkable molecular metal TTF-TCNQ was synthesized from the combination of equimolar quantities of the two precursor reagents , TTF (tetrathiofulvalene , the electron donor , or reducer) , and TCNQ (7,7,8,8tetracyano-p-quinodimethane , the electron acceptor , or oxidizer) . Its component molecules were found to be self-stacking , and the compound had an extraordinary electrical conductivity behavior : it peaked at about 9000 ohm⁻¹cm⁻¹ near 58 K , but when cooled further toward absolute zero the conductivity "crashed" and the material became almost insulating (ref. 52 , page 398 ; see also Miller and Epstein's article , "Linear-Chain Conductors" , ref. 44 , page 396 , pp. 57 and 59) . It is interesting to note that above 58 K TTF-TCNQ behaves like a true metal , with an inverse conductivity-temperature relationship , but below this Mott transition temperature , the compound has the direct relationship characteristic of a pseudometal .

It was found that , although TTF-TCNQ is indeed composed of equal numbers of TTF and TCNQ molecules , not all the charge was transferred from TTF to TCNQ ; to be precise , only 59% of the available valence electrons in TTF were transferred . That is , the compound's formula could realistically (if awkwardly) be written as :

TTF⁰_{0.41}TTF¹⁺_{0.59}TCNQ⁰_{0.41}TCNQ¹⁻_{0.59}

The driving force behind the electron transfer from TTF to TCNQ is thought to be the aromatization of the "zerovalent" precursor reagents :



In the TTF case, there are seven valence electrons available to the pi cloud system in each ring [3 x carbon $2\pi + 4$ x sulfur 3σ (lone pairs)]. Transfer of one of these electrons to TCNQ, or another acceptor, will leave six pi type electrons in one of the rings. The very stable aromatic pi cloud can now form over that TTF ring. However, resonance between the TTF¹⁺ ring and the TTF⁰ ring can occur, with the second ring also becoming aromatic. When that happens, the "seventh" electron gets pushed out of the pi system

and into an outer frontier orbital . Again , as with poly(sulfur nitride) , I believe that this outer orbital is the 4s AO , with maybe a small contribution from the 4p AOs . It seems that TTF can promote only one of its seventh valence electrons to the 4s AO , and not two , as in the zerovalent molecule . Promotion of this extra electron can thus occur only when the second seventh electron is transferred to the acceptor molecule or oxidizer . That is , the 4s AO will readily accept one promoted electron , but will resist receiving a second one . We see this same reluctance on the part of s AOs in the divalent metals such as magnesium , zinc , and so on , where there is significant leakage of ns^2 AO electrons into adjacent np AOs , to form the familiar "s-p conduction band" .

When TCNQ accepts an electron from TTF, it also becomes electronically aromatic, changing from its quinone ring to the stabler benzene ring. The three radical anion electrons are delocalized by resonance over the entire molecule.

When the seventh sulfur electrons in the TTF^{1+} radical cations are boosted up into the 4s AOs – according to this orbital picture of the metallic bond in molecular stack metals – the orbitals are now half-occupied by valence electrons, and as they overlap in the stacks a 4s sigma XO can form along the stacks which (I believe) is the metallic bond in these compounds. It is because of this metallic bond that the TTF molecules are self-stacking in the crystals, and aren't alternating with TCNQ molecules in them.

We can also readily see why a full exchange of TTF valence electrons to TCNQ doesn't occur . If it did , all the TTF molecules would be TTF¹⁺ radical cations , which would strongly repel each other and weaken the 4s AO overlap to the point of rupturing the metallic bond . To dilute down the destabilizing coulombic force , "zerovalent" , electrically neutral TTF molecules are intercalated here and there in the stack until the stabilizing force of the metallic bond balances and exceeds it somewhat . The result is a non-integral redox state of the TTF and TCNQ molecules in the compound . By the same token , there are also a similar number of neutral TCNQ molecules in the acceptor stacks . It seems that crystallization of the compound TTF-TCNQ from its precursor reagents must be a delicate

balancing act of several opposing forces in the stacks (coulombic , metallic , van der Waals), with the final architecture of the molecular structure – in this case a "herringbone" pattern [see the nice sketch in Epstein and Miller's <u>Scientific American</u> article, "Linear-Chain Conductors", p. 57, ref. 44, page 396] – a compromise between them .

We would expect that because the metallic bond in TTF-TCNQ is the nodeless 4s sigma XO, the compound should be a true metal all the way down to absolute zero. Why then does its conductivity crash below 58 K? If anything, the metallic bond usually strengthens with cooling !

The source of the problem may be the neutral , "zerovalent" molecules that must be intercalated between the TTF^{1+} cations and $TCNQ^{1-}$ anions in order to "dilute down" the destabilizing coulombic charges , and so permit the XO to form along the stacks . It has been suggested that a wave of aromaticity passes along the stacks – both TTF and TCNQ – when they are conducting an electric current (ref. 53 , page 398) . The two types of molecules are behaving like Robin-Day Class IIIB mixed-valent compounds with a facile transfer of valence electrons between the "zerovalent" parent molecules and their corresponding univalent radical cations and anions . Moreover , the waves are synchronized , so that a TTF wave will be matched by a TCNQ wave . In this way , the anionic and cationic charges on adjacent molecules will be exactly balanced .

In TTF the "extra" electrons from the TTF⁰ molecules will be accommodated and transferred in the 4s sigma XO without any problem . In TCNQ molecules , however , only their outer 2p pi clouds can overlap in the solid to provide a weak nodal XO , which can permit the passage of the aromatic wave . Of course , we know from our experience with KCP what happens to the metallic bond based on a nodal XO when it is cooled down : it fades away , with disproportionation of the NIOS valence into the two component valences , and localization of free electrons on parent kernels . This is likely what happens in the TCNQ stacks below 58 K . And when the aromatic wave is frozen in the TCNQ stacks , it also freezes in the neighboring TTF stacks . There , the zerovalent molecules act as insulating plugs in the conduction pathway , and electrical conductivity in the TTF stacks plummets below 58 K .

Suppose we were to try other oxidizing agents in place of TCNQ , or even carry out electrocrystallizations of TTF under oxidizing conditions , to form salts of the type TTF-X_n , where X is an inert anion such as BF_4^- , PF_6^- , and so on . Would these TTF compounds still be electrically conducting , with an aromatic wave mechanism ? Actually , TTF halides have been prepared , where X is chloride , bromide , and iodide ; for example , the compounds TTF-Br_{0.71-0.76} (ref. 54 , page 398) and TTF-I_{0.71} (ref. 55 , page 398) have been studied and well characterized with respect to their electrical conductivity properties . Both are modest room temperature conductors ; the bromide compound's conductivity ranges from 200-500 ohm⁻¹cm⁻¹ , while that of the iodide is about 350 ohm⁻¹cm⁻¹ . Unlike TTF-TCNQ , both the bromide and iodide analogues are pseudometals , with a direct temperature-conductivity relationship . The Mott transition temperatures are 170 K for the bromide and 210 K for the iodide , below which both compounds become semiconductors .

I don't have any electrical data for TTF mixed-valent chloride compounds, but TTF^+ Cl⁻ was found to be a good semiconductor (0.27 ohm⁻¹cm⁻¹ at room temperature), while the parent compound TTF was – not surprisingly – shown to be an insulator (10⁻¹² ohm⁻¹cm⁻¹; ref. 56, page 398).

A simple picture that might help to clarify these observations is again based on the types of orbitals used in forming the metallic bond , following Krebs's Theorem . Where true metal behavior of the compound is noted , the 4s AOs on the sulfur atoms will form a nodeless sigma XO as the metallic bond . Where pseudometal behavior is observed in the compound , it is conceivable that the pi MOs in the aromatized TTF molecules can overlap to a certain extent between the stacked molecules , to form a weak nodal pi XO along the stack axis . This latter XO would support an aromatic wave as the conduction mechanism in the solid . In the former sigma XO the sulfurs' 4s electrons would all be "crunched" in the Fermi-Dirac distribution typical of metallic solids with an s-p conduction band . In TTF-TCNQ the metallic bond would switch from the nodal pi XO to the nodeless sigma XO at the Mott transition temperature , 58 K , as the TTF⁰ and TTF¹⁺ valences begin to reproportionate with rising temperature . Such a reproportionation apparently doesn't occur in the TTF mixed-valent halides , and their conduction mechanism is based on an aromatic wave passing through the stacks via a nodal pi XO metallic bond , over a wide temperature range .

An alternate explanation for the TTF stack compounds' conductivity behavior might be found in the corresponding results for the mixed-valent salts of tetramethyltetraselenofulvalene (TMTSF), the selenium analog of TTF [plus four additional methyl groups]. In this case, the 5s AOs over the selenium atoms could form the sigma XO which functions as the metallic bond in the molecular stacks :



(TMTSF)₂PF₆ molecular metal stack compound

In this case , hexafluorophosphate anions , PF_6^- , are shown as the inert spectator anions which accompany the TMTSF^{0.5+} cations , and are packed in the interstack spaces . However , several other anions can be used in place of PF_6^- , with significant changes in the conductivity properties of the salts . For example , $(TMTSF)_2PF_6$ is a pseudometal under ambient pressure , but it becomes a true metal when compressed to 12,000 atmospheres , and under such pressure has a superconductor T_c of about 1 K . The perchlorate salt ,

 $(TMTSF)_2ClO_4$, by contrast is a true metal, and becomes superconducting at 1.2 K, under ambient pressure (ref. 57, page 399). The following sketch illustrates a possible mechanism, in orbital terms, that might account for the different conductivity behavior of the two salts:



In this simple picture, an incomplete overlap of the 5s AOs over the selenium atoms in the PF_6^- salt results in the presence of nodes along the sigma XO chain, and this salt accordingly is a pseudometal. Applying pressure to the compound's crystals forces the molecules more closely together; the nodes are eliminated, the sigma XO becomes nodeless, and the salt becomes a true metal. In the perchlorate salt there is sufficient overlap of the 5s AOs to produce a nodeless sigma XO as the metallic bond in it, and as a result it is a true metal under ambient pressure conditions.

A similar situation might exist for the various TTF stack compounds . Pseudometal behavior in certain of them may be evidence for poorly overlapping 4s AOs on the sulfur atoms , and nodal surfaces in between them , rather than utilization of pi XOs as the metallic bond in the stacks . The 4s AOs would be much more voluminous than the 2,3p AOs used in the aromatic rings of the TTF molecules , and so should have a higher probability of overlap along the stack axes than the latter orbitals .

As can be well imagined , the extraordinary success of TTF-TCNQ aroused considerable interest among researchers in molecular metals and stack compounds , with many analogues being prepared and studied in subsequent years . The current record for the highest superconductor T_c , of 12.8 K, for a molecular metal is held by a TTF derivative , κ -(ET)₂Cu[(CN)₂N]Cl. "ET" is shorthand for bis(ethylenedithio)tetrathiofulvalene , whose molecular structure is sketched as follows :



bis(ethylenedithio)tetrathiofulvalene, "ET"

As with all of the other sulfur-based molecular metals discussed in this section , we can consider this ET compound as being a form of metallic sulfur , with the surrounding organic molecule as being a sort of "window dressing". Of course , the organic molecule environment and the accompanying spectator anions – which may or may not be all that chemically inert – will have a significant effect on the metallic bond along the stacks' major axes . In fact , the conductivity properties of these stack compounds must be very sensitive to the molecular packing , which in turn will be influenced by the internal forces (the coulombic , van der Waals , and hydrogen bonding) acting to set the molecules in place in their stacks . The metallic bond that subsequently forms in the crystals is really a sort of an "afterthought" , which , however , produces the extraordinary physical effect of electrical conductivity in them . To date , it seems that the electron promotion creating the sigma XO occurs only in the chalcogenide atoms sulfur , selenium , and tellurium in the electron donor compounds .

Niobium Monoxide, NbO

I have alluded on page 62 to the complexity of the electronic nature of the metallic solids comprised of transition metal elements with nonmetallic elements such as oxygen, sulfur, and nitrogen. Nevertheless, I would like to present a brief discussion of several interesting transition metal oxides with metallic properties, to see if they can be analyzed by the orbital model employed above in earlier case studies. I must emphasize right away that the results obtained in these analyses are quite simple – some might say simplistic – and may be at odds with conventional solid state theory. However, they might help in the understanding of the chemical bonding in these materials, and in particular of their metallic bonds. I hope the reader, even if skeptical of my analyses, will be intrigued by my descriptions of these fascinating crystal systems, and will be inspired to give them more thought and study.

The first of these transition metal compounds we'll look at is niobium monoxide, NbO. It is a highly refractory compound (m.p. 1940 °C) that is black as a powder, but "....exhibits a bright metallic sheen" as a fused button when prepared in an arc furnace (ref. 58, page 399). Niobium monoxide was first prepared in 1868 by the nineteenth century French chemist, Henri Sainte-Claire Deville (1818-1881). A more recent (1973) preparation has been described in detail in <u>Inorganic Syntheses</u> by Reed and Pollard (ref. 58). They reproportionated Nb(0) from powdered niobium metal, and Nb(V) from Nb₂O₅, fusing these starting materials together in an arc furnace, to obtain a button of pure NbO :

 $3/5 \text{ Nb}^0 + 1/5 \text{ Nb}_2\text{O}_5 \longrightarrow \text{NbO}$

The electrical conductivity of NbO at room temperature is about 50,000 ohm⁻¹cm⁻¹, compared to that of pure niobium metal at 80,000 ohm⁻¹cm⁻¹. Its conductivity rises to around 1.43 million ohm⁻¹cm⁻¹ at 4.2 K, and NbO becomes superconducting at 1.38 K (compared to niobium's T_c, at 9.3 K). With such an inverse conductivity-temperature relationship, niobium monoxide must be a true metal .

Several solid state chemistry references I consulted (examples in ref. 59, page 399) concerning the crystal and electronic structures of niobium monoxide stated that it has a "defect rocksalt" structure , that is , like rocksalt , but with regularly spaced atomic vacancies . Actually , the point can be raised that given the compound's AX formula , why doesn't it have a genuine rocksalt structure , like magnesium oxide , for example ? The obvious reason is that niobium(II) is quite different , both chemically and electronically , than the magnesium cation .

The crystal structure of NbO is shown in the M3D model below :



Figure 22 : The M3D structure of niobium monoxide , NbO . The small red spheres are niobium atoms , and the larger green spheres represent oxygen atoms . This structure is based on that one shown in Fig. 14.14 , p. 191 , of Krebs's excellent textbook , <u>Fundamentals of Inorganic Crystal Chemistry</u> , cited in ref. 8 , page 391 .

In addition to the expected niobium-oxygen bonds, I have also shown in this model the Nb-Nb metal-metal bonds, resulting in a square bipyramid "cage"

of niobium atoms . We have encountered such metal cage structures before in the discussion of Robin-Day Class IIIA mixed-valent compounds (see page 52), like the polyatomic metal cation $(Ta_6Cl_{12})^{2+}$, whose structure somewhat resembles that of NbO . It is interesting to note in this regard that the metallurgical metals niobium and tantalum , among others , have the body-centered cubic (bcc) crystal structure . We can see contained within the bcc structure an infinite array of these six-atom octahedrons :



Figure 23 : An M3D model of the body-centered cubic (bcc) crystal structure , showing two unit cells , outlining with black solid lines (covalent bonds) the Nb₆ octahedral "metal cage" structure found in NbO .

This suggests to me that the Nb₆ octahedron is chemically a very stable , cohesive structure , and must be held together by strong bonds of some sort or other . Conventionally , such bonding is thought to be coulombic , with Nb²⁺ cations and oxide anions ; crystal field theory is then applied to derive a suitable picture of the electronic and crystal structure in accordance with the observed physical and chemical properties of the material .

I would like to present a somewhat different picture of the chemical bonding in NbO . First , let's start by noting that the alkali metals , from lithium through to cesium , all have the bcc crystal structure . This same bcc atomic organization is shared with over a dozen transition metal elements , including – as noted above – niobium , tantalum , as well as vanadium , chromium , manganese , iron , molybdenum and tungsten . The alkali metals and these transition metals have wildly different physical properties , the former being very soft and low melting , while the latter are very hard and refractory materials [Note 4 , discussion of niobium carbide , page 376] .

We can attribute these differences quite simply to the fact that the alkali metals are held together entirely by a rather feeble metallic bond, mostly "s" (sigma XO) in nature, while the transition metals probably rely on sigma covalent bonds for their great internal strength. They have an overlaid weak sigma XO metallic bond, as well (they are true metals, after all), that would contribute little to the overall atomic cohesiveness of the transition metals.

In niobium monoxide , these sigma MO covalent bonds are retained in the Nb₆ "metal cage" octahedrons we see in its crystal structure . Electronically , all six niobium(0) atoms (4d⁴ 5s¹) hybridize four of their 4d AOs to form d⁴ square pyramid hybrid AOs , placing their four 4d valence electrons in the lobes . The six niobium atoms then form covalent Nb-Nb bonds to create the octahedrons .

Note that four oxygen atoms coordinate each niobium atom in a square plane pattern . The niobiums generate the classic dsp² square planar hybrid AO , with four empty lobes , from their $4d_{x}^{2}-_{y}^{2}$, 5s , and $5p_{x,y}$ AOs . The oxide anions can donate electron pairs into these empty lobes to form additional coordinate covalent Nb-O bonds . Finally , the niobiums' fifth valence electrons are promoted – slightly – from their formal 5s orbital to the unused $5p_{z}$ AO .

Here's where things get really interesting , because this is the source of the metallic bond in NbO . Is there a direct overlap of the niobiums' $5p_z$ AOs to obtain a pi XO ? I doubt it , because the overlap geometry is unsuitable in

the octahedrons . Rather , I think it's likelier that the niobiums' $5p_z^{-1}$ AOs overlap to some extent with the oxide $2p_z^{-2}$ AOs to form a "blended" XO in the crystal . This latter "composite" XO would act as the metallic bond in niobium monoxide . The electronic structure of the compound is summarized in the following simple sketch :

Proposed Electronic Structure of Niobium Atoms in NbO 4d 5s 5p (xy) (xy) (xy) (xy) (00) (00) (00) (x) d^4 sq. pyramid dsp^2 square plane $5p_z^1$ x = niobium valence electron y = neighboring niobium valence electron (in Nb-Nb bonds)o = oxygen links' valence electrons donated to niobiums

The picture that emerges from this admittedly simple analysis is that during the formation of NbO , the strong , stable Nb₆ octahedrons are preserved in the reaction environment , but in the presence of oxide ligands are coordinated in a square planar geometry to form the Nb₆O₁₂ superstructure shown in Figure 22 above . If additional oxidation of NbO with more oxygen atoms occurs , the Nb₆ "metal cages" are broken down by the aggressive oxides , and the higher valence compounds Nb₂O₃ , NbO₂ , and finally Nb₂O₅ are formed . NbO is thus a sort of "bridge" between niobium metal and the higher valence compounds .

A magnetic susceptibility study of NbO by Khan and co-workers in 1974 (ref. 60, page 399) seems to support the above picture of the metallic bond in the compound. If the niobium atoms in NbO were purely ionic, that is, as Nb^{2+} (4d²), the compound would have an intermediate magnetic susceptibility strength, comparable to Fe²⁺, Ni²⁺, and the like. However,

this is not the case . It turns out that NbO exhibits a weak form of magnetic susceptibility , Pauli paramagnetism , also called "temperature-independent paramagnetism", which is typical of many metallurgical metals , being produced by the free electrons above the Fermi level in the metallic bond . We can definitely rule out the presence of Nb²⁺ cations in NbO . The simple orbital picture presented above of Nb-Nb covalent bonds , Nb-O coordinate covalent bonds , and the niobiums' $5p_z^{-1}$ unpaired fifth valence electrons being the basis of NbO's metallic bond , at least is not ruled out , and may even be supported by this experimental evidence .

The picture I thus have of NbO isn't the conventional one of a defect rocksalt structure , but rather one of the strong Nb₆ octahedrons , when undergoing limited oxidation by oxygen , retaining their integrity while being surrounded and coordinated by oxide anions . The resulting Nb₆O₁₂ superstructures are fitted together into an infinite atomic lattice , which comprises the macrostructure of the NbO crystal .

Before leaving the topic of niobium monoxide , I wanted to mention that Pauling had speculated on the electronic structure of iron , in valence bond terms , in his textbook , <u>The Nature of the Chemical Bond</u> , pp. 414-416 . The ground state electronic configuration of iron atoms is $3d^6 4s^2$, for the valence shell . Pauling pointed out that relatively little energy would be required to promote 3d and 4s electrons to the 4p level , to provide an excited state hybrid AO , d^5sp^2 . Such a hybrid AO would be a face-centered [square] prism ; see Sanderson's list , bottom of Table 3 , page 64 . This is the VB equivalent to the crystallographic body-centered cubic structure . Pauling calculated the promotion energy for this hypothetical iron hybrid to be 92 kcal-mol⁻¹ . Compare that to the 200 kcal-mol⁻¹ for the carbon transition from the ground state $2s^2 2p^2$ to the excited state $2s^1 2p^3$ for the tetrahedral hybrid AO , sp^3 .

It would be nice if the iron hybrid was the d^5p^3 AO instead of the d^4sp^2 AO as Pauling suggested . That way , the 4s AO would be left open for use as the primary metallic bond in iron , via its 4s sigma XO . Unfortunately – and Nature seems to be perverse sometimes – the d^5p^3 AO represents a square antiprism structure , that is , a cube whose two opposing square ends have

been twisted through 45° with respect to each other . Bad luck ! This suggests that the metallic bond in iron may occur when free electrons enter the unused , available 4p AOs on the iron atoms , forming a pi XO . This is certainly a possible scenario . However , I suspect that the metallic bond in iron may really be a complex composite of several contributing XOs , both nodal (the d⁴ AO sigma covalent bonds in the interlocking iron octahedrons) and nodeless (3d level delta XOs ; 4s sigma XO ; and 4p pi XOs) . Since there aren't enough valence shell electrons – eight – to fully occupy all of these XOs simultaneously , it is possible , as Pauling suggested , that a sort of electron resonance occurs in iron and other such metals , as in the benzene molecule , for example . That is , these various XOs would have only a partial , fluctuating occupancy of XOs by electrons is a hallmark of metallic bonds , and of the s-p conduction band , in band theory .

In any case , the great strength and refractory nature of the transition metals (those with the bcc crystal structure , at least) can be attributed to those d⁴ MO sigma covalent bonds in the M₆ octahedrons , with only a very minor contribution from the sigma , pi , and delta XOs of the (nodeless) metallic bond . The close , tight packing of the spherical metal atoms in the crystal also results in very short M-M bond lengths , which again permits the formation of strong covalent metal-metal bonds in the solid .

Chromium Dioxide, CrO₂

The interesting metallic solid chromium dioxide [chromium(IV) oxide], a brownish-black or dark gray powder, has been used for a couple of decades as the recording medium in magnetic ribbon for tape recorders and compact cassettes, in competition with the more mundane iron(III) oxide. It has been described as a "half-metallic ferromagnet" (Cox, reference on page 62 above). Chromium dioxide's credentials as a metallic solid have been well authenticated; its electrical conductivity at room temperature is about 10,000 ohm⁻¹cm⁻¹, and it rises steadily as the material is cooled toward absolute zero. I haven't seen a reference saying that CrO_2 actually becomes superconducting at any temperature , but its conductivity certainly becomes very high at liquid helium temperature (see the temperature-conductivity graph for CrO_2 in Figure 9 , p. 13 , of Chamberland's review of the chemical and physical properties of chromium dioxide in ref. 61 , page 399) . Again , as with NbO , CrO_2 is a true metal , which I have placed in Class 1 (page 56) of the metallic solids categories .

Chromium dioxide has the TiO_2 , or rutile structure (6:3,3 coordinations) :



Figure 24 : The rutile structure generally ; specifically for chromium dioxide , the small blue spheres are octahedral chromium(IV) atoms , while the larger green spheres represent trigonal oxygen linking atoms . This M3D model was based on the sketch of rutile shown in Figure 7.4 , p. 97 , in Wold and Dwight's textbook (ref. 24 , page 394) . The model is idealized in its geometry , of course ; actual bond angles and lengths will usually be somewhat distorted from the ideal values shown in the model . Goodenough

(ref. 62, page 399), in his review of the electronic structures of a selection of transition element-based metallic solids (among which is chromium dioxide, incidentally), presents a nice sketch of titanium dioxide in his Fig. 5, p. 1203, which shows the bond angles and lengths in TiO_2 . This drawing shows the distortions in the real-life material rutile.

Chromium in CrO₂ is in the Cr(IV) valence state , and must be considered as covalent in nature , rather than the ionic Cr⁴⁺ . In discussing CrO₂ in VB terms , two possible hybrid AOs could be reasonably considered for the chromium atoms , the conventional "inner octahedral" one , d²sp³ , and a new one I would like to propose , d⁵s (Table 3 , page 64) . This latter hybrid orbital could be thought of as a combination of three separate hybrid AOs : $d_{xy} + d_x^{2-y^2}$ (x-y plane , bent 90°) ; $d_{xz} + d_{yz}$ (x-y plane , bent 90°) ; and $3d_z^2 + 4s$ (z axis , linear) . The use of either of these octahedral hybrid AOs by Cr(IV) will have an important effect on the electronic structure of the solid .

There are six chromium-oxygen covalent bonds per formula unit of CrO_2 that will require twelve valence electrons to fill . Since the chromium atoms in the compound are Cr(IV), they will use four of the six available valence electrons in Cr(0), which is $3d^5 4s^1$ electronically, leaving two "extra", unused electrons in frontier orbitals . The covalent oxygen linking atoms, with trigonal sp^2 hybrid AOs, must supply the remaining eight electrons for the skeletal framework, or four per atom . Since oxygen(0) has six valence electrons, four will be in two of the sigma lobes of the hybrid, and the remaining two will be in the unhybridized $2p_z$ orbital , as shown in the sketch at the top of the next page . "Polymerization" of the chromium octahedral AOs with the oxygen atoms' trigonal AO links produces the rutile crystal structure in CrO_2 .

The two "leftover" valence electrons in CrO_2 after the skeleton formation are responsible for its metallic properties . According to a density of states diagram in Cox's textbook (page 62; Fig. 5.10, p. 222), in CrO_2 the chromium 3d states and the oxygen 2p states don't mix, but remain separated by an energy gap. I'm wondering, though, how we can account for the metallic bond in the material, which is definitely a true metal, in



Trigonal sp² Oxygen Atom Link Hybrid AO

orbital terms , when the chromium atoms are separated from each other by oxygen atom spacers .

Wold and Dwight (ref. 24, page 394) present an energy level diagram for the electronic structure of chromium dioxide (Figure 7.13, p. 108). They locate the Fermi level for the material in a partially filled band comprised of contributions from the t_{2g} orbitals on chromium and the unhybridized $2p_z$ orbital on the oxygen atom links. This suggests a "classical" inner octahedral hybridization of d^2sp^3 for the chromiums. The partially filled band also has sigma and pi* attributes, both of which would result in a nodal XO, and result in CrO_2 having the properties of a pseudometal, which it isn't.

Instead , let's consider a different scenario : suppose the chromiums have the d^5s inner octahedral hybrid AO , which isn't too improbable , considering that chromium is an "early" transition metal , in which d orbitals are quite prominent . For example , in the macromolecular solid chromium trioxide , consisting of long chains of $[CrO_3]_n$, the chromium atoms all have a tetrahedral coordination by the oxygens . They will use the d^3s hybrid AO for the tetrahedrons , rather than the more familiar sp³ AOs , simply because the d orbitals are so prominent in the transition metal elements , while the

pre- and post-transition elements will tend to use s and p native orbitals in forming their hybrid AOs, and tend to avoid the d orbitals for this purpose. In the "later", or heavier transition metal elements, s and p native orbitals begin to play a more important role in hybrid AO formation, as we will see later with copper.

If the chromiums in CrO_2 actually do have d^5s hybrid AOs forming their covalent skeletons, then the two "extra", unused Cr(IV) valence electrons will be promoted into the 4p native frontier orbitals :

Proposed Electronic Structure of Chromium Atoms in Chromium Dioxide



If the outer p orbitals in the chromiums are the location of the extra electrons in the compound, we will have a plausible mechanism for the formation of nodeless XOs that might function as the metallic bond in CrO_2 and permit it to behave as the true metal that it is . It should be possible for the chromium 4p AOs and the oxygen links' $2p_z$ AOs to overlap together to form a continuous pi XO in the solid which will operate – with its contained electrons, of course – as the crystal's metallic bond.

I presume that Hund's Rule applies to singlet electrons in p orbitals as well as in the usual d orbitals . Thus , I have shown in the above sketch the two extra chromium electrons as singlets in two separate p orbitals . This is rather interesting , as only one set of the p AOs (the $4p_z$) will be able to

overlap continuously with the set of oxygen links' $2p_z AOs$. This combination of 2-4 $p_z AOs$ will form the pi XO, which could well function as the metallic bond in chromium dioxide. As for the other non-overlapping chromium $4p_{x,y} AOs$, the electron in them will be localized, and should make chromium dioxide exhibit magnetism of some sort or other.

In fact, chromium dioxide displays the "intermediate" strength type of magnetism, Curie paramagnetism [the weak type of magnetism is Pauli paramagnetism, observed in most, if not all true metals; and the strong type of magnetism is ferromagnetism, as is seen in strongly magnetic materials such as iron, nickel, magnetite, and so on]. Chromium dioxide has an ambient magnetic susceptibility of 2.0 BM (Bohr magnetons), a value typical of many transition metal salts and compounds. Using the simple formula for calculating spin only magnetic moments,

 $\mu = [n(n+2)]^{\frac{1}{2}}$,

where μ is the magnetic susceptibility in Bohr magnetons , and n is the number of unpaired valence electrons in the transition metal atoms in the solid , if n = 1 , then μ = 1.73 BM , while if n = 2 , then μ = 2.83 BM . The value for chromium dioxide is closer to n = 1 than 2 , so as with niobium monoxide , the basic test of magnetic susceptibility seems to support – or at least does not refute – the simple picture presented on the previous page of the proposed electronic structure of the chromium atoms in chromium dioxide .

The simple formula above for the magnetic susceptibility of compounds with "n" unpaired valence electrons in their transition metal atom components is reasonably accurate for magnetically dilute compounds , that is , those in which there is no significant interaction between the unpaired singlet electrons . As it turns out , the singlet $4p_{x,y}$ electrons in chromium dioxide responsible for its magnetism apparently have an overall parallel orientation of their spins in the three dimensional structure of the crystal . That results in a weak ferromagnetism appearing in the material . Because of the diluting effect of the oxygen atom links in the structure , this ferromagnetism is within the Curie paramagnetism range , in effect no more than a slight enhancement of the magnetically dilute spin only value of 1.73 BM . However , this magnetic ordering regime in chromium dioxide results in it being , as Cox says , a "half-metallic ferromagnet" , with one of the extra valence electrons creating a metallic bond in the crystal , and the second electron making it a weak ferromagnet .

When I was reading various references concerning chromium dioxide, such as Chamberland's review article (ref. 61, page 399), I was struck by the relative scarcity of good preparative methods for this interesting material. According to Ridley, in a rather dated (1924) review of syntheses of CrO₂ (ref. 63, page 400), the "best" preparation of it was by a controlled decomposition of chromium trioxide up to 250 °C. There appears to be no verified preparation of chromium dioxide published in <u>Inorganic Syntheses</u>, for example. I was wondering if several simple procedures for its preparation, discussed briefly below, might be **carefully** looked at.

First , let's recognize that CrO_2 is an oxidizing agent , and a remarkably powerful one , at that , as illustrated by its standard reduction potential E^0 at STP :

 $CrO_2 + 4 H^+ + e^- \longrightarrow Cr^{3+} + 2 H_2O$; $E^0 = 1.48 V$.

(This redox equation was from the <u>Handbook of Chemistry and Physics</u>, 80^{th} edition, 1999).

The acidic standard reduction potentials of dichromate and chromate (from aqueous chromic acid or chromium trioxide), by comparison are 1.232 V and 1.350 V, respectively. These are generally considered to be quite powerful oxidizing agents. It may seem paradoxical and counterintuitive that a metallic solid can be an oxidizing agent; we usually visualize metallic substances as being reducing agents. Note, however, that the famous high T_c superconductor YBCO is also a relatively powerful oxidizer, being capable of chemically oxidizing water molecules to oxygen at room temperature. Clearly, the metallic bond can exist and function in either chemically reducing or oxidizing environments.

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The following are a half-dozen or so ideas for preparing CrO_2 that I think may be novel . The interested reader should verify their novelty by a thorough literature search before embarking on laboratory trials . I personally enjoy laboratory work and designing new syntheses of interesting materials , both organic and inorganic . Also , I would like , in this presentation , to depart from theory now and then to discuss practical topics such as "real" chemical substances . For me , laboratory synthesis is much more fun – and sometimes more frustrating – than theorizing !

I cannot overemphasize the great need for **safety** if the following procedures – and any others mentioned in this text – are carried out . The reader must assume full responsibility for the safe manipulation of the reagents cited and in carrying out any actual trial runs . Of course , I expect all my readers are mature , responsible chemists , and are well versed in chemical theory and practice . As a basic minimum precaution , however , I would suggest that no more than semi-micro quantities of reagents (a gram or less) be utilized , that the experiments be carried out in a clean , vacant area with air aspiration (an empty fume hood) , and that protective equipment be deployed by the researcher , **especially** eye protection (the latter I can personally certify !) .

Caution is especially required in several of the following cases , since they will involve the combination of a reducer (Cr^0 or Cr^{2+}) with an oxidizer , Cr(VI), and will be in intimate contact with another strong oxidizer , Cr(IV) itself . The reader has probably already guessed that these will be reproportionation reactions , in which a low-valent chromium reagent is blended with a high-valent reagent , to obtain the mid-valent product , Cr(IV). In the middle of these is Cr(III), which is the "low energy" form of chromium . Unfortunately , the only useful Cr(III) reagent available is the highly refractory (m.p. 2535 °C) chromium sesquioxide , Cr_2O_3 , which doesn't lend itself very well to reproportionation with other reagents .

The combination of a chemical reducer with an oxidizer **may** often be a sure recipe for a **detonation**, especially with well-mixed solid reagents; the example of gunpowder comes to mind here. It might be possible to use a modified technique to avoid such an explosion, such as by adding one of the

reactants to the other in a slow, carefully controlled manner, and permitting most of the exothermic reaction to have been completed before more reagent is added to the reaction container. As is often the case in preparative chemistry, the researcher generally learns through experience, improving and refining synthesis techniques until a safe, acceptable procedure for a preparing the desired compound has finally been developed.

The following are several suggestions for a possible new preparation of chromium dioxide :

1. Simple metathesis (using the chloride salt as an example) :

$$CrCl_2 + Na_2CrO_4 \xrightarrow{(water solution)} Cr^{2+}CrO_4 + 2 NaCl$$
.

The intermediate product , chromium(II) chromate , may be water-soluble ; most , if not all , chromate salts are . It may also be "metastable" ; that is , stable at room temperature , but violently decomposing at higher temperatures . Note that it contains a reducer species , Cr(II) , together with an oxidizing species , Cr(VI) , in the same compound . This is reminiscent of certain solid rocket fuels , such as ammonium perchlorate and hydrazinium perchlorate , and of the familiar explosive , ammonium nitrate . Perhaps gentle heating , or even reflux , of the reaction solution may be necessary to achieve a suitable decomposition of $Cr^{2+}CrO_4 \rightarrow 2 CrO_2$. A catalyst such as platinum foil or wire might also induce a safe , smooth transfer of electrons from Cr^{2+} to CrO_4^{2-} .

2.
$$Cr^{0} + Cr(VI)$$
:

Dissolve powdered chromium metal in chromic acid $(CrO_3 + H_2O)$. Chromium metal dissolves in aqueous acids to first produce Cr^{2+} , which should then combine with chromate anion , as above :

 $Cr^{0} + H_{2}CrO_{4} \longrightarrow Cr^{2+}CrO_{4} + H_{2}(g) ;$

The intermediate hydrogen gas likely would instantly reduce chromate anion

to unknown by-products , possibly to CrO_2 itself . This suggests a third scheme to prepare chromium dioxide :

3. Reductive deoxygenation of CrO_3 :

By hydrogen, possibly on platinum as a catalyst :

 $H_2CrO_4 + H_2(g) \xrightarrow{(water solution)} CrO_2 + 2 H_2O$. (platinum)

By organic phosphines and phosphites, which have a noted affinity for oxygen atoms, and readily "scavenge" them (cf. the Wittig reaction) :

 $CrO_3 + (\phi)_3P \xrightarrow{\text{(organic solvent,})} CrO_2 + (\phi)_3PO ;$ eg. $CH_2Cl_2)$ the symbol " ϕ " is shorthand for triphenyl, C_6H_5 .

 $CrO_3 + (EtO)_3P \longrightarrow CrO_2 + (EtO)_3PO$.

By hypophosphorous acid, which is a good reducing agent :

 $H_2CrO_4 + \frac{1}{2}H_3PO_2 \xrightarrow{\text{(water solution)}} CrO_2 + \frac{1}{2}H_3PO_4 + H_2O.$

Suggestion : add the H_3PO_2 slowly, dropwise to the chromic acid solution, ensuring a complete reaction between aliquots. Note that the intermediate phosphorus acid, H_3PO_3 , will likely be formed as a transient species in this reaction. It is also a good reducing and deoxygenating agent, but would immediately be consumed by the chromic acid. This suggests an additional reduction experiment, reduction of Cr(VI) with phosphorus acid :

 $H_2CrO_4 + H_3PO_3 \longrightarrow CrO_2 + H_3PO_4 + H_2O$.

I should point out that all the reagents cited in this work are commercially available from familiar chemical supply sources such as Alfa-Aesar, Aldrich Chemical Company, and so on, unless otherwise noted (and if that is the case, I will try to suggest a possible preparation from literature sources or from cognate syntheses).

The redox equation for chromium dioxide on page 137 suggests that it should be reduced spontaneously in acidic conditions at STP (although redox reactions never say how fast the reactions would be), and would be deoxygenated by their protons to Cr^{3+} . We should therefore try to avoid acidic reaction conditions if possible, at least in strong acids and for extended reaction times and at elevated temperatures. So, for example, milder pH aqueous solutions could be tested :

$$Na_2CrO_4 + H_3PO_3 \longrightarrow CrO_2 + Na_2HPO_4 + H_2O$$
.

By hydrazine :

 $H_2 CrO_4 + \frac{1}{2} N_2 H_4 \quad \xrightarrow{\text{(water solution)}} CrO_2 + \frac{1}{2} N_2 (g) + 2 H_2 O .$

Hydrazine is a very powerful reducer , both in acidic and basic media . It is well known to reduce chromate anion to Cr^{3+} ; in fact , one valuable industrial use of hydrazine is to convert water-soluble (and very eco-toxic) chromate to the insoluble chromium(III) hydroxide sludge , precipitating this toxic element from industrial wastewater streams . My question – and it is certainly appropriate to the other reduction experiments mentioned above – is : can the reduction of Cr(VI) be selectively controlled to stop at Cr(IV) , in the form of the insoluble chromium dioxide , rather than continue on to the undesirable Cr(III) stage ? I have written the above equations with a stoichiometry corresponding to the production of CrO_2 , but I'll readily admit that in at least several of the cases , only a Cr(III) product may be formed .

The reduction of chromate by hydrazine might in this case be limited to the Cr(IV) stage by the slow, dropwise addition of the hydrazine component in

water solution , with rapid mechanical stirring of the reaction mix , and probably with cooling of the mix in an ice bath , to the chromate solution . That way , there is an excess of chromate in the solution most of the time (a slight stoichiometric excess of chromate might be used in the reaction) . An unfortunate possibility in all these cases is that the CrO_2 product we desire may actually react faster than chromate with the various reducers cited , to produce the uninteresting Cr(III) sludge .

4. Dehalogenation of chromyl chloride :

Chromyl chloride is a dense (s.g. = 1.911) reddish-brown liquid (b.p. 117 °C) resembling bromine . It is commercially available – but expensive ! – and is fairly easy to prepare ; for example , by heating a mixture of sodium chromate , sodium chloride , and concentrated sulfuric acid , and distilling the deep red vapor in an all-glass apparatus . A quantitative yield of chromium dioxide can be obtained by pyrolysing chromyl chloride vapor at 370 °C for a prolonged period of time at an elevated pressure (ref. 64 , page 400) . I wonder if it would be possible to dehalogenate chromyl chloride with a reagent such as zinc dust , for example :

Since zinc dust is a moderate strength reducing agent, and chromyl chloride is as strong an oxidizer as chromic acid, this last proposed reaction is potentially rather hazardous. Perhaps the chromyl chloride, as a solution in the benzene, could be added dropwise to the rapidly stirred suspension of zinc dust in the reaction flask, with heating if necessary, thereby controlling the rate of the reaction within acceptable limits.

5. Oxidation of Cr^{3+} to Cr(IV)

The redox reaction on page 137 for the reduction of chromium dioxide to

 Cr^{3+} might be turned around (that is , oxidation of Cr^{3+} to CrO_2) and teamed up with a suitable oxidizer's standard reduction reaction to produce an overall net chemical reaction for the production of CrO_2 from Cr^{3+} . But which oxidizer shall we choose ?

It must be an oxygenating oxidizer, at least. For example, we could look at hypochlorous acid, the familiar "Javelle water" as its sodium salt, NaOCl :

HClO + H⁺ + 2e⁻ \longrightarrow Cl⁻ + H₂O ; E⁰ = 1.482 V ; 2 Cr³⁺ + 4 H₂O - 2e⁻ \longrightarrow 2 CrO₂ + 8 H⁺ ; E⁰ = -1.48 V .

Net chemical equation :

$$2 \operatorname{Cr}^{3^+}$$
 + HClO + $3 \operatorname{H}_2 O$ \longrightarrow $2 \operatorname{CrO}_2$ + $7 \operatorname{H}^+$ + Cl⁻
 $\operatorname{E}^0_{T} = 0.002 \operatorname{V}$.

Hypochlorous acid can be generated by bubbling a stream of chlorine gas through water , or in this case , it could be produced in situ for the reaction by passing the chlorine stream through a solution of a water-soluble chromium(III) salt , such as $CrCl_3$ [to produce the intermediate $CrCl_4$?].

A more convenient oxygenating oxidizer for trial in the synthesis of chromium dioxide might be hydrogen peroxide :

 $H_2O_2 + 2 H^+ + 2e^- \longrightarrow 2 H_2O$; $E^0 = 1.776 V$.

Combining this redox half-reaction with that for Cr^{3+}/CrO_2 , we have the net chemical reaction for the redox couple Cr^{3+}/H_2O_2 :

$$2 \operatorname{Cr}^{3^+} + \operatorname{H}_2\operatorname{O}_2 + 2 \operatorname{H}_2\operatorname{O} \longrightarrow 2 \operatorname{Cr}\operatorname{O}_2 + 6 \operatorname{H}^+;$$

 $\operatorname{E}_T^{\ 0} = 0.296 \operatorname{V}.$

Fairly concentrated solutions of hydrogen peroxide, around 30% by weight or so, are commercially available and are reasonably priced, making this latter reaction of some interest. Concentrated solutions of hydrogen peroxide , and indeed all peroxides , should be handled very carefully by chemists who have acquainted themselves with the safety precautions required for such energetic chemicals . The anion associated with the Cr^{3+} cation should not be oxidizable by the peroxide . For example , chloride anion could be oxidized to chlorine by hydrogen peroxide :

 $2 \text{ Cl}^2 - 2e^2 \longrightarrow \text{Cl}_2(g)$, $E^0 = -1.3583 \text{ V}$ (versus +1.776 V for hydrogen peroxide reduction , above).

Sulfate and nitrate should be satisfactory spectator anions for this hypothetical oxidation of Cr^{3+} to Cr(IV) as – we hope – CrO_2 . A drop or so of parent acid (sulfuric or nitric) to make the starting reaction mix acidic might be necessary as a catalyst to induce the peroxide oxidation. As the reaction proceeds, by-product acid will accumulate in the product mix, to the point where a buffering chemical such as sodium acetate could be added to reduce the pH of the mix somewhat.

As mentioned earlier on page 131, the main industrial use of chromium dioxide at present is in magnetic recording media such as compact cassettes. As I see it, though, the trend in audio and audiovideo recording these days seems to be moving toward photonic digital recording such as in CDs and DVDs and away from magnetic devices (although magnetic metal discs, such as the hard drives in computers, will be around for a long time, no doubt). I can predict a decline in the market requirements for chromium dioxide, and a decrease of interest in it as magnetic material.

Rhenium Trioxide, ReO3

Rhenium trioxide is a colorful solid , having been described variously as red with a green luster , or blue , or purple . It disproportionates to ReO_2 and Re_2O_7 when heated to 400 °C . The most interesting thing about rhenium trioxide in the present context is its remarkably high electrical conductivity , 149,300 ohm⁻¹cm⁻¹ at room temperature . Compare that to the values for nickel (146,200) or rhenium itself (58,140) . It has an inverse temperature-conductivity relationship ; see , for example , Bowen's Figure 5 , p. 299 in
ref. 25, page 394. Rhenium trioxide apparently never becomes superconducting, even very close to absolute zero. However, there is no doubt that it is a true metal, and I have placed it in Class 1 of the general categories of metallic solids (page 56).

Rhenium trioxide gives its name to this general crystal structure type, and has a very simple "supercubic" framework :



Figure 25 : the M3D structure of rhenium trioxide . The small red spheres are octahedrally-coordinated rhenium(VI) atoms , and the larger aqua spheres represent linear covalent oxygen atom links .

I referred to this structure as being "supercubic", because it is indeed cubic in shape but has a large central cavity. This is in comparison to the rocksalt crystal structure, which is "simple cubic", with no central cavity. If a large cation ("A", generally) is located within the central cavity of the ReO₃ structure ("MX₃", generally), the resulting AMX₃ structure is a perovskite. One reference I checked said that ReO₃ is diamagnetic , but another said it has a very weak , temperature-independent paramagnetism ("t.i.p.") ; in the Handbook of Chemistry and Physics (eighty-second edition , 2001) its molar magnetic susceptibility , χ_m , is given as +16 10⁻⁶cm³mol⁻¹ , which is the same as that for sodium metal (and close to those values for the other alkali metals , except for cesium , which is somewhat higher) . This is clearly Pauli paramagnetism in the compound . Hall and Seebeck effects measurements on rhenium trioxide show that it has only one valence electron per formula unit as the free electrons in its metallic bond (see the review article in ref. 65 , page 400 , for a discussion of rhenium trioxide) . Since rhenium(0) has the 5d⁵ 6s² electron configuration in its valence shells , the other six valence electrons must be used for skeletal covalent bonding ; Re(VI) is definitely covalently bonded , and isn't the ionic Re⁶⁺ .

As with chromium dioxide before , let's suppose that the rhenium atoms in ReO₃ have inner octahedral d⁵s hybrid AOs . There are six Re-O covalent bonds per formula unit , requiring twelve electrons for complete filling . Six of these electrons will come from the rhenium atom , and will occupy each of the six sigma lobes of the d⁵s hybrid AO . The other six electrons will come from the three oxygen atom links , or two valence electrons per oxygen . The covalent oxygen links are linear in geometry . They will undoubtedly use the linear sp + $2p_y + 2p_z$ hybrid AO , with a single electron in each of the two sigma lobes , and lone pairs of electrons in each of the unhybridized $2p_y$ and $2p_z$ AOs (see the sketch at the top of the next page) .

Polymerization of the octahedral rhenium and linear oxygen atoms' AOs with their contained electrons produces the supercubic structure of rhenium trioxide . The seventh valence electrons in the rhenium atoms become "extra" to this covalent skeleton , and are relocated to the unhybridized $6p_{x,y,z}$ AOs . This represents no great energy requirement , since in the bulk rhenium metal the $6s^2$ valence electrons will actually leak to a certain extent into the 6p AOs anyway : this is the s-p "conduction band" in the native element .

We know these seventh extra electrons from the rheniums are in , or form , the metallic bond in the solid . Why are they responsible for the compound's extraordinarily high electrical conductivity ?



Linear sp covalent oxygen atom link AO

Proposed Electronic Structure of Rhenium Atoms in Rhenium Trioxide



- x = rhenium valence shell electrons
- o = oxygen links' valence shell electrons

Cox (ref. 18, page 393; Fig. 4.32, p. 123), in his band structure diagram for rhenium trioxide, shows the energy levels for the rhenium 5d and oxygen 2p orbitals separated by an energy gap, and the Fermi level (i.e. metallic bond) located in the former orbitals. Nevertheless, he states on p. 122, "Another solid showing covalent mixing of p and d orbitals is the transition metal compound rhenium trioxide" The general consensus nowadays is that the oxygen atom links in ReO₃ participate somehow in the metallic bond in the solid, the 5d orbitals either being too small, or being physically blocked by the oxygens, to form direct Re-Re metal bonds. Wold and Dwight (ref. 24, page 394; Figure 8.5, p. 135) show an energy band correlation diagram for rhenium trioxide. They located the Fermi level for the solid in a π^* band, but I am doubtful of this assignment because, as noted earlier, ReO₃ is a true metal which must utilize a nodeless XO as its metallic bond, and all antibonding AOs, and by extension, ABXOs, are highly nodal in nature.

At this point I would like to introduce the concept of the **bilayer metallic bond**. The oxygens' $2p_y^2$ and $2p_z^2$ AOs have the correct shape, size, symmetry, and physical orientation in the crystal skeleton to overlap successfully with the rheniums' $6p_{x,y,z}^{-1}$ AOs. The hypothesis – and I must stress that this is only a suggested "picture" of the metallic bond in ReO₃ – is that these oxygen and rhenium 2p and 6p orbitals, respectively, blend together in the solid over the covalent framework to form a crystal-wide pi XO that, with its contained valence electrons, forms the metallic bond in rhenium trioxide.

There is , however , an energy mismatch in the two component sets of p native orbitals . The oxygen 2p AOs are at a very low energy level , while the rhenium 6p AOs are at a much higher energy level (refer to Figure 4 , page 35) . The picture I have here is that the rhenium 6p AOs "float" on top of the oxygen 2p AOs ; that is , there are two layers in this metallic bond , like oil floating on water . Cox placed the Fermi level for these mixed orbitals in the rhenium 5d AOs ; however , the only nodeless XO possible from such d AOs would be the delta XO (illustration on page 79) , and this is unlikely because of the oxygen links separating the rheniums , as mentioned earlier . Also , because of shape and symmetry considerations , d and p AOs can't blend together in a crystal to form any sort of nodeless XO .

We could locate the Fermi level in rhenium trioxide in the rhenium 6p AOs, though, and still have an acceptable type of nodeless XO (pi) for use in a true metal. The question arises once again : how can this proposed

electronic structure for ReO₃ rationalize the remarkably high electrical conductivity of the compound , two and a half times higher than that of the parent rhenium metal ?

A possible explanation is that in rhenium metal there is a monolayer, or if you will, a single layer, homogeneous metallic bond. The energies of the valence electrons in this metallic bond are "crunched" [distributed] in the Fermi-Dirac energy distribution, according to the quantum mechanical theory of metals. This results in relatively few of the valence electrons actually being "free" and itinerant within the solid at room temperature ; they are located above the Fermi level in the material, as singlet electrons occupying their own energy levels, and contribute to the electrical conductivity (and other typical properties of metallic solids) in it.

Most of the valence electrons in the solid's metallic bond are located below the Fermi level . They are paired together , with opposite spins , at the same energy level in the crystal , but not necessarily as geographical neighbors . In fact , most of the sub-Fermi level valence electrons are widely separated in the physical sense , having "energy mates" located distant from them in the lattice . This results in the metallic bond being very weak , energetically speaking , compared to true covalent bonds .

Ellis and coauthors (ref. 66, page 400, pp. 191-192) give the example of sodium metal, with a $3s^1$ valence shell electronic configuration. From the Fermi-Dirac distribution of energies in these valence electrons it has been calculated that only one percent of them are located above the Fermi level and are able to contribute to the electrical conductivity in the metal. A similar situation undoubtedly occurs in rhenium metal. It is possible that in rhenium genuine covalent bonds may utilize some of the element's valence shell electrons, as was pointed out earlier for niobium, iron, and other transition metal elements with the bcc crystal structure (rhenium has the hcp – hexagonal closed-packed – crystal structure). The few remaining valence electrons may then form the metallic bond in the element, but after crunching in the Fermi-Dirac distribution, are too few in number to impart but a mediocre electrical conductivity to the metal.

The picture for rhenium trioxide, however, is that its bilayer metallic bond

alters the Fermi-Dirac distribution so as to promote many more rhenium valence electrons (in the $6p_{x,y,z}$ ¹AOs) above the Fermi level than would be the case in rhenium metal. Could it be that the Fermi level in ReO₃ is actually at the interface between the oxygen 2p and rhenium 6p AOs , so that all the rhenium 6p valence electrons are boosted above the Fermi level?

It is conceivable that even some of the oxygen 2p electrons might be promoted above the Fermi level, depending on the degree of mixing of the two layers of the metallic bond. The prime factor encouraging such a mixing of the two layers is the **polarizing power** of the cation in the compound. An oxidizing cation, or metal atom center, will pull valence electrons from the non-metal atoms or anions surrounding it toward it. Oxygen covalent links and oxide anions are very difficult to oxidize, so they will resist the electron pulling effect from the cations, but some polarization of the metal-oxygen pi bond will nonetheless occur.

I wouldn't expect low energy cations, such as the alkali metal cations, or chemically reducing cations, to polarize the metal-ligand bond very much, if at all. On the contrary, the anion may actually polarize the outer electron shell of such a cation; see, for example, Fig. 2.1, p. 65 in A.R. West's textbook, <u>Basic Solid State Chemistry</u> (ref. 34, page 395), which shows the polarization and distortion of the $1s^2$ electron shell of lithium cations by the coordinating fluoride anions in the rocksalt structure of lithium fluoride.

The reverse action may occur with oxidizing cations or metal atom centers (in covalent structures). Rhenium(VII) is known to be a moderately strong oxidizer, and rhenium(VI) is probably a mild oxidizer, although I can't find a redox reference for it (Note 8, page 384). Some polarization of the Re-O pi XO metallic bond in rhenium trioxide is likely, and this would tend to pull oxygen 2p electrons up toward the rhenium 6p layer in it. A small population of oxygen 2p electrons might be drawn up above the Fermi level with the rhenium 6p electron population. Polarization of the metallic bond would thus have the effect of substantially increasing the population of free, itinerant electrons above the Fermi level, which would result in a significantly higher electrical conductivity for the compound, compared to materials with a homogeneous, monolayer metallic bond.

Sanderson (ref. 32, page 395, p. 142) has provided a list of factors influencing the strength of covalent and metallic bonds. Polarization is one such factor. Polarized covalent bonds are often stronger than the corresponding nonpolar bonds, although nucleus shielding effects may mask the polarization enhancement, as illustrated for the bond strengths of the hydrogen halides:

H–H 435.99 kJ-mol⁻¹ H–F 569.87 H–Cl 431.62 H–Br 366.35 H–I 298.41

Similarly, polarization by electrophilic metal atom components in a compound may enhance the strength of the metallic bond in the solid by increasing the mobility of its free electrons. An excellent example of an enhanced polarized metallic bond is provided by the series of graphite intercalation compounds with Lewis acid electrophiles.

As is well known, the flaky structure of graphite can serve as a host for a wide variety of chemical reagents, which penetrate into the flakes and bond in between the separate sheets of carbon atoms. Both electrophiles, such as Lewis acids, and nucleophiles, such as amine bases and alkali metal atoms, can be readily accommodated in the graphite host. The electrical conductivity of the native, virgin graphite (about 25,000 ohm⁻¹cm⁻¹ at room temperature) can be dramatically increased by some of these intercalated reagents. For example, in 1973 a research team at the Université de Sherbrooke, Quebec, Canada, intercalated graphite with a powerful electrophile, antimony pentafluoride, SbF₅ (up to 75% by weight), producing a "black, glossy powder" (ref. 67, page 400). I believe their experiments were aimed toward the preparation of an easier to handle form of a Friedel-Crafts reaction catalyst for organic condensation reactions, since that is an important application for pure antimony(V) fluoride.

Four years later , it was found that the 75% by weight graphite-SbF $_5$ intercalated product had the extraordinary ambient electrical conductivity

of around one million ohm⁻¹cm⁻¹, which far exceeded that of pure silver, at $629,000 \text{ ohm}^{-1}\text{cm}^{-1}$, the previous record holder for electrical conductors (ref. 68, page 400). I believe that 75% SbF₅-graphite still holds the record for ambient electrical conductivity, although obviously the superconductors exceed this performance below their transition temperatures.

The antimony(V) fluoride probably forms a charge transfer compound with the graphite , with charge partially donated to the SbF₅ from the pi cloud over the carbon skeleton . Antimony(V) is a mild oxidizer ; its standard reduction potential at STP is $E^0 = 0.82$ V in a chloride environment (0.66 V in an oxide environment) . It should therefore act to polarize the pi XO in the graphite . An exchange equilibrium , strongly favoring the graphite , could conceivably be established in which a small population of pi XO electrons were resident near the antimony atoms . This would result in a sort of pseudo "mixed-valent" state being created in the graphite sheets , enabling the carbons' pi electrons to move more easily through the XO .

I doubt that any of the graphite carbons are actually oxidized to carbocations by the SbF₅; that would require a much more powerful oxidizer to accomplish. In fact, graphite has been cleanly oxidized to delocalized carbocations by the superelectrophilic oxidizer dioxygenyl hexafluoroarsenate, $O_2^+AsF_6^-$ (ref. 69, page 400), whose reduction potential must be around 3V or so. The AsF₆⁻ anions would have been deposited in between the carbon sheets as inert spectator ions, with ejection of oxygen molecules from the reaction mixture.

I should point out that electronegative atoms (such as the fluorine in the hydrogen fluoride molecule), or electrophilic atoms, such as highly oxidized metal atoms, are capable of polarizing the fairly strong sigma type of chemical bonds, as in H-F. It seems reasonable that they will polarize and distort to an even greater extent the "softer", more easily deformable pi bonds. We should therefore be alert to the possibility of observing some interesting electronic effects when these strongly electron-attracting chemical species are present in solid state materials. It is possible that such polarization effects may be the cause of the enhancement of the transition temperature in high T_c superconductors, as will be discussed later on.

If there is a polarized bilayer metallic bond in rhenium trioxide , might there also be one in chromium dioxide and niobium monoxide ? In the former compound , the chromium(IV) atoms are strongly oxidizing species , and should polarize the Cr-O pi XO surrounding the covalent skeleton . The ambient electrical conductivity of CrO_2 (10,000 ohm⁻¹cm⁻¹) is less than one tenth of that of ReO₃ (149,300) . Factors other than the state of polarization of the pi bond may also be significant in their effect on the conductivity . For example , there is one less formula oxygen atom in CrO_2 than in ReO₃ . Their crystal structures are quite different , and the metal-oxide distances are also dissimilar in the two materials .

In niobium monoxide, with an ambient electrical conductivity of around $50,000 \text{ ohm}^{-1}\text{cm}^{-1}$, there shouldn't be any significant polarization of its bilayer pi XO; if anything, the niobium in this compound is chemically reducing in nature. There will also be an appreciable contribution to the conductivity via the Nb-Nb bonds in the octahedral "metal cages". Direct comparison of NbO to ReO₃ and CrO₂ is difficult, since it has a crystal structure radically different than them, it has only one formula oxygen, and its unit cell dimensions are different from theirs. Nevertheless, in all three of these metallic solids, it is likely that a bilayer metal-oxygen pi XO forms a highly effective metallic bond in them. Whether or not, or to what extent this pi XO is polarized by redox-active metal atom components in the solid, and what effect such polarization might have in them, are questions that must be set aside for now. The bilayer pi XO remains a very useful concept that will be employed extensively throughout this narrative.

The Tungsten Bronzes and Perovskites

I mentioned earlier that if the rhenium trioxide supercube structure , " MX_3 ", contained a large cation , "A", then the resulting solid state structure AMX_3 was termed a perovskite , which was borrowed from the mineral of the same name . Perovskite mineral is calcium titanate , $CaTiO_3$, and has the generic perovskite crystal structure , shown on the next page . Many ternary compounds with extended atomic lattices are known to be perovskites .

Two reviews about perovskites are listed in ref. 70, page 400. Models of perovskites can be viewed in two ways, with the A cation in the center of the supercube (the "A type" unit cell), or with the M atom component in the center of the cube (the "B type" unit cell):



Figure 26 : The M3D model of the perovskite crystal structure , A type unit cell . For the mineral perovskite , $CaTiO_3$, the small red spheres are the octahedrally coordinated titanium(IV) atoms , the large aqua spheres represent covalent linear oxygen atom links , and the large central violet sphere represents a calcium cation . For example , see Smart and Moore's textbook , <u>Solid State Chemistry , An Introduction</u> , ref. 49 , page 397 , Figure 8.6 , p. 265 .

This is probably the commonest representation of the perovskite crystal structure found in chemistry texts, and the one I prefer. The B type of unit cell model is occasionally used as an illustration by some writers, especially when the A cation needs to be emphasized for some reason or other. The B type of model does this, and "hides" the M atom component in the interior :



Figure 27 : The M3D model of the perovskite crystal structure , B type unit cell . As in Figure 26, for the mineral perovskite , $CaTiO_3$, the violet spheres are Ca^{2+} cations , the small red sphere is Ti(IV), and the aqua spheres are covalent oxygen atoms . The full black lines represent covalent Ti-O bonds , while the dashed black lines are meant only to outline the cubic structure of the unit cell (Smart and Moore , Figure 8.7 , p. 265).

The transition metal bronzes are a family of solid state compounds with the perovskite structure (some of cubic symmetry, as shown in Figures 26 and 27, others of lesser symmetry); they are oxides of the transition metal element and a second metallic element, usually a very reactive reducer from the alkali, alkaline earth, or rare earth families.

Many of the elements can form perovskites as the M atom component, and the larger and more reactive atoms can participate in perovskites as the A component, but the term "bronze" is reserved for those perovskites that exhibit bright colors, a metallic luster, and a significant electrical conductivity. For example, the common laboratory chemical potassium iodate, KIO_3 , has the perovskite structure, but it is a white, water-soluble, salt-like crystalline substance, and therefore isn't a bronze.

Most, if not all of the transition metal elements can form perovskites as the M atom component, but again the bronze designation is usually applied to only nine of them : titanium, zirconium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, and rhenium; also, the actinide element uranium is said to form a series of bronze compounds (several reviews of the chemistry of the bronzes and of the tungsten bronzes in particular are listed in ref. 71, page 400).

The tungsten bronzes were first prepared by the prominent German chemist Friedrich Wöhler (1800-1882) in 1824, but have been studied extensively since about 1950. Apart from their striking colors and noticeable metallic luster, the bronzes were found to be excellent electrical conductors. The compound $K_{0.4}WO_3$, for example, has an ambient conductivity of 26,200 ohm⁻¹cm⁻¹. Some sodium tungsten bronzes have conductivities up to 70,000 ohm⁻¹cm⁻¹ (see Figure 2, p. 240, in the review paper by Shanks, Sidles, and Danielson, cited in ref. 71, page 400, for a graph of the electrical conductivity of alkali metal bronzes versus their alkali metal content expressed as a mole fraction). As with rhenium trioxide, however, few of the tungsten – or other – bronzes, despite their impressive ambient electrical conductivities, ever become superconducting, even very close to absolute zero. The highest transition temperature for an alkali metal tungsten bronze was 1.98 K, and tetragonal $K_{0.5}MOO_3$ has an exceptionally high T_c of 4.2 K.

The precursor structure to the tungsten bronzes is tungsten(VI) oxide , WO_3 , which has a distorted ReO₃ crystal structure . The tungsten bronzes may be thought of as WO_3 with varying mole ratios of zerovalent metal atoms inserted into the supercube centers . Tungsten trioxide itself is a yellow insulator ; the tungsten atoms' valence electrons (six each) are fully used in the W-O covalent bonds . Insertion of a zerovalent metal atom – let's take sodium as an example – into the supercube center will result in the powerfully reducing sodium atom donating its $3s^1$ valence electron to the WO₃ skeletal framework , with the electrostatic embedding of the sodium cation into the central cavity .

As with ReO_3 , we hypothesize that this "extra" valence electron will be located in the tungstens' unhybridized $6p_{x,y,z}$ AOs (sketch, middle of

page 147) . "Fully loaded" WO_3 , that is , $NaWO_3$, would thus be isoelectronic with ReO_3 . In practice , the mole ratio of inserted metal is always less than 1.00, which results in a NIOS mixed-valent condition of the tungsten atoms . For example , the compound $Na_{0.5}WO_3$ could be thought of as a "blend" of the two valence states , W(V) and W(VI), and could be represented (somewhat clumsily) as $Na_{0.5}W^{5.5+}O_3$. This is a true Robin-Day Class II mixed-valent compound , with separation of the tungsten atoms by oxygen atom links , and a complete blending of the W(V) and W(VI) valences . As such , and noting that they are true metals , I have placed the tungsten bronzes in Class 3 of the general classification of metallic solids .

As with rhenium trioxide (which could itself be considered as a sort of "bronze" compound), we anticipate that the pi XO in the tungsten bronzes is a bilayer metallic bond, and is likely polarized to a certain extent; W(VI) is a mild oxidizer, having $E^0 = 0.26$ V to W(V). This could provide at least part of a reasonable explanation for the excellent electrical conductivities of the tungsten bronzes, but an understanding of their visual appearance – bright colors and metallic luster – would require a more sophisticated physical approach for both qualitative and quantitative analyses.

Sulfur Hexafluoride and the sp³ds Hybrid Orbital

I would like to digress briefly to discuss the electronic structure of sulfur hexafluoride, SF_6 , with a specific reference to the involvement in it of the proposed new octahedral hybrid orbital, sp^3ds .

Sulfur hexafluoride is a very dense , chemically inert , colorless gas at room temperature . It resembles carbon dioxide in that its liquid phase exists only under high pressure . Its solid sublimes without melting , like dry ice . The SF_6 molecule has an octahedral structure , with six equally long S-F bonds . Its extraordinary chemical inertness , and resistance to attack by aggressive reagents , have been attributed to the steric hindrance of the fluorine atoms around the sulfur atom . Incoming nucleophiles merely bounce harmlessly

off the surrounding protective layer of fluorine atoms :



Figure 28 : An M3D model of sulfur hexafluoride, spacefill version (instead of the usual ball-and-stick model). The yellow center sphere represents sulfur, which is surrounded octahedrally by green fluorine spheres. The electronegative fluorines help to repel incoming nucleophiles, and will reduce the sulfur's electropositive "target area" to them.

There has been considerable argument and discussion in the literature concerning the electronic structure of sulfur hexafluoride . It is tempting to apply an sp^3d^2 outer octahedral hybrid AO to the sulfur atom , then place each of the six sulfur valence electrons in the s-type lobes . Overlapping these lobes with those from the six fluorine atoms (possibly having the unhybridized valence shell structure $2s^2 2p^5$, or in an sp linear or sp^3 tetrahedral hybrid AO) completes the SF₆ molecule .

It was pointed out, though, that in the pre- and post-transition metal elements, the d orbitals are either very diffuse, or form inner non-valence electron shells in the kernels. As such, they are unlikely to participate in hybrid AO formation in the valence shells :

"It was discovered that the d orbitals in some states of atoms like sulfur could be so diffuse that they could not reasonably be expected to participate to a significant extent in bonding" (ref. 72, page 401).

Reed and Weinhold rather more bluntly state (ref. 73, page 401):

"Models of SF₆ requiring sp^3d^2 hybridization should be discarded".

These latter authors favored an ionic model of bonding in SF_6 , and suggested that d orbitals could contribute to its stabilization via a backbonding process. They calculated the following contributions to the hybrid AO by native AOs in the sulfur atom : 32% by 3s ; 59% by 3p ; 8% by 3d ; and 1% by 4p . I'm surprised that no mention of the 4s AO was made in this analysis , since it and not the 4p AO is probably used in the metallic bond sigma XO of poly(sulfur nitride). Also , the 4s AO is lower in energy than either the 3d or 4p AOs ; refer back to Figure 4 on page 35.

What bothers me most about Reed and Weinhold's electronic structure is its ionic nature . Is sulfur hexafluoride an ionic gas ? No , I think it's really a covalently bonded molecule . We just have to find a suitable combination of six native orbitals to comprise the new octahedral hybrid orbital .

My suggestion for the hybrid AO in SF₆ would therefore be somewhat like the Reed and Weinhold combination of AOs, but substituting the 4s for the 4p AO, and totaling up the 3s and 4s share to about a third of the overall contribution to the hybrid AO: 33% by 3s and 4s; 59% by 3p; and 8% by 3d. This would be the sp³ds hybrid orbital. I would add the important provision that the energy of the nd orbital making the contribution to an sp³ds hybrid AO generally should be roughly comparable to that of the n and n+1 s and p native orbitals contributing to it.

Construction of the new sp³ds AO from its component native AOs can be rationalized as follows: $3s + 3p_x = (sp)_x$; $4s + 3p_y = (sp)_y$; and $3d_z^2 + 3p_z = (dp)_z$ [these are all linear hybrid orbitals]. Then, $(sp)_x + (sp)_y + (dp)_z = sp^3 ds$, an octahedral hybrid orbital. It should be noted that there are chemical analogues of SF₆: for example, PF₆⁻, AsF₆⁻, SbF₆⁻, and SiF₆²⁻. The AlF₆³⁻ anion, if it is indeed such, in the important industrial chemical cryolite, Na₃AlF₆ (the molten solvent for alumina in the electrowinning of aluminum metal from bauxite ore) may also be isoelectronic with sulfur hexafluoride.

Tin(III) Phosphide

In 1970 Donohue published his synthesis and study of an interesting new metallic solid , tin(III) phosphide , SnP (ref. 74 , page 401) . It was prepared by the reaction of powdered tin with red phosphorus at 800 °C and under 65 kbars pressure in an anvil press . The product , SnP , had the rocksalt crystal structure , but was composed mostly of a tetragonally-distorted phase . When this phase was heated to 100-200 °C under ambient pressure , it was converted irreversibly into the cubic form , with a = 5.54 Å .

Several properties of interest to us of the tetragonal and cubic phases of tin(III) phosphide, with a comparison to white tin metal, are summarized in the table below :

Comparison of Tin Metal and Tin(III) Phosphides

Material Ambient Elec. Cond.		Superconductor Tc	<u>Sn-Sn length</u>	
Tin Metal	87,000 ohm ⁻¹ cm ⁻¹	3.7 K	3.16 A	
SnP cubic	50,000	2.8 - 4.8	3.92	
SnP tetrag.	50,000	none	3.83	

Although the tetragonal form of SnP fails to become superconducting , its electrical conductivity at liquid helium temperature has risen to about 333,000 ohm⁻¹cm⁻¹ , and both it and the cubic form of SnP are true metals . It would be interesting to describe and compare the crystal and electronic structures of the SnP phases , and those of tin , in VB terms .

All three materials have fairly simple crystal structures . Cubic SnP has an

undistorted rocksalt structure :



Figure 29 : The M3D model of cubic tin(III) phosphide . The aqua spheres are octahedrally-coordinated tin atoms , and the brown spheres represent octahedrally-coordinating phosphorus atoms .

Tin compounds are generally covalent in nature , especially those of Sn(IV), and even those of the lower-valent Sn(II). Thus , SnP will have a covalent skeletal framework , as it can be thought of as really being $Sn(IV)(e^{-})P(III)$. That is , the covalent framework is that of tetravalent tin , with the "extra" electron in a metallic bond , and delocalized over the entire crystal structure .

In one formula unit of SnP, there will be six Sn-P covalent bonds, which require twelve valence electrons for completion. The phosphorus atoms, which are $3s^2 3p^3$ electronically (valence shell), can supply five of them. The tin atoms, which have the $4d^{10} 5s^2 5p^2$ configuration, must provide seven more valence electrons to the covalent skeleton. Since there are only four electrons in tin's "normal" valence shell, it must "dig down" into its 4d shell to obtain more. The 4d electrons are roughly at the same energy level as the 5 s-p electrons; see Figure 4, page 35. It should be possible, then,

for the tin atoms to utilize some of the 4d shell electrons for the allimportant step of skeletal construction in the crystal. On the other hand, phosphorus doesn't have any 3d electrons to use for skeleton building, so tin has no choice but to include several of its 4d electrons for this purpose.

To get the full complement of the seven required valence electrons, tin must include four of the higher energy $e_g 4d$ electrons in the construction of its VB hybrid AO (since there is an octahedral coordination around each tin atom). That is, the tins will use an inner octahedral hybrid AO to build the covalent framework : $(4d_x^2 \cdot y^2)^2 + (4d_z^2)^2 + 5s^2 + 5p_x^2 + 5p_y^0 + 5p_z^0)$. These six native orbitals, together with their contained valence electrons, will be blended together to form the octahedral hybrid AOs, with a single electron in each of five s-type lobes, plus two electrons in the sixth one (since we need a contribution of seven electrons from tin). That will leave one extra unused electron to be promoted up into the 6 s-p orbitals, which we anticipate will participate in the metallic bond in SnP.

Meanwhile , the phosphorus atoms will also use octahedral hybrid AOs to participate in the rocksalt structure . This is where the sp³ds hybrid AO will likely come into play , as it probably does in sulfur hexafluoride and its isoelectronic cousin , the PF_6^- anion (page 159) . The five valence shell electrons in the phosphorus atoms will be placed in five of the six s-type lobes of this hybrid AO , then the tin and phosphorus atoms will be "polymerized" together to form the rocksalt extended lattice structure of cubic tin(III) phosphide .

The high electrical conductivity of SnP, and its nature as a true metal, suggest that the metallic bond in this solid is comprised of a nodeless XO with strong overlapping of its component AOs. Given the rocksalt structure of the compound, we have to accept that the outer orbitals of the phosphorus atoms must participate in the XO. Since all of the phosphorus atoms' valence electrons are used in the covalent bonds, the phosphorus can only contribute empty frontier orbitals to the XO. If we further accept that the phosphorus uses sp³ds hybrid AOs for the covalent bonds, its 3s and 4s AOs will be unavailable for the XO. That leaves the 5s AOs, but they might be at too high an energy level above the 3 s-p valence level in phosphorus

(refer back to Figure 4, page 35) to be usable. That is, a free electron in the metallic bond might "avoid" the phosphorus atoms, being too strongly destabilized in the 5s regions. They would be "pinned" to the tin atoms, and the material would be an insulator or semiconductor.

The most likely scenario for the metallic bond in cubic SnP is the phosphorus $4p^0$ AOs overlapping continuously with the tins' $6p^1$ AOs to form a nodeless three-dimensional pi XO in the lattice. The 4p AOs are both available and are at a somewhat lower energy level than the 5s AOs.

The inert pair effect (see Figure 13, page 69) is observed in the crystal structure of the tetragonal form of tin(III) phosphide :



Figure 30 : the M3D model of tetragonal tin(III) phosphide . The small blue spheres are tin atoms , and the larger brown spheres represent the phosphorus atoms in this compound . The full black lines are covalent Sn-P bonds ; the dashed black lines outline the tetragonal shape of the unit cell of SnP . The empty spaces underneath the tin atoms actually contain the inert pairs of valence electrons (not shown) . This model was based on Donohue's

Figure 1, p. 336 of his article (ref. 74, page 401).

Again , the tins have the inner octahedral hybrid AOs , and again there are singlet valence electrons in five of its s-type lobes . This time , though , the sixth and seventh electrons form the inert pair in the sixth lobe . The eighth valence electrons are extra to the covalent skeleton , as before , and will be promoted to the 6 s-p native frontier orbitals , where they will create the metallic bond in tetragonal SnP .

The phosphorus atoms will use the square pyramid hybrid AO, which is usually the sp³d AO $[3s^2 + 3p_x^{1} + 3p_y^{1} + 3p_z^{1} + (3d_x^{2} \cdot y^{2})^{0}]$, in this system. The five valence electrons are assigned to each s-type lobe of the hybrid AO, and the tin and phosphorus atoms are polymerized together to form the covalent skeleton of tetragonal SnP. The inert pairs of electrons on the tins aren't bonded to the phosphorus atoms, as with the cubic phase of SnP, but instead occupy the interlayer space, causing a noticeable bulge in the layers of atoms, the tin atoms pushing upward and the phosphorus atoms pushing downward.

If the tin atoms in the tetragonal phase do indeed use the sp³d hybrid AO for framework building, then their 4s AOs will be available, and at a reasonable energy level, for overlap with the tins' 6s AOs to form a sigma XO as the metallic bond in the solid. This is quite interesting, at least by comparison with the cubic form of SnP, which might have a pi XO as its metallic bond. Might that be all the difference required to result in the latter cubic phase becoming a superconductor at temperatures near absolute zero, while the former tetragonal phase fails to do so ?

Tin : The Inside Story

The third material listed in the table on page 160 is tin (also called white tin , β -tin , or tin metal) , and I include it for discussion because , interestingly enough , it also exhibits the "inert pair" effect . Wells (ref. 21 on page 394 , p. 495) has pointed out a simple chemical test for the presence of the inert

pair $(5s^2)$ of valence electrons on the tin atom in the metal . When gray tin, with the diamond crystal structure and **no** inert pairs, is dissolved in acid, the tetravalent $(5s^0)$ compound is formed; but when tin metal is similarly dissolved in acid, the divalent $(5s^2)$ compound is obtained:

white Sn +	concentrated HCl (aq)	 SnCl ₂ .2H ₂ O;
gray Sn +	concentrated HCl (aq)	 SnCl ₄ .5H ₂ O.

This suggests that first, the tins' $5s^2$ valence electrons are chemically more resistant to removal by oxidation – "inert" – than are its $5p^2$ electrons, or for that matter, singlet electrons in hybrid AOs in tin and its compounds; and second, we infer that there are inert pairs of electrons in tin metal itself.

The crystal structure of white tin seems to hint at the presence of inert pairs :



Figure 31 : the M3D model of the crystal structure of tin metal . This model was based on Müller's Fig. 57 , p. 110 in ref. 23 , page 394 .

The inert pairs are presumed to be located in the long axial "bonds", which may not be bonds at all, as we will see.

In this structure , each tin atom is surrounded by six neighbors , with four short Sn-Sn bonds (3.016 Å) and two longer axial "bonds" (3.175 Å) ; the bond lengths in gray tin are a uniform 2.81 Å by comparison . In white tin we have the tetrahedron – somewhat squashed – found in gray tin , plus the inert pair , plus the metallic bond . Clearly , the normal valence $(5s^2 5p^2)$ electrons of tin , plus some of its 4d level electrons , must be involved in the bonding in tin metal , as with the two forms of SnP . The presence of the directional inert pair in the structure indicates that the Sn-Sn skeletal bonds are covalent in nature , and that the tin atoms use hybrid AOs with valence electrons to form those bonds . As usual , the metallic bond in tin will be an opportunistic "add-on" that will form over the skeleton when extra , unused electrons enter frontier orbitals capable of crystal-wide overlapping .

There is no really suitable single hybrid AO that seems appropriate to the crystal structure of white tin, so I will suggest instead that **two** hybrid AOs might conceivably provide an overall satisfactory geometry to the crystal :



The first is the "classic" sp² trigonal planar hybrid AO, so familiar in organic chemistry .The inert pair occupies one of the three s-type lobes of the composite orbital, with singlet electrons in each of the other two. The second is the bent d² hybrid AO, with a singlet electron in each of the two s-type lobes . The $4d_{x-y}^{2}$ and $4d_{xy}$ native AOs would be used to construct this d² composite orbital.

The two hybrids are fused on each tin atom to provide the overall geometry for the formation of the white tin crystal structure :



Composite sp2+d2 hybrid orbital

In this scheme, the nominally $5s^2$ inert pairs would occupy the space generally assigned to the long axial "bonds" in the structure. The lack of covalent bonds between the sheets of tetrahedrons would lead to a weaker structure than if they were really there, and indeed tin is a rather soft, low melting (232 °C) metal that emits a "squeak" when bent. The electronic structure of white tin is summarized in the simplified sketch below :



 \mathbf{x} = inner 4d electron , valence electron , or inert pair electron

y = neighboring valence electron in Sn-Sn covalent bonds

Six of the eight electrons drafted by tin for this structure (four normal valence 5 s-p electrons , plus four more hypervalent 4d electrons) are

accounted for in the above scheme . Four are singlets used in the Sn-Sn covalent bonds of the squashed tetrahedron , plus two more form the inert pair . The remaining two electrons are surplus to the skeleton , and will enter higher energy level frontier orbitals . The $5p_z$ native AO , while unused for the skeletal hybrid AOs , would likely be strongly destabilized by the presence of the inert pairs in their space . The inert pairs would strongly repel any electrons trying to enter the $5p_z$ AOs in this structure . The next available frontier orbitals would be the 6 s-p AOs , which is where I would predict the metallic bond is located in white tin ; that is , mostly in the 6s sigma XO , plus some leakage into the 6p pi XOs , thus permitting tin to have metallic properties , as is the case with mercury (6s²) , for example , or magnesium or zinc .

The study of the two forms of tin(III) phosphide has provided us with the insight necessary to propose a reasonable electronic structure for white tin in VB terms. We have thereby been able to look under the shiny surface of tin to examine the framework of covalent bonds inside the crystal that provides most of the bonding strength in that metal.

The Zintl Concept and Zintl Structures

Around 1932-33 the German solid state chemist Eduard Zintl (1898-1941) and his students were studying intermetallic compounds such as sodium thallide , NaTl . It was noted that on occasion , when two metals were combined together , the resulting material was more of a chemical compound than a metal alloy . The intermetallic compounds would often be rather brittle substances with poor electrical conductivities in the semiconductor range . Some even resembled salt-like ionic solids , without any noticeable metallic luster . There seemed to be no logical explanation for why the intimate mixture of two genuine metals would result in a product having greatly diminished metallic properties .

The combination of equimolar quantities of sodium (m.p. 98 °C) and thallium (m.p. 303 °C) metals will produce the intermetallic compound

sodium thallide, NaTl (m.p. 305 °C, without decomposition; I haven't been able to find any other properties of NaTl, such as physical appearance or electrical conductivity, especially over an extended temperature range. See ref. 75, page 401).

Sodium thallide was found to have a crystal structure resembling, although not exactly like, rocksalt:



Figure 32 : the M3D model of sodium thallide , NaTl . The green spheres are thallium atoms , connected by solid black covalent bonds , and the smaller red spheres represent sodium cations . The dashed black lines outline the cubic structure of the crystal . This model was based on the sketch of the NaTl structure in Müller's Figure 65 , p. 123 , in ref. 23 , page 394 .

Zintl proposed that the powerful reducer sodium donated its $3s^1$ valence electron to the thallium , which would form the thallide anion , Tl^{1-} :

 $Na^{0} (3s^{1}) + Tl^{0} (6s^{2} 6p^{1}) \longrightarrow Na^{1+} (3s^{0}) + Tl^{1-} (6s^{2} 6p^{2}).$

I haven't read Zintl's papers in their original German text, so I can't state

with certainty that he expressed his findings or theory in VB terms . The interpretation of them in such terms , though , suggested that the thallide anions used hybridized atomic orbitals of the tetrahedral sp^3 variety to form a diamond-like skeleton in the crystal , in whose interstices the sodium cations were periodically embedded . Zintl discovered that the sodium and thallium atoms in NaTl both had similar radii of 1.62 Å (ref. 76 , page 401) . This result can be compared to the known radii of sodium and thallium atoms in the parent metals , ionic salts , and covalent compounds :

Atomic Radii of Sodium and Thallium

	<u>metallic</u>	<u>ionic</u>	<u>covalent</u>	<u>in NaTi</u>
Sodium	1.91 A	1.16 A (1)	1.54 A	1.62 A
Thallium	1.71	1.64 (2)	1.52	1.62
(1) 6-coord	dinate Na ¹⁺	(2) 6-coord	dinate TI ¹⁺	

Addition of the sodium's valence electron to the thallium's 6p orbital shouldn't increase the thallium atom's radius very much , if at all . We would expect a significant decrease in the radius of the sodium atoms , though , more than is actually observed in NaTl . Possibly the sodium cations are able to attract the sigma MO electrons in the tetrahedral Tl-Tl bonds , and in polarizing them , draw off and retain a fraction of them . In other words , NaTl may be a charge transfer compound $(Na^{\delta 1+}Tl^{\delta 1-})$ and **not** fully ionic $(Na^{1+}Tl^{1-})$.

Another interesting intermetallic compound is strontium digallide, $SrGa_2$, in which the gallium atoms form graphite-like sheets with the "spent" strontium cations intercalated between them (Figure 33, next page). In this case, each of the strongly reducing strontium atoms donates its two valence electrons to two gallium atoms :

$$Sr(5s^2) + 2 Ga(4s^2 4p^1) \longrightarrow Sr^{2+}(5s^0) + 2 Ga^{1-}(4s^2 4p^2)$$



Figure 33 : the M3D model of strontium digallide , $SrGa_2$. The aqua spheres are strontium cations , and the smaller red spheres represent anionic gallium atoms . The flat sheets of gallium atoms resemble the structure of graphite , with an extended array of fused hexagonal rings of atoms . This model is based on the sketch of the structure of $SrGa_2$ in Figure 65 , p. 123 , in Müller's textbook , ref. 23 , page 394 .

In this case it is thought that the gallium anions form trigonal planar sp² hybrid orbitals with their four valence electrons, $\sigma_a^{\ 1} + \sigma_b^{\ 1} + \sigma_c^{\ 1} + 4p_z^{\ 1}$, which then overlap continuously in the solid to form the graphite-like sheet structure. The strontium cations are electrostatically intercalated between the gallium sheets. The metallic bond here would be the 4p pi XO.

If this picture of the electronic structure of sodium thallide and strontium digallide is correct, we would expect to find experimentally that the former solid is a pseudometal (direct temperature-conductivity relationship), while the latter compound is a true metal, with an inverse temperature-conductivity relationship. In NaTl, the nodal separation [band gap] between the thallium atoms must be quite narrow, narrower than in gray tin, which has an ambient electrical conductivity of 2090 ohm⁻¹cm⁻¹ (page 30).

The ambient conductivity of NaTl should exceed this figure ; however, I am not aware of any published electrical conductivity data over a range of temperatures for NaTl, studied in the form of a bulk sample or purified single crystal.

In the case of strontium digallide , if the metallic bond in it is indeed the 4p pi XO , it should behave as a true metal , and its ambient electrical conductivity – I'm guessing – would be roughly comparable to that of pure elementary gallium , which is $73,530 \text{ ohm}^{-1} \text{cm}^{-1}$.

An analogue of strontium digallide , with lower atomic weight elements , and isostructural with it , is the interesting compound magnesium diboride , MgB_2 . This material caused a stir in the solid state science community in the Spring of 2001 , when a team of Japanese researchers announced that it was a "medium temperature range" superconductor , with a transition temperature of $T_c = 39$ K (ref. 77 , page 402) . While this is far lower a temperature than the 133 K of the mercury-based copper oxide superconductor , it is nevertheless quite a remarkable finding from two points of view . First , it is one of the highest transition temperatures found for a chemical compound not containing copper ; and second , it is isoelectronic with graphite , which apparently never becomes superconducting , even very close to absolute zero .

Metal diborides are a well-known class of boron compounds (for example , see ref. 78 , page 402) . Both magnesium and aluminum diborides are offered commercially , eg. from Alfa Aesar . Has aluminum diboride been examined for possible superconducting properties ? It might be interesting to dope magnesium diboride with increasing mole ratios of aluminum diboride to examine the effect on the superconducting T_c of increasing the free electron density in the 2p pi XO metallic bond of the boron layers :

x MgB_2 + (1-x) AlB_2 \longrightarrow $Mg_x Al_{1-x} B_2$, where "x" is a mole fraction between zero and unity.

Going in the opposite direction , that is , decreasing the free electron density in the borons' metallic bond , might be achieved by doping MgB_2 with a

compound MB_2 , where "M" is formally univalent . Alkali metal compounds with boron are known, but not in the desired MB_2 stoichiometry . The reaction of thallium metal (caution : highly toxic !) with boron in a one-to-two mole ratio, contained in a tightly sealed ampoule at high temperature and pressure – possibly in an anvil press ? – might produce the compound TIB_2 , with the formally univalent thallium cations located between the boron sheets . Doping MgB_2 with this latter material, as with AIB_2 above, should result in a decreased free electron density in the borons' 2p pi XO. The solid state chemistry of the metal diborides, new methods of synthesizing them, and their electronic properties, are all potentially fruitful new fields of endeavor for researchers.

Purple Plague, Al₂Au

Before leaving the topic of Zintl structures and intermetallic compounds , I wanted to discuss briefly another such material , "Purple Plague", aluminum auride , Al_2Au . Actually , while Al_2Au is an intermetallic compound , it isn't a Zintl structure , but nevertheless its chemical bonding is quite interesting and deserves some comment .

Both gold and aluminum are used extensively in modern electronics equipment . It was found that if exposed surfaces of gold and aluminum , in close proximity , were warmed or heated , a purple metallic substance would sometimes gradually form between them . Because this new material is a good electrical conductor , the gold and aluminum components would short out , causing the equipment to malfunction . The detested purple solid came to be known as "purple plague" , and was found to be the intermetallic compound aluminum auride (Ellis et al. , ref. 66 , page 400 , p. 119) .

Actually, purple gold – as it has been called – has been known for quite a long time. I came across a reference to it from 1892. It consists of 78.49% gold and 21.51% aluminum by mass, and would thus correspond to a gold "alloy" of about 19 karats or so (24 karats is pure gold). I doubt, though, that purple gold has ever been, or ever will be used for jewelry purposes.

First, intermetallic compounds are generally rather brittle, so I suspect purple gold would likely be unworkable at a goldsmith's bench. Second, people like gold for jewelry because of its pretty golden color. Purple would probably be considered too bizarre a color for gold jewelry.

Several selected properties of purple plague , and of its component elements aluminum and gold , are shown in the following table :

<u>Material</u>	<u>MP.</u>	<u>S.G.</u>	<u>M-M(1)</u>	<u>Elec. Cond.(</u> 2)	<u>Tc</u>
Aluminum	660 C	2.70	2.863 A	365,900 ohm ¹ cm ¹	1.18 K
Gold	1063	19.3	2.884	440,300	none
Al ₂ Au	1060	7.60	2.58	119,000	0.074
(1) AI-AI , Au-Au , and AI-Au bond lengths respectively (2) at 300 K					

Selected Properties of Aluminum, Gold, and Purple Plague

The melting points of gold and purple plague are nearly similar , suggesting that the chemical bonding in the latter solid is more closely related to that in gold than in aluminum . The specific gravities suggest , in this same theme , that purple plague might be thought of as an "expanded form" of gold . The metal atom-to-atom bond lengths aren't directly comparable , since both gold and aluminum have the simple fcc/ccp atomic packing structures of the metallurgical metals , while purple plague has the fluorite (CaF₂) crystal structure typical of chemical compounds , not of metals and alloys . The fluorite structure is shown in the M3D model presented in Figure 19 , page 99 ; in this case , the smaller red spheres would be the gold atoms , and the larger green spheres would represent aluminum atoms .

Purple plague is a true metal and a superconductor, the latter only at extremely low temperatures. Comprehensive electrical studies of Al_2Au and related compounds such as Ga_2Au and In_2Au have been carried out by J.-P. Jan and W.B. Pearson, and by J.H. Wernick et al.; see ref. 79, page 402. A conductivity-versus-temperature graph for these three compounds is presented by the former authors in their Figure 1, p. 280, of ref. 79.

Although aluminum is a fairly strong reducing agent , and gold is capable of accepting an electron from really powerful reducers (as in the ionic solid cesium auride , Cs^+Au^-), relatively little charge – about 0.18 e⁻ – has apparently been transferred to gold in aluminum auride (ref. 80 , page 402). The lower electrical conductivity of Al₂Au relative to gold and aluminum suggests that some of the valence electrons that would normally constitute the s-p conduction band , or sigma-pi XOs , as in gold and aluminum , have been diverted to form covalent bonds in the compound . However , as purple plague is a true metal and superconductor , it still must have a nodeless metallic bond as its main pathway for the electrical current .

The gold atoms in Al₂Au are eight-coordinated , with gold in the center of a cube of aluminum atoms . Assuming that there actually are covalent Al-Au bonds in the material , the VB hybrid orbital corresponding to this geometry about gold would be the face-centered prism , d^5sp^2 ; refer back to Table 3 , page 64 . The "Coordinated Polymeric Model" of covalent bonding in extended atomic lattice compounds , discussed above on page 71 , proposes that entire outer shells of electrons , and not just the usual limited numbers of valence electrons , may be brought into the covalent bonding of atoms with higher coordination numbers . This will be necessary in the case of purple plague .

The gold atoms in the compound have eight covalent Au-Al bonds per formula unit . They will therefore require sixteen valence and hypervalence electrons to complete . Gold's outer shells have the normal configuration of $5d^{10} 6s^1$. All five 5d AOs , complete with their contained electrons , will be used to form the d^5sp^2 hybrid AO . Each aluminum atom will provide three valence electrons $(3s^2 3p^1)$ to fill its tetrahedral (sp^3) hybrid AO , for a total of six electrons contributed . That completes the eight Al-Au covalent bonds per formula unit . However , the gold's $6s^1$ valence electron is unused in the formation of the fluorite crystal's skeleton , and will provide the metallic bond in the structure . It will likely end up in the unused $6p_z$ AO , a relatively minor promotion from the 6s AO . Looking at a simplified model of Al₂Au (next page) , we can see that the gold atoms are lined up in layers that might reasonably permit a side-to-side overlap of the voluminous $6p_z$ AOs to form a pi XO in the crystal . This nodeless XO could



Figure 34 : the M3D model of aluminum auride , "purple plague". The larger yellow spheres portray gold atoms , while the smaller blue atoms represent aluminum atoms . This is a simplified version of the fluorite structure . It was based on Figure 5.20A on p. 118 of the textbook , <u>Teaching General Chemistry</u>, <u>A Materials Science Companion</u>, by A.B. Ellis et al. (ref. 66 , page 400) . The black lines between the gold atoms could represent the $6p_z$ pi XO metallic bonds in the crystal .

reasonably serve as the metallic bond in the solid . This proposed electronic structure is summarized in the diagram at the top of the following page .

Ellis et al. (ref. 66, page 400, their p. 147) describe a simple semimicro preparation of purple plague from the reaction of two molar equivalents of aluminum powder mixed with one molar equivalent of gold powder. The reactants are combined in a small quartz tube, and are heated together until the aluminum component melts; at that point, the reaction of the two metals becomes exothermic, with the rapid production of purple aluminum auride.

Let's suppose that the metallic bond in Al_2Au actually is the $6p_z$ pi XO in the layers of gold atoms, ignoring the aluminum atoms. In pure Al_2Au each gold atom contributes a single valence electron to the XO. Suppose also we





were to replace an aluminum atom in the compound with one that will contribute only two valence electrons to the covalent framework of the crystal , rather than aluminum's three electrons . In this case , a gold atom would be obliged to surrender its normally free $6s^1$ (or $6p_z^1$) electron to the skeleton , in accordance with the Aufbau principle . That is , formation of the lower energy covalent skeleton will take priority over that of the higher energy metallic bond . Then , a "hole" would be produced in the $6p_z$ pi XO over the gold layers . Additional doping of the compound with more divalent metal atoms would produce more vacancies in the pi XO . Introducing the holes , or vacancies , into the pi XO might result in a more favorable environment for superconductivity , raising the transition temperature for aluminum auride from a chilly 0.074 K to a higher value , by analogy with the electronic condition of many mixed-valent Class 3 compounds .

Dopants such as magnesium and zinc in purple plague might be useful in this regard . Zinc could have an advantage over magnesium , since its compounds tend to be more covalent in nature than those of magnesium (compare the ionic MgO and MgCl₂ versus the covalent ZnO and ZnCl₂) :

 $(2-x) Al^0 + x Zn^0 + Au^0 \longrightarrow Al_{2-x} Zn_x Au$,

where "x" is a mole fraction taken experimentally between zero and two theoretically ; in reality it would be a very low quantity , probably no more than 0.25 in actual practice .

Purple plague is an interesting and instructive metallic solid : to theorize about ; to experiment with ; and of course , to look at .

Controlled Valence in Mixed-Valence Chemistry

I pointed out earlier , on pages 39-41 inclusive , in the new proposed general classification of metallic solids , how important a role mixed-valent compounds play in the chemistry of the metallic bond . Four classes of these materials (3 , 4 , 7 , and 8) are comprised of mixed-valent compounds in various structural arrangements . It seems fitting , therefore , to at least briefly discuss a key chemical process in the synthesis of mixed-valent compounds , that of **controlled valence** . We'll see later how controlled valence played a critical role in the development of high transition temperature superconductors .

An outstanding pioneer in the rational synthesis of mixed-valence compounds, and originator of the controlled valence process for producing them, was Evert Johannes Willem (E.J.W.) Verwey [Dutch spelling: Verweij]. He was born in Amsterdam, Holland, on April 30, 1905. Verwey joined the Philips Electronics Company's Research Laboratory in Eindhoven, the Netherlands, in 1934, becoming its Director in 1946. He retired from Philips in 1966. While at Philips, Verwey and his co-workers studied several solid state systems such as spinels and rocksalts, discovering that those with mixed-valent transition metal cations often had useful electronic properties, such as greatly enhanced electrical conductivity. He referred to the synthesis technique used to produce these new mixed-valent compounds as "induced valence" (ref. 81, page 403), but that term seems to have been replaced in later years by the present name, "controlled valence". I don't think that Verwey's important contribution to solid state chemistry has really received the recognition it so richly merits , although admittedly this comes with the benefit of some hindsight (as in the advent of the high T_c superconductors). I would like to take this opportunity to thank Ms. Miriam Mobach , Public Relations Assistant at the Philips Electronics Research Laboratory , Eindhoven , the Netherlands , for providing me with detailed information on Verwey's life and career up to his retirement from Philips in December , 1966 .

One interesting solid state system investigated by Verwey and his fellow researchers at Philips was doped nickel(II) oxide (ref. 81, page 403). Pure, virgin nickel(II) oxide, NiO, is a green, refractory (m.p. 1984 °C) solid, although the commercial chemical is generally black, which is caused by the unavoidable slight oxidation of some of the Ni(II) to Ni(III) during processing. Nickel oxide has the rocksalt crystal structure, which is somewhat distorted from cubic symmetry, a result of the high spin electronic configuration of the Ni²⁺ cations in the crystal, with the consequent asymmetrical "bulging" of the 3d eg orbitals. Octahedrally coordinated Ni²⁺ can never be low spin; in simple Ni(II) salts, the 3d orbital electron configuration is always $d_{xy}^2 d_{xz}^2 (d_{x^2-y}^2)^1 (d_z^2)^1$. In these salts, where magnetic dilution is observed, their magnetic susceptibilities usually conform fairly well to the simple relationship, $\mu = [n(n+2)]^{\frac{1}{2}}$ BM (spin only); refer to page 136 above.

Nickel(II) oxide is antiferromagnetic at room temperature , with its Néel temperature , $T_N = 525 \text{ K} (252 \text{ °C})$, a remarkably high value [from the <u>Handbook of Chemistry and Physics</u>, 82^{nd} edition , 2001 , p. 12-125]. Its 3d e_g singlet electrons have an increasingly antiparallel orientation with respect to each other , in a three-dimensional pattern in the crystal , as the solid is cooled down more and more . The intervening oxide anions apparently help in this magnetic ordering by the process of superexchange .

Nickel(II) oxide was at the center of some controversy at one time, leading to a temporary crisis in the electron theory of metals. It was predicted from band theory that NiO should be a metallic solid and an electrical conductor, since the Fermi level in it was originally thought to lie in the nickel 3d orbitals. However, nickel oxide is actually an insulator. The solution to this perplexing problem is explained in W.J. Moore's excellent textbook, <u>Seven</u> <u>Solid States</u>, cited in ref. 14, page 392. Moore devotes an entire chapter (5, pp. 133-162) to nickel oxide, so the interested reader is best referred to this source.

Verwey and co-workers found that doping nickel oxide with lithium cation , that is , a gradual replacement of Ni^{2+} with Li^{1+} , while still retaining the cubic rocksalt structure , resulted in it changing from an insulator into a semiconductor . The chemical reaction they investigated was :

$$\frac{1200 \text{ °C}}{1200 \text{ °C}}$$
 + (1-x) NiO + $\frac{14}{4} \times O_2(g)$
air Li_x Ni_{1-x} O,

where "x" is a mole fraction taken experimentally from zero to 0.5, that is, from NiO (zero) to LiNiO₂ (x = 0.5), where nickel is in the trivalent oxidation state. In actual practice, it seems that the upper limit of lithium substituted was 0.9% by mass of lithium cation, at which point the ambient electrical conductivity of the doped product was 0.8 ohm⁻¹cm⁻¹, making it a fair semiconductor. For each lithium cation added to the structure, a nickel(II) cation was oxidized (by the atmospheric oxygen) to Ni(III). In that way, a precise electrical charge balance was maintained in the crystal at all times.

This system might also be investigated by a second method , in a two-step procedure . First , the pure , well-characterized nickel(III) dopant , $LiNiO_2$, could be prepared , possibly by the reaction :

$$\frac{1200 \text{ °C}}{1200 \text{ °C}} + \text{NiO} + \frac{1}{4} \text{ O}_2(g) \xrightarrow{1200 \text{ °C}} \text{LiNiO}_2 + \frac{1}{2} \text{ CO}_2(g).$$

In the second step , the nickel(II) oxide substrate would be doped with increasing mole fractions of the Ni(III) dopant , $LiNiO_2$:

x
$$\text{LiNiO}_2$$
 + (1-2x) NiO \longrightarrow $\text{Li}_x \text{Ni}_{1-x} \text{O}$;
again, "x" is a mole fraction taken between zero and 0.5. This method should provide a series of rocksalt compounds of lithium-doped NiO whose physical properties, including electrical conductivity, can be studied.

Since doped NiO is a conductor , it must have a functional pathway for the flow of free electrons in the solid . It apparently has semiconductor properties ; that is , I assume it has a direct temperature-conductivity relationship . If so , $\text{Li}_x \text{Ni}_{1-x} \text{O}$ must be a pseudometal , utilizing a nodal sort of XO as its metallic bond (I have placed it in Class 7 of the general classification of metallic solids ; refer to page 58) . One such nodal XO in doped NiO might be formed from the continuous overlap along the z axes in the crystal of the nickels' $(3d_z^2)^1$ AOs with the linear hybrid $(2sp_z)^4$ AOs on the oxide anions :



If the oxide anion can't form what is , after all , a covalent hybrid AO , then the unhybridized $2s^2$ AO , with a positive symmetry , would be a suitable candidate for the XO . In both cases a nodal crystal orbital would result , which is appropriate to the semiconducting pseudometal . Also in both cases a bilayer metallic bond (refer back to page 148) would be formed in the crystal , with the higher energy level nickel free electrons "floating" on top of the lower energy level oxide valence electrons . We can predict from this simple model that lithium-doped , semiconducting nickel oxide should be a half-metallic antiferromagnet , by analogy with chromium dioxide (refer back to page 137) . That is , the $(3d_x^{2-2})^{1}$ singlet electron will participate in the collective antiparallel magnetic coupling with other such electrons throughout the solid , resulting in the observation of antiferromagnetism in nickel oxide (but is Li_x Ni_{1-x} O antiferromagnetic also ?) , while the $(3d_z^{2})^{1}$ electrons will participate in the sigma XO that functions as the metallic bond in the doped NiO . If this is true , then why is pure NiO an insulator ? The answer may be that nickel(II) oxide could be considered as a latent or potential metallic solid . The metallic bond XO , with its necessary "extra" valence electrons , are in place , but those electrons are "frozen" or – to use the common phrase in solid state chemistry – are pinned to their respective atomic kernels . The pinning forces are described in works more technical than this one ; for example in W.J. Moore's nice textbook , <u>Seven Solid States</u> , referred to above . I am more interested in what unpins the valence electrons and frees them to move through the metallic bond in the crystal .

Note that the series of compounds $\text{Li}_x \text{Ni}_{1-x} \text{O}$ are Robin-Day Class II mixedvalent in nature . They each contain a certain amount of Ni(III) species blended into the Ni(II)-oxide matrix . It turns out that Ni(III) is a fairly strong oxidizing agent , at $\text{E}^0 = 1.17 \text{ V}$ with respect to Ni(II) . Compare this to the value of $\text{E}^0 = 0.82 \text{ V}$ for the antimony(V) in the SbF₅ which so successfully polarizes the metallic bond in graphite (page 151) , dramatically increasing its electrical conductivity from about 25,000 ohm⁻¹cm⁻¹ (virgin) to around one million ohm⁻¹cm⁻¹ (doped) . I believe that the Ni(III) acts in a similar manner to polarize the metallic bond in the lithium-doped nickel oxide samples , converting it from an insulator into a fair semiconductor . It probably accomplishes this by setting up an electron resonance in the solid :

$$Ni_{A}^{3+}e^{-} + Ni_{B}^{3+}$$
 \checkmark $Ni_{A}^{3+} + Ni_{B}^{3+}e^{-}$

The species "Ni³⁺e⁻" is , of course , Ni(II) ; it was written that way to show the electron exchange between the Ni(III) base atomic kernels . That is , in the Li_x Ni_{1-x} O doped compounds , we can look at the structure as an assembly of Li¹⁺ , Ni(III) , and oxide anions , with "extra" 3d e_g AO electrons from the nickel atoms superexchanging between them via the oxide anion bridges . That sort of resonance exchange of the outer "extra" electrons is a common feature in Robin-Day Class II mixed-valence compounds .This mixed-valence electron exchange is what activates the dormant metallic bond and permits the solid to become a conductor , albeit only in the semiconducting range .

In Verwey's "Induced Valence" paper cited in ref. 81, page 403, a second example of his doping technique to enhance electrical conductivity in solid

state systems is provided . When the cubic perovskite strontium titanate , $SrTiO_3$, was doped with 1% lanthanum(III), its conductivity rose from 10^{-7} ohm⁻¹cm⁻¹ to 0.6 ohm⁻¹cm⁻¹, again in the "fair" semiconductor range .

The compound LaTiO₃, also a perovskite, has been described as "black, slightly iridescent crystals" (ref. 82, page 403), and is a metallic solid (ref. 83, page 403). A series of doping experiments could be carried out to study the change in the electrical conductivity of, and possibly even the onset of superconductivity in, the compounds produced in the following reaction :

x LaTiO₃ + (1-x) SrTiO₃ \longrightarrow La_x Sr_{1-x}TiO₃,

where "x" is a mole fraction taken experimentally from zero to unity . The compounds SrTiO₃, CaTiO₃, and BaTiO₃ are commercially available, and could be examined in this study . However, LaTiO₃ would have to be prepared by the researcher, best by the method of Kestigan and Ward, described in ref. 82. The titanium(III) in LaTiO₃ is a mild reducing agent, so this system would have to be manipulated under an inert atmosphere such as nitrogen or argon. The mixed-valent titanium-based spinel, LiTi₂O₄, with titanium (III) and (IV), was a superconductor with a transition temperature of $T_c = 13.7$ K (ref. 84, page 403). I doubt that the transition temperatures, if any, for the La_x Sr_{1-x}TiO₃ and related systems would much exceed this value.

Verwey's experiments with controlled valence in solid state systems such as the rocksalts $\text{Li}_x \text{Ni}_{1-x} O$, the perovskites $\text{La}_x \text{Sr}_{1-x} \text{TiO}_3$, and various spinels such as magnetite, Fe₃O₄, demonstrated that the variable valence metal atom components of these systems had to be in a similar coordination geometry by nonmetal atoms in order for them to have enhanced electrical conductivity properties. This condition for electronic activity in such systems is now referred to "Verwey's Rule". We can readily understand the basis for this observation in VB/MO terms : the frontier orbitals comprising the XO in the crystal structure must be of a similar nature ; they should be similar if the underlying hybrid AOs on the metal atom components , defining their coordination geometry and creating the crystal architecture , are similar . Different coordination geometries will result in "extra" valence

electrons entering different frontier orbitals, which may or may not be able to continuously overlap in the structure to produce a viable XO to function as the material's metallic bond.

There is little doubt that Verwey's mixed-valent solid state systems , produced by the controlled valence technique , were early precursors – by about forty years – of the revolutionary research of the mid to late 1980s , in which a whole new chemistry of high T_c cuprate superconductors rapidly evolved . Controlled valence is now one of the most valuable synthetic methods available to chemists working in the field of metallic solids .

The Modern Superconductors

Superconductivity was discovered in 1911 in a sample of mercury, frozen in a Dewar flask of liquid helium at 4.2 K, by another Dutch scientist, Heike Kamerlingh Onnes, who was a pioneer in the new physical field of cryoscopy, the study of matter at very low temperatures. In the decades that followed, researchers discovered dozens, then hundreds of substances – about two dozen or so pure elements; the rest were intermetallics and simple chemical compounds – that were superconducting, all at temperatures close to absolute zero, chilled in liquid helium.

Intermetallic compounds in the A15 crystallographic group , having a simple A₃B formula , were found to be a rich source of these "classical" superconductors . In the A15 compounds the B atoms form a bcc structure ; lines of A atoms traverse the faces of the B cube , with two atoms lined up on each face . See the M3D model of the A15 crystal structure at the top of the next page . In 1973 the A15 compound Nb₃Ge was found to have the highest transition temperature of any member of that family , 23.2 K . This also proved to be the highest T_c for any known superconductor up to the discovery of the cuprates in 1986-87 by Bednorz and Müller . An influential physics paper on superconductivity theory , published in 1968 ,



Figure 35 : the M3D model of the A15 crystal structure , for intermetallic A_3B compounds such as Nb_3Ge (the structure shown above has the formula A_6B_2 , excluding the outer A atoms). The red spheres are the A atoms (Nb), and the blue spheres represent the B atoms (Ge). This model is based on Simon and Smith's sketch of the A15 structure (ref. 85, page 403, p. 115).

suggested – incorrectly, as later events proved – that there was an "upper limit" of about 30 K to the transition temperature of any future superconductors (this unfortunate analysis has been sympathetically discussed by T.P. Sheahen; see ref. 86, page 403). With the benefit of hindsight, it would have been quite illuminating for a physicist at that time to have studied the electrical conductivity of magnesium diboride (page 172) from liquid helium temperature to , say , ambient temperature , discovering its transition temperature at 39 K. Note that MgB₂ was then , and is now , a well-known , commercially available chemical . That result alone would have blown away the misleading physics analysis and prediction .

On the other hand , if such a result for MgB_2 had indeed been discovered at that time , we might not have had the inspired guesswork and dedicated laboratory experimentation by the two solid state chemists in Switzerland ,

J. G. Bednorz and K.A. Müller , who finally succeeded in surpassing that "psychological barrier" of 30 K for superconductivity researchers in 1986 and 1987 . I have read their famous report on the 30+ K transition temperature for the Ba-La-Cu-O system (ref. 87 , page 403) half a dozen times , and I'm still unsure of what prompted them to carry out such a thorough investigation of it . Whatever their working hypothesis may have been at the time , their discovery prompted an excited surge of interest and activity in high temperature superconductivity and a revitalization of solid state chemistry in general .

Replacement of the barium in the Ba-La-Cu-O system with strontium resulted in a slightly higher T_c of 38 K or so ; the "optimized" formula for this modified system is generally considered as $(La_{0.925} Sr_{0.075})_2 CuO_4$ (ref. 88, page 404 ; see also p. 10 in the textbook by Poole , Datta , and Farach , ref. 17 , page 393) . The overall K_2NiF_4 crystal structure of the parent material , La_2CuO_4 , was maintained in the strontium-doped samples , with Sr^{2+} cations replacing some of the La^{3+} cations here and there . An M3D model of the Sr-La-Cu-O system is presented on the next page .

Looking at the M3D model of strontium-doped La_2CuO_4 , we can focus on the $(CuO_6)^{2-}$ unit in the center of the vertically oriented "box". The two axial oxygen atoms are really terminal oxides , -O⁻, while the four equatorial oxygen atoms are covalent linear (sp hybrid AO) links , which are shared equally with adjoining copper oxide units . We thus have , in effect , $^{-}O_{-}(CuO_2)-O^{-}$ as the "CuO₄" part of the formula La_2CuO_4 .

There are six Cu-O covalent bonds in each CuO₄ unit , requiring twelve valence electrons for completion . The copper is in valence state 2+ , so it contributed two electrons . The two La³⁺ cations have provided three each , or six in total from them . Each oxygen atom provides one electron from its sp hybrid AO (sketch , top of page 147) , for a total of six . The total of all contributed valence electrons is 2 + 6 + 6 = 14. Twelve of these electrons complete the six Cu-O covalent bonds , while the remaining two go to each of the axial oxygens , making them terminal oxides , -O⁻. The precursor compound La₂CuO₄ fulfills the criteria of a Zintl-concept structure . Of course , it could also be reasonably thought of as purely ionic , as well ,



Figure 36 : the M3D model for the Sr-La-Cu-O system . Red spheres : copper atoms ; green spheres : oxygens ; yellow spheres : lanthanums ; aqua spheres : strontiums (I arbitrarily selected two of them , placed in those locations for a symmetrical , "artistic" appearance) . This model was based on the nice , clear sketch of the Sr-La-Cu-O system , Fig. 15 , p. 318 in Goodenough's review of ceramic superconductors , ref. 89 , page 404 .

with its formula written simply as $(La^{3+})_2 Cu^{2+} (O^{2-})_4$. However, since I am trying to describe the metallic bond in these crystal structures in VB/MOT terms, I must first provide them with an underlying strong, low energy covalent skeletal structure.

If one of the La^{3+} cations in La_2CuO_4 is replaced by an Sr^{2+} cation, one of the copper atoms has to increase its cationic charge to 3+ in order to maintain electrical neutrality in the crystal : $(La^{3+}Sr^{2+})(Cu^{3+})(O^{2-})_4$. Thus, when the pure precursor compound La_2CuO_4 is doped with strontium in an

oxidizing atmosphere, copper(II) atoms are oxidized to copper(III) in numbers equal to the numbers of strontium cations added to the structure. Strontium-doped lanthanum copper (II,III) oxide is a Robin-Day Class II mixed-valent compound, synthesized by Verwey's controlled valence process, and compliant with Verwey's Rule regarding coordinations.

Copper(II) is $3d^9$, and copper(III) is $3d^8$ electronically. Low spin $3d^8$ transition metal atoms are usually square planar (dsp² hybrid AO) in coordination by ligands. As mentioned on page 179 with nickel (II), high spin $3d^8$ transition metal species have an outer octahedral (sp³d²) coordination with ligands. In the case of strontium-doped lanthanum copper oxide, however, both of the formally copper(II) and copper(III) atoms have a 4+2 distorted octahedral coordination – also sometimes called tetragonal – by oxygen atoms. That is, there are four short equatorial Cu-O bonds, and two long axial Cu-O bonds in the CuO₆²⁻ units. The **base of copper(III)** atoms in the structure **must be in a low spin electronic configuration**, in order for the compound to become superconducting.

Copper(II), $3d^9$, is never symmetrically octahedral in coordination by ligands, because of the strongly repulsive nature toward them by the ninth valence electron in the $3d_z^2$ orbital; this is the **Jahn-Teller effect**. This $3d_z^2$ orbital and its electron are very prominent stereochemically, causing the copper(II) to "bulge out" axially quite noticeably, along the arbitrary z axis. How can we explain the apparent contradiction of the requirement of low spin base copper(III) atoms, but an obvious Jahn-Teller effect in evidence, requiring the ninth valence electron in the $3d_z^2$ orbital?

The answer in this case may be that the copper atoms in this system are using a hybrid AO for the two long axial Cu-O bonds that are just as stereochemically prominent as the $3d_z^2 AO$. A conventional square planar hybrid AO (using the $3d_x^2 - y^2 AO$, plus the 4s and $4p_{x,y} AOs$) would accommodate the four short equatorial Cu-O covalent bonds. A second hybrid AO, the rather voluminous linear sp AO, formed from the $4p_z$ and 5s native AOs, would accommodate the two long axial Cu-O bonds. The combination of the two separate hybrid AOs, the dsp² and the sp, could be used to produce the recognizable 4+2 distorted octahedral coordination in

lanthanum copper(II) oxide and its doped, mixed-valent derivatives.

With the copper(III) atoms in this structure, there will be a low spin base of the $3d^8$ inner shell electrons. With the **formally** copper(II) atoms, the ninth of the $3d^9$ electrons will be **promoted to the** $5p_{x,y,z}$ **AOs**, above the lower energy covalent skeleton of the structure (eight inner shell electrons, plus two in the skeleton, plus one in the metallic bond, from $Cu^0 = 3d^{10} 4s^1$). This electronic configuration is illustrated in the following simple diagram :





Note that I haven't included any 4d orbitals in the above diagram . Referring to the energy level sketch in Figure 4, page 35, we see that the 3d, 4s, and 4p levels have roughly the same energy, and therefore they should be able to form the dsp² square planar hybrid AO fairly easily . The 4d, 5s, and 5p levels similarly are approximately the same in energy, so there probably isn't too much difference in the hybridization energies for the formation of either z-axis linear hybrid, the dp $(4p_z + 4d_z^2)$, or the sp $(4p_z + 5s)$. True, the transition metal elements, with valence and hypervalence shell electrons in d orbitals, tend to favor d native orbitals in forming hybrid AOs for their covalent bonds . However, if the sp hybrid is used here for the two long axial Cu-O bonds, the copper(II) "ninth" (of 3d⁹) electron will be located in the 5p_{x,y,z} AOs. These, in turn, can successfully overlap with the oxygen

links' $2p_{y,z}$ AOs to form a pi XO as the proposed metallic bond in the superconducting Sr-La-Cu-O system. If 4d orbitals become involved in the Cu-O bonding, we cannot be assured of the formation of a nodeless XO in the crystal. However, we know that the Sr-La-Cu-O compounds are true metals and superconductors; this points to the sp hybrid AO as the probable covalent axial Cu-O bond source, and the 5p AOs as the likely location of the "ninth" copper(II) valence electron.

Please also note in the diagram above , that "an electron is an electron is an electron"; that is , regardless of their source , the electrons are all uniformly identical . I have labeled them differently , to show the reader their different sources , according to the Zintl and coordination concepts .

Yttrium-Barium-Copper-Oxide (YBCO)

A major advance in high temperature superconductors came in 1987 with the discovery of the yttrium-barium-copper-oxide series of compounds , which were optimized with the composition , $YBa_2Cu_3O_7$ (an idealized formula , since it was experimentally difficult to obtain samples with precisely seven oxygen atoms per formula unit) . We can write this formula out in full to see clearly the mixed-valent nature of its copper atoms : $(Y^{3+}Ba^{2+}Ba^{2+})(Cu^{2+}Cu^{3+}Cu^{2+})O_7^{-14-}$. I have collected the electronically inert spectator cations together , separated from the group of electronically active copper cations .

In a sense , YBCO was "designed" by its inventor , C. W. Chu , who , with his co-workers at the University of Houston , and a second research team under M. K. Wu at the University of Alabama , carried out and reported on their detailed investigation of the Y-Ba-Cu-O system (ref. 90 , page 404) . Chu was interested in studying the effects of pressure on superconductors , and thought that by substituting the smaller yttrium cation for the larger lanthanum cation in the lattice an "internal pressure" on the copper atoms would be produced . The resulting optimized samples had the remarkably high transition temperature of around 93 K , high enough for the replacement of the costly liquid helium refrigerant with the cheap and

abundant liquid nitrogen , which boils at 77 K , for use with the new cuprate superconductors .

YBCO had a somewhat different crystal structure than the Sr-La-Cu-O compounds :



Figure 37 : the M3D model of YBCO , $YBa_2Cu_3O_7$ (idealized formula) . Red spheres : copper ; green spheres : oxygen ; violet spheres : barium cations ; and yellow sphere : yttrium cation . This model was based on the nice , clear sketch of the YBCO crystal structure presented by Ourmazd and Spence (ref. 91 , page 404 ; their Figure 1 , p. 426) .

Although many writers portray YBCO as having an "oxygen defect perovskite" structure, I prefer to think of it – and the other cuprate superconductors – as having more of a **sheet structure**, with crosslinking oxygen atoms. To the best of my knowledge, copper(II) never has a

symmetrical octahedral coordination by any ligand ; its favored coordinations are square planar (dsp^2) , tetrahedral (sp^3) , square pyramid (dsp^3) , and 4+2 distorted octahedral $(dsp^2 + sp)$, as discussed above. It will never be able to form the perovskite structure because of the geometrical restrictions imposed by these preferred coordinations.

Also , because of a strong preference of copper(II) for a square planar coordination geometry , the copper oxide skeleton in the high T_c superconductors tends to be sheet-like in its overall appearance . It is sometimes flat , and sometimes "kinked" in a regular wavy pattern , with the oxides folded around a smaller spectator cation (in this case , yttrium) . The five-coordinate square pyramids can be thought of as planar (or kinked) copper oxide sheets that have been crosslinked with oxygen links .

Referring back to Figure 37, for the empirical formula unit $YBa_2Cu_3O_7$, in the copper oxide part, " Cu_3O_7 ", we have a square pyramid-square plane-square pyramid arrangement. Hence, we will have 5 + 4 + 5 = 14 covalent Cu-O bonds per formula unit. We will need twenty-eight valence electrons to comprise those bonds. In the Zintl concept, some of those electrons will be supplied by the powerful reducer metals yttrium and barium, in the formal if not experimental sense. They will supply their seven valence electrons to the copper oxide skeleton ($Y^{3+}Ba_2^{2+}$).

The oxygen linking atoms have a linear sp hybridization , like those in rhenium trioxide (top of page 147) . Each link supplies two electrons to the copper atoms it bonds to . There are seven oxides per formula unit , so the oxides contribute fourteen more valence electrons to the skeleton . Finally , the three copper atoms per formula group provide seven of their valence electrons to the structure . The total of the contributions is 7 + 14 + 7 = 28 electrons , which complete the framework of the Cu-O covalent bonds , with the inert yttrium and barium cations embedded in cavities in the structure . YBCO thus could be considered a Zintl-type compound , in the more general sense of the term that I have pointed out earlier .

In the formula group of three copper atoms, two have a square pyramid coordination by the oxygen links, and the third is square planar coordinated by them. The square pyramid coordinated copper atoms should have an

electronic structure similar to that of the 4+2 distorted octahedral coppers in lanthanum copper(II) oxide (page 189). The hybrid AO used for the square pyramid coordination is dsp³, from the copper(II) atoms' $3d_{x-y}^{2} + 4s + 4p_{x,y,z}$ native AOs . As in La₂CuO₄, the copper(II) "ninth" valence electron will be promoted into either the 4d, 5s, or 5p AOs, which all lie at roughly the same energy level . Again , as with La₂CuO₄ , the 5 s-p AOs seem a more likely location for the "ninth" valence electron . However , the 5s AOs on the coppers can't overlap properly with the neighboring oxygens' $2p_{y,z}$ native AOs with their electron pairs (because of symmetry considerations); only the coppers' $5p_{y,z}$ AOs can do that , since they have the proper shape , symmetry , and spatial orientation for a continuous overlap along the crystal axes with their neighboring oxygen links .

The electronic structure of the square planar coordinated copper(II) atoms in YBCO is even simpler than that of the square pyramidal coppers :

Proposed Electronic Structure of the Copper(II) Atoms in YBCO



I would predict in this case that the "ninth" copper(II) valence electron will be promoted to the $4p_z$ frontier orbital. Here it can readily overlap with the oxygen links' $2p_z^2$ AOs to form a pi XO and the principal metallic bond in YBCO. It will be a bilayer metallic bond, with the copper(II) "ninth" valence electrons "floating" over the lower energy level oxygen electrons. As with the nodal metallic bond in Verwey's lithium-doped nickel oxide, the pi XO metallic bond is polarized , in this case by the powerful copper(III) base of cations . Partial oxidation of copper(II) by controlled valence doping of yttrium into the lattice , partially replacing some of the bariums without disturbing the crystal structure , has "exposed" these copper(III) atoms . Since YBCO is a Robin-Day Class II mixed-valent compound , the Cu²⁺– Cu³⁺– Cu²⁺ cationic charges in the formula unit copper atoms are perfectly blended to provide an overall copper cationic charge of (2+3+2)/3 = 2.33+, for the idealized YBCO formula . This NIOS valence , lying between 2+ and 3+ , will result in YBCO having distinctly oxidizing properties . In fact , YBCO is known chemically to oxidize water , with the evolution of oxygen (ref. 92 , page 404) :

The following is thus what probably happens chemically when a sample of YBCO is left exposed to the humidity in the atmosphere, or to liquid water :

 $YBa_2Cu_3O_7 + \frac{1}{2} H_2O \longrightarrow YBa_2Cu_3O_6OH + \frac{1}{4} O_2(g)$.

The hydroxy cuprate, in pure form, would be an insulator. The relatively high reaction redox potential of 1.171 V indicates that the chemical reaction as shown should proceed spontaneously, and indeed vigorously if kinetically unhindered.

We can reasonably expect the presence in YBCO of a polarized , bilayer metallic bond as the electron pathway in the crystal . Of the two possible pi XOs which will form such a metallic bond , that one based on the copper $4p_z$ and oxygen $2p_z$ AOs , over the Cu-O "diamonds" with square planar coordinated copper atoms , is probably the stronger and more functional of

the two . This is anticipated because – glancing at Figure 37 on page 191 above – it will be less sterically blocked and destabilized by oxygen atoms than will the copper $5p_z$ – oxygen $2p_z$ pi XO in the copper oxide layers formed by the square pyramids . I am assuming in the square pyramid case that the pi XO can indeed form , despite the "kinking" in the Cu-O chains . This might cause a thinning or weakening of the XO . The $5p_z$ based pi XO will also be more diffuse than the $4p_z$ based pi XO of the planar "diamonds" layer . The copper 5s – oxygen 2s sigma XO might provide a functional metallic bond for the kinked "pyramids" Cu-O layer .

We will see in the further examples to follow of high T_c cuprate superconductors that most of them have the planar "diamonds" with the square planar coppers and the 4p-2p pi XO. It might be possible for a high T_c cuprate to have only the pyramids and no diamonds, but in this case its high T_c value could be attributed to a cause, or causes, other than the oxide coordination of the copper atoms in the material.

Antiferromagnetism and Superconductivity

All the modern physical theories of superconductivity agree that the electrical charge carriers in the superconducting state are **pairs** of electrons, now called "Cooper pairs", after their principal exponent, L.N. Cooper. Each electron in the pair has a spin component opposite to the other; one's spin is "up", while the other's is "down". In that sense, Cooper pairs somewhat resemble the pairs of electrons comprising covalent bonds, an idea that found expression in the "resonating valence bond" theory of superconductivity (P.W. Anderson, referred to at the top of page 76).

The presently accepted physical theory of superconductivity, generally referred to as the "BCS theory", was published in 1957 by J. Bardeen, L.N. Cooper, and J.R. Schrieffer. This is a highly abstruse, mathematical treatment of the subject, which sought to explain how electrons can couple together to form the electrical energy and charge carrying entities in superconductors. The BCS theory was the most successful, and enduring, of several rationalizations of the phenomenon, in that it was able to explain

many of the known features of classical superconductivity (that is , precuprate superconductors) in quantitative terms . However , it made no reference to the chemical nature of superconductors ; it ignored the metallic bond in them , and their metallic properties ; it made no predictions regarding future sources of these materials ; and it failed to anticipate the high transition temperature superconductors . Nevertheless , "in the country of the blind , the one-eyed man is king" , and the BCS theory satisfied condensed matter physicists for three decades (this was also a notable period of dormancy or stagnation in the field) . There has been some debate as to whether or not the BCS theory is applicable to the high T_c cuprate and related superconductors , or if a new theory – and many competing ones have been proposed since 1987 – will be required to encompass both the classical low temperature and modern high temperature superconductors .

Superconductivity is a complex , multidisciplinary phenomenon , including physics , chemistry , crystallography , and materials science and engineering in its domain . The aim of this present work is to provide an overview of the chemistry of superconductors within the framework of the metallic solids , the more general class of materials in which they are found . While the superconductors are all metallic solids , the constitution of their metallic bond is quite unlike that of the conventional metallic solids we have been examining so far in this report . I don't want to venture into the field of superconductor physics , in which I am completely lost ; but in order to describe the metallic bond in superconductors in even a basic , simple manner , I will have to refer to the subject of **antiferromagnetism** in extended atomic lattice structures .

Antiferromagnetism is the engine that drives high T_c superconductivity . Specifically, antiferromagnetism within the metallic bond in a solid creates the critical condition for high T_c superconductivity in that solid . Both antiferromagnetism and the metallic bond are necessary for the presence of superconductivity. Either condition alone will produce in the solid only a feeble sort of bulk magnetism, or an electrical conductor, respectively. When they are combined together in a solid, we may observe the onset of superconductivity in it at a reduced temperature. Antiferromagnetism is the mechanism whereby the free valence electrons above the Fermi level in the crystal are able to couple together to form Cooper pairs .

In the BCS theory, formation of Cooper pairs is mediated by phonons, the lattice vibrations in the crystal. This coupling mechanism of the free electrons at extremely low temperatures had received experimental support from observation of the "isotope effect" in 1950. A good account of the development of the BCS theory, and a clear explanation of Cooper pair formation via phonon-electron coupling, is provided by (for example) Vidali in ref. 93, page 404.

Actually, the idea of electron pairs being the charge and energy carriers in superconductors was suggested twenty-four years before the BCS theory was published. In 1933, the creative and eclectic Russian physicist Yakov Ilich Frenkel (1894-1952), whose name now graces Frenkel excitons and Frenkel defects, proposed that,

"...... the normal state must be characterized by an opposite orientation of the resulting orbital and spin angular moments a metal in the superconducting state must behave like a diamagnetic body with a large negative susceptibility"

This paper (ref. 94, page 404) seems to have been completely overlooked by subsequent workers in the field of superconductivity, and indeed, even by Frenkel's biographer (ref. 95, page 405).

In 1945-46, the American physicist R.A. Ogg published a series of research reports (ref. 96, page 405) describing his work with metal-ammonia electrides . In one of these papers, "Bose-Einstein Condensation of Trapped Electron Pairs . Phase Separation and Superconductivity of Metal-Ammonia Solutions", he suggested that electron pairs might form in the ammonia solvent cavities, thereby allowing the frozen ammonia-electride solution to become superconducting (which he claimed to observe) . Unfortunately, Ogg's results could not be reproduced, at least by one other team of researchers (ref. 97, page 405), and he seems to have abandoned his efforts in this field . I believe that Ogg had the right physics, but the wrong

chemistry, and I'll be discussing the chemistry of electrides later, with respect to their potential as a source of superconductor compounds. It is interesting to note, though, that modern thinking about metal-ammonia electrides agrees with Ogg concerning the trapped pairs of electrons in the solvent cavities.

I have always been somewhat uncomfortable with the explanation of the phonon-electron coupling in superconductors to produce the Cooper pairs . After all , common sense tells us that the like charges of the electrons should inhibit their bonding . What force might overcome this repulsion to permit their association in the superconducting state ? Frenkel thought that the electromagnetic inductive forces in the valence electrons might be responsible , but his mathematical analysis didn't seem to lead to any definite conclusion to this hypothesis .

The clue to solving this mystery is the required antiparallel spin orientation for the electron pair comprising the Cooper pair . The "spin" of the electron (which apparently isn't a mechanical spin , like a top) implies that it has a surrounding magnetic field , with a north and a south pole , like the Earth itself , for example . This bipolar magnetic field around the electron permits it to act somewhat like a spherical bar magnet . When the electrons in the pair have antiparallel spins , their poles are aligned north-south and southnorth . This attraction between the poles provides the magnetic force required to overcome the repulsive electrical force that would otherwise keep the two electrons apart .

Can we quantify this idea ? First , we know that the electric charge "e" on a single electron is $e=1.6022 \ x \ 10^{-19}$ coulomb (C) . We also know , from Coulomb's Law of Electric Force , what the electrical repulsive force F_e (in newtons , N ; I'm using MKS-SI units throughout this discussion) between two electrons , separated by any distance , "r" metres , will be :

$$F_e = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} ,$$

where ε_0 is the electrical permittivity of free space , a universal constant

whose value is 8.8542 x $10^{-12} \text{ C}^2 \text{ N}^{-1}\text{m}^{-2}$.

The next question is , what is the attractive magnetic force F_m , in newtons , between two coupled electrons with antiparallel spins in a Cooper pair ? There is also a Coulomb's Law of Magnetic Force (not as well known as the electric force law; see in Semat's physics textbook, ref. 98, page 405) :

$$F_{\rm m} = \frac{1}{4\pi\mu_0} \frac{\Phi^2}{r^2} ,$$

where Φ is the magnetic pole strength or magnetic flux of the electrons, and μ_0 is the magnetic permeability of free space, another universal constant whose value is 1.2566 x 10⁻⁶ Wb² N⁻¹m⁻². The MKS-SI unit of magnetic pole strength or flux is the weber (Wb), or volt-second. The intensity, or density, of the magnetic field is called its "magnetic flux density", and its unit is the weber per square metre, Wb-m⁻². This latter unit is usually called the "tesla" (T), and is equal to 10,000 gauss (G).

The magnetic field is quantized in superconductors, although it apparently isn't in normal magnetism (Poole, Farach, and Creswick, p. 309 in ref. 17, page 393). The magnetic quantum is that of the individual electron in the Cooper pairs; it is usually called the "fluxoid", and its value is :

$$\Phi_0 = \underline{h}_2$$
, where "h" is Planck's constant, 6.6261 x 10⁻³⁴ J-s.

The value of the magnetic flux quantum or fluxoid, which is applicable only to the electrons in the Cooper pairs, is $\Phi_0 = 2.0678 \times 10^{-15}$ Wb.

In both expressions for F_e and F_m , the only variable is the distance , "r" metres , separating the two electrons in the Cooper pair . We can eliminate this variable by taking the ratio , F_m/F_e , and cancelling the "r²" terms ; the fraction , $1/4\pi$, common to both force terms , is also cancelled :

$$F_{m} / F_{e} = \varepsilon_{0} (\Phi_{0})^{2} / \mu_{0} e^{2} = \varepsilon_{0} \frac{(h / 2e)^{2}}{\mu_{0} e^{2}} = \varepsilon_{0} \frac{h^{2}}{4 \mu_{0} e^{4}}$$

Recalling the numerical values for the constants e , h , ϵ_0 , μ_0 , and Φ_0 :

Physical Constants for Calculating F_m / F_e				
Physical Constant	<u>Symbol</u>	MKS-SI Value		
electrical permittivity of free space	ε ₀	8.8542 x 10 ⁻¹² C ² N ⁻¹ m ⁻²		
magnetic permeability of free space	μ ₀	1.2566 x 10 ⁻⁶ Wb ² N ⁻¹ m ²		
Planck's constant	h	6.6261 x 10 ⁻³⁴ J-s		
electronic charge	е	1.6022 x 10 ⁻¹⁹ C		
fluxoid (magnetic flux quantum)	Φ_0	2.0678 x 10 ⁻¹⁵ Wb		

The ratio of the attractive magnetic force , F_m , between the two electrons in the Cooper pairs , to the repulsive electric force between them , F_e , is calculated to be :

 $F_{\rm m}/F_{\rm e} = 1173.6574$, which I'll round off to 1174.

The attractive magnetic force – only if the two electrons have an antiparallel spin orientation to each other – is thus almost twelve hundred times as great as the corresponding repulsive electric force pushing them away from each other .This seems to me to be a simple and readily understood mechanism for the association of the two free electrons in the Cooper pair . It does not at the same time preclude the phonon-electron interaction to do the actual "pushing together" of the two electrons in the crystal . In fact , the **absolute value** for the net attractive force between the two electrons may be extremely small in most cases , especially with the very low temperature "classical" superconductors . Hence , destructive lattice vibrations at higher temperatures may be more than enough to overcome the magnetic coupling and break up the Cooper pairs .

I wondered if this predominance of the magnetic coupling force over the repulsive electrical force might also provide a rationale for the covalent bond, comprised as it is of two electrons with antiparallel spins. However, whatever magnetic coupling there is in the two electrons of the covalent bond apparently is negligible compared to the electrostatic force between the electrons and the positively-charged nuclei of the atoms. Holden writes :

"The prevalence of electron-pair bonds has often been rashly interpreted as betokening a mysterious force that comes into being with the pairing of electrons . But the hydrogen moleculeion dispels that mystery by showing that a bond approximately half as strong as an electron-pair bond arises from half as many electrons . The reason that electron-pair bonds are more common is simply that there are usually enough electrons available to form them whenever atoms offer suitable unoccupied orbits". – A. Holden , ref. 99 (page 406) , p. 91 .

Pauling discusses the one-electron bond in his textbook , <u>The Nature of the Chemical Bond</u>, third edition, providing values on p. 340 for the strengths of the hydrogen molecule's H-H bond (102.62 kcal-mol⁻¹, 429.36 kJ-mol⁻¹), and for the hydrogen molecule-cation's H-H⁺ bond (60.95 kcal-mol⁻¹, 255.01 kJ-mol⁻¹). The latter value is 59.4% of the former figure . This shows conclusively that the coulombic electron-nucleus force is bonding the atoms together , with no assistance observable from any putative magnetic coupling force between the two electrons in the H-H covalent bond .

This is a rather sad conclusion . For , if the magnetic coupling actually **was** responsible for the strength of the covalent bond , we might hope some day to design and synthesize superconductors in which the Cooper pairs were bonded together as strongly as , say , the electron pair in the hydrogen molecule's covalent bond . If that were the case , we might reasonably hope to produce **ambient temperature superconductors** . Alas , it seems that if the magnetic coupling force really does exist , it must be very feeble indeed , which gives us faint hope – excluding the discovery of another mechanism for producing high temperature superconductivity – of ever finding them .

Another brief comment about the fluxoid : as noted above , its value was calculated from $\Phi_0 = h/2e$. We can rewrite this relationship as $h = 2e \Phi_0$.

That is, Planck's constant is the product of the electronic and magnetic flux quanta. Considering the central role played by Planck's constant in quantum-related processes in physics and chemistry, I find that relationship to electromagnetism quite profound.

Returning to antiferromagnetism and its influence in superconductivity, I shall assume that the magnetic coupling force in the Cooper pairs really does exist, even though it may be extremely weak. Note that the $F_m / F_e = 1174$ ratio will remain constant in whatever physical or chemical environment the Cooper pairs are located, and regardless of the distance of separation, "r", between their constituent pairs of electrons. In the classical superconductors with transition temperatures close to absolute zero, the two electrons with antiparallel spins may be located near to each other, or very far away, at the opposite ends of the crystal. They are always paired off in energy space at the same energy level in the metallic bond, but not necessarily close to each other physically. On the average – I'm guessing – they are probably separated fairly distant from each other , resulting in the two forces , F_m and F_e , being extremely weak. In turn, the net magnetic coupling force will be, in absolute terms, also extremely weak. While phonons may nudge the antiparallel electrons together, they will also scatter them, preventing their condensation into Cooper pairs. This process will be reflected in the deep cryogenic range (liquid helium) transition temperatures for the classic superconductors.

The situation with the modern high T_c cuprate superconductors is quite different in two significant aspects . First , the metallic bond in them is bilayered and polarized , as opposed to monolayered and homogeneous in the classical , low T_c materials . We hypothesize that in the bilayer metallic bonds the copper free electrons are all promoted above the Fermi level , with the oxide electron contribution to the XO paired off in the lower energy levels below the Fermi level . This is in comparison with , say , copper metal itself , in which the 4s¹ valence electrons are subjected to the Fermi-Dirac distribution , with only a small percentage – perhaps 1% or so , as with sodium metal – rising as singlets above the Fermi level .

If we are correct about the promotion of the cuprate free electrons above the Fermi level, then neighboring valence electrons in the cuprates will find

themselves above the Fermi level . This is very unlikely to happen in copper metal , in which , geographically speaking , the singlet electrons above the Fermi level in it are sprinkled about here and there with wide separations (copper never becomes superconducting , even near absolute zero) . The neighboring valence electrons in the cuprates will be guaranteed to always have much shorter separation distances than they would in copper metal . Their magnetic coupling forces will be much stronger than in the low T_c materials , making their Cooper pairs more resistant to scattering at higher temperatures . However , will they have the necessary antiparallel spins required for magnetic coupling ?

The answer is , maybe , and certainly more likely than in copper . That's where the second major difference between high T_c and low T_c superconductors comes into play . That difference is that the cuprates are all antiferromagnetic at relatively high temperatures ; that is , they have high Néel temperatures (T_N). When they are cooled down below room temperature , their antiferromagnetism , with the three-dimensional antiparallel ordering of the outermost copper valence electrons , becomes stronger and stronger . Most importantly , this antiferromagnetic régime is also imposed on the free electrons in the metallic bond . With deeper and deeper cooling , the neighboring valence electrons become more and more antiparallel with respect to each other , and their magnetic coupling increases in strength , until pairs of neighboring electrons are able to couple together into Cooper pairs .

In copper metal , no such antiferromagnetism has been measured at any temperature ; on the contrary , copper exhibits a weak temperature independent Pauli paramagnetism , typical of most metallurgical metals . This sort of magnetic régime indicates that the spins of the free electrons above the Fermi level in copper must be almost entirely parallel in orientation, with very few , if any of them , having antiparallel spins . If anything , this parallel spin orientation of the free electrons will inhibit their magnetic coupling into Cooper pairs . This fact is reflected in the wellknown inhibiting effect magnetic (parallel spin) impurities have on superconductors . For example , traces of iron or other such magnetic contaminants in superconductor precursor materials are highly undesirable . As discussed earlier, I have proposed a new general classification of metallic solids into eight new Classes (YBCO, for example, is in Class 3). We can now identify two new "casual" (non-rigorous) types of metallic solids, the **bronzes** and the **blacks**. I have named the bronzes after the tungsten bronzes, because of their metallic luster and high electrical conductivity. Other classic bronzes are, well, bronze [copper/tin] itself, other alloys, those intermetallic compounds that have a metallic nature (such as Purple Plague, NaT1, and SrGa₂) and the metallurgical metals. More "modern" bronzes would include synthetic metals such as KCP, Alchemist's Gold, and silver subfluoride, and molecular metals such as poly(sulfur nitride) and (TMTSF)₂ PF₆.

Typical properties of bronze metals include a metallic luster , color (gold , silver , bronze , brass) , high ambient electrical conductivity , and an extremely low – close to absolute zero – transition temperature , if any . I would hypothesize that their free electrons , above the Fermi level in their metallic bond , are in a predominately , if not exclusively , parallel orientation . The population of these free electrons is rather low , because their valence electrons participating in the metallic bond have been "crunched" in the Fermi-Dirac distribution , with only about 1% of them rising above the Fermi level . Because of the low population of these "active" electrons , they will be scattered throughout the crystal , with long separation distances between them .

The black metals are derived from precursor compounds, such as nickel(II) oxide, NiO, and copper(II) oxide, CuO, whose latent, or potential metallic bond has been chemically activated, usually by doping or some other method of chemical modification. Such an activation is accomplished by polarizing the latent metallic bond, and by producing a mixed-valent state in the metal cation components of the compound.

I have named the black metals after the jet-black color , or appearance , of copper(II) oxide , the precursor to the high T_c superconductors (which are also all black) . We find that the black metals all have rather poor ambient electrical conductivities ; for example , that of YBCO at 300 K is around 500 ohm⁻¹cm⁻¹ , which is in the "good semiconductor" range . However , the

black metals have transition temperatures much higher than those of the bronzes ; in the case of the cuprates , they can range from 30 K to as high as 135 K (so far) under ambient pressure .

The black metal precursors are generally antiferromagnetic at room temperature, sometimes strongly so. This antiferromagnetism is conferred on the valence electrons when they are located in the metallic bond. Because the black metals have a bilayer metal-oxygen metallic bond (compared to the bronzes, which are metal-only bonds, with no anion participation), most if not all of their valence electrons in the metallic bond will be raised above the Fermi level in the crystal. This means that there will be a relatively large, dense population of free electrons in the metallic bond, and free electrons from neighboring metal atoms will be next to each other with quite short separation distances :

"These new pairs [in the high T_c cuprates , i.e. blacks] differ from BCS pairs [in the low T_c classical superconductors , i.e. bronzes] in one respect at least : the distance between the charge carriers of each pair in the new superconductors is much shorter , by a factor of around 100 . Furthermore , the isotope effect is almost absent in the new [cuprate] superconductors this seems to indicate that the role of phonons in the new materials is non-existent or , at least , different than in BCS superconductors" . – G. Vidali , ref. 93 , page 404 , p. 137 .

Recalling that the magnetic coupling force is inversely proportional to the square of the separation distance , r^2 , it will therefore be $(100)^2 = 10,000$ times as strong in the cuprates as it is in the classical , low T_c (BCS) superconductors . It could well be , then , that magnetic coupling actually does take place in the black metals , while BCS phonon-electron coupling is the predominate Cooper pair forming mechanism in bronze metals close to absolute zero . The separation distance of the free , antiparallel spin electrons in the bronzes is simply too great for the magnetic coupling to play any significant role in the formation of Cooper pairs at low temperatures .

The following are examples of antiferromagnetic compounds, selected from the list of them in the <u>Handbook of Chemistry and Physics</u>, 82^{nd} edition, 2001, p. 12-125, together with their structures and Néel temperatures, T_N :

<u>Material</u>	Crystal Structure	<u>Néel ten</u>	perature
MnO	rocksalt	122 K	- 151 °C
FeO	rocksalt	198	- 75
CoO	rocksalt	291	18
NiO	rocksalt	525	252
CuO	CuO	230	- 43
LaFeO ₃	perovskite	750	477
NdFeO ₃	perovskite	760	487
BiFeO ₃	perovskite	673	400
NiS	NiAs	263	- 10
CrS	NiAs	460	187
Cr_2O_3	corundum	318	45
Fe_2O_3	corundum	948	675

Noting that the Néel temperature for copper(II) oxide , $T_N = 230$ K , looked somewhat low for the series , and that a reference mentioned that CuO shows a "very strong magnetic exchange reaction" , having only a weak paramagnetism with a maximum at 561 K (ref. 100 , page 406) , I drew a simple graph of these T_N values versus the increasing formula weight of the transition metal oxides concerned . This graph is reproduced on the next page . We see that the NiO Néel temperature is rather high for the series , while at 230 K the value for CuO (not on the graph) would be abnormally low . The projected value for CuO – the upper horizontal line – would be more like a minimum of 500 K , if there was no magnetic interaction in the CuO crystal .

It would be interesting to look more closely at CuO, which is the critical precursor for all of the high transition temperature superconductors. The M3D model of copper(II) oxide is shown in Figure 38 on page 208 below.



This is a somewhat crude graph showing the relationship between the formula weight of transition metal oxide (in the rocksalt series) and its Néel temperature , T_N , in kelvins . Obviously , the drawing of the graph is open to some interpretation . However , under normal circumstances – that is , excluding magnetic interactions in the copper(II) oxide crystal – we would expect a T_N for CuO of at least 500 K (the upper horizontal line) . This is probably a reasonable value for CuO with regard to its place near the end of the transition metal oxides . We should also recognize that copper(II) oxide has a crystal structure quite different from the rocksalt oxides in the series .



Figure 38 : the M3D model of copper(II) oxide , CuO . The small red spheres are square planar coordinated copper atoms , and the larger green spheres represent tetrahedrally coordinating oxygen atoms . This model was based on Wells's drawing of CuO (tenorite) , Fig. 152(a) , p. 463 (ref . 21 , page 394) .

The three-dimensional ball-and-stick representation of CuO is a really beautiful structure . I urge the reader who has the Molecules 3D software program installed on his or her computer (a free trial version is available from the manufacturer ; see page 42) to open the M3D file for CuO on the "3D Molecule Builder" window , then study its crystal structure in 3D by twirling it about and rocking it back and forth . You can see the interlocking ribbons of "diamonds" , joined to other ribbons at right angles , in a "spiro" manner – to use an organic chemistry phrase – at the tetrahedrally coordinating oxygen atoms . The copper atoms in the parallel planes of ribbons are all nicely lined up , one on top of the other . This geometry may be favorable for a direct copper-to-copper magnetic exchange interaction . Unfortunately , such a 3D geometry cannot be very well appreciated by the static JPEG illustration above in Figure 38 . The "skeletal" ball-and stick version of the M3D model is the best one to view and study .

The valence bond description of the chemical bonds in CuO is quite simple . In one formula unit of CuO there are four covalent Cu-O bonds , requiring eight valence electrons . Copper(0) provides two of them , and oxygen(0) furnishes the remaining six . The copper atoms are square planar , using dsp² hybrid AOs . The oxygen atoms have a tetrahedral coordination , and use sp³ hybrid AOs . There are no unhybridized AOs remaining on the oxygens .

Since copper(0) is $3d^{10} 4s^1$ electronically, and two of these valence electrons are used in the Cu-O covalent skeleton, the nine remaining outer shell electrons must be accommodated in only four available 3d AOs, because the fifth one, $3d_x^{2} \cdot y^2$, has been taken for the dsp^2 hybrid AO. Where will the "ninth" copper valence electron go? Copper is a 4 s-p element, so it will require very little energy for it to be relocated to the $4p_z AO$. In turn, the $4p_z AO$ might conceivably form a linear dp hybrid AO with the $4d_z^2 AO$; this composite orbital would be voluminous enough to form a nodal sigma XO along the z axis in the crystal, linking up the copper atoms directly. This could serve as the latent metallic bond in CuO. Note that the electrons in the tetrahedral oxygen links are entirely occupied in the covalent bonding of the skeleton. They have no available unused 2p AO electrons to form a bilayer metallic bond with the coppers, and in any case, the geometry would be unfavorable for the formation of such an XO in this crystal.

The "ninth" valence electron in CuO should normally impart to it a significant Curie paramagnetism (about 1.73 BM, spin only), but the compound is only weakly paramagnetic, as mentioned earlier. Feeble Cu-Cu bonds might form via the $4p_z$ AOs, or $4p_z - 4d_z^2$ linear dp hybrid AOs; weak Cu-Cu bonds are thought to occur in copper(II) acetate dihydrate (Figure 14, page 80). Such low density Cu-Cu bonds would be a plausible mechanism for lowering the magnetic susceptibility in copper(II) oxide.

Seeing all those copper atoms nicely lined up in rows reminds me of KCP. Would it be possible to partially oxidize the coppers to activate the latent Cu-Cu metallic bond? That should form a nodal sigma XO as in KCP, and the partially oxidized CuO would behave as a pseudometal with a greatly increased electrical conductivity. The standard oxidation potential of Cu(II) to Cu(III) is $E_{ox}^{0} = -2.4$ V, so we'll need a very powerful oxidizer to do the job . One such oxidizer might be fluorine , whose standard reduction potential is $E_{red}^{0} = 2.866 \text{ V}$. The reaction ,

 $Cu(II) + \frac{1}{2} F_2(g) \longrightarrow Cu(III) + F^-$,

should be spontaneous at STP, but in practice might need some warming; and it might also be advisable to dilute the highly reactive (and toxic !) fluorine with an inert carrier gas such as helium, argon, or nitrogen.

Fluorine is such a reactive substance – violently so, in many cases, with the substrate being incinerated if precautions aren't taken – that chemists have been rather cautious in its use in the past. Almost twenty-five years ago a gentler, more selective technique of direct fluorination was devised, sometimes called "LaMar fluorination" after its two principal developers, R.L. Lagow and J.L. Margrave (ref. 101, page 406). They found that when fluorine is diluted to about 10% concentration in an inert carrier gas, such as helium, argon, or nitrogen, it is much easier to handle and work with than the pure, undiluted halogen. Direct fluorination of many organic molecules can now be carried out efficiently and selectively by the LaMar procedure. It might also be applied successfully to inorganic substrates.

Partial fluorination of copper(II) oxide, at low mole fraction contents of fluorine, should generate the corresponding quantity of copper(III) in it, sufficient to activate the latent metallic bond in the substrate :

$$CuO + \frac{1}{2} x F_2(g) \xrightarrow{10\% \text{ in argon}} CuOF_x ,$$

where "x" is a mole fraction ; I suspect it would be rather low , possibly from 0.05 to 0.10 or so .

The question is : could the fluoride anions (with a crystal ionic radius , per Shannon-Prewitt , of 1.19 Å) be fitted into the CuO crystal structure without disturbing , or altering it , or blocking the formation of the Cu-Cu metallic bond ? Of course , the M3D models presented in this study are "exploded"

or expanded illustrations , while in reality the atoms in these solids are all packed very tightly together . Substrates with a pronounced layer structure , such as graphite and the transition metal dichalcogenides (MoS_2 and TiS_2 , for example) can be chemically and electronically modified by oxidizers and reducers that deposit their inert spectator ions in between the layers after reaction . Similar sorts of reactions won't occur in nonlayered structures with extended atomic lattices , because there is nowhere "to put out the trash", so to speak . Combination with the reactant may occur , but the substrate's crystal structure may have to shift into a different form to accommodate the added chemical residue .

Palladium monoxide, PdO, has a similar sort of structure to CuO:



Figure 39 : the M3D model for palladium(II) oxide , PdO . The small blue spheres are square planar coordinated palladium atoms , and the larger green spheres represent tetrahedrally coordinating oxygen atoms . The model was based on Wells's drawing of PdO , Fig. 152(b) , p. 463 , ref. 21 , page 394 .

In effect, Figures 38 and 39 are identical. The CuO model on page 208 above could also reasonably be that of PdO as well. In copper(II) oxide the diamonds in one layer of ribbons are bent over slightly with respect to the diamonds with which they are joined in a spiro manner. The overall result is that the planes of ribbons are "tilted" slightly with respect to each other, with the tilt alernating from one layer to the next, making the unit cell of

CuO rhombohedral in structure . In palladium(II) oxide , however , the alternating layers of ribbons are perpendicular to each other , making the PdO unit cell tetragonal in form . My M3D model of PdO is thus reasonably accurate . I must confess , though , that because of my laziness (you can set the bond angles accurately when making the M3D models , but it is a lot of work when building extended atomic lattice structures) , the CuO M3D model isn't exactly correct , although the reader will get the general idea of its structure , especially when viewing it in three dimensions in the M3D application . You can see the difference in CuO and PdO right away in Wells's sketches , which I can't reproduce here , for obvious reasons .

The standard oxidation potential of Pd(II) to Pd(IV) [in a chloride environment] is $E_{ox}^{0} = -1.288 \text{ V}$. Again, fluorine could be used to try to activate the sigma XO by partial oxidation of the $4d_z^2$ AOs on the palladium atoms, by analogy with the $5d_z^2$ AOs in KCP. The standard reduction potential of chlorine is $E_{red}^{0} = 1.358 \text{ V}$, so it should be able to oxidize the palladiums. Bromine, with $E_{red}^{0} = 1.066 \text{ V}$, would be unsuccessful in this endeavor. Another interesting oxidizer to try would be the nitrosonium cation, NO⁺, which forms crystalline, stable salts with several inert, nonnucleophilic anions (BF₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻, etc.). The standard reduction potential of NO⁺ is a surprisingly high 1.45 V, so the following reaction might be interesting to try :

PdO + x NO⁺BF₄⁻ $\xrightarrow{\text{solvent}}$ PdO(BF₄⁻)_x + x NO (g). eg. propylene carbonate

Again, we would question whether or not even a very low mole fraction "x" of tetrafluoroborate anions could squeeze into the PdO solid state lattice without forcing it to undergo a radical transformation to a new structure. My aim here, though, was to point out the possibility of creating a new palladium-based synthetic metal (although a pseudometal, like KCP), with a Pd-Pd nodal XO and metallic bond. This objective could be reached through an understanding of first, the crystal and electronic structure of the substrate, palladium(II) oxide, then second, of the redox and synthetic

chemistry of the PdO and of the oxidizers contemplated for use with it .

Neodymium Copper(II) Oxide, Nd₂CuO₄

On page 195 I pointed out that the main metallic bond in YBCO would likely be over the square planar "diamonds", rather than through the square pyramids, because of orbital considerations. If we are looking for new superconductor candidate compounds, it would be desirable to have in them these copper-oxygen "diamonds", rather than the pyramids, if at all possible. In copper oxide itself, we don't have flat sheets of copper and oxygen atoms. Certainly, both copper(II) and (III) show a distinct preference for a square planar coordination with oxygen ligands; however, there is no square planar hybrid appropriate to the oxygens, which instead prefer linear (sp), trigonal planar (sp^2) , and tetrahedral (sp^3) coordinations, and possibly a "composite" hybrid, the $sp+p^2$ "seesaw" shaped orbital. In CuO, with equimolar quantities of copper and oxygen, and with copper(II) offering a square planar coordination, the oxygens must provide a four-fold coordination, and the tetrahedral form proved to be the one chosen, with the very distinctive and beautiful atomic architecture of the CuO crystal resulting from their union.

If there are plenty of oxygen ligands present in the reaction environment in which a copper-oxygen compound is created , we run the risk of having the copper atoms coordinated by too many oxygen ligands , with the formation of Cu-O square pyramids and the 4+2 distorted octahedrons $(dsp^2 + sp)$. We would like to try to maintain the presence in the cuprate compound of the square planar diamond structures , so as to optimize the Cu-O bilayer , polarized metallic bond in the material . This should give us a good chance of observing high T_c superconductivity in the new cuprate .

It turns out that several ternary cuprates are known in which the Cu-O layers are apparently planar – not kinked – and which retain intact the square planar coordination of the copper atoms by the oxygen ligands . One of these

compounds is neodymium copper(II) oxide , Nd_2CuO_4 , which has a modified structure related to that of La_2CuO_4 (the K_2NiF_4 structure) :



Figure 40 : the M3D model of neodymium copper(II) oxide , Nd_2CuO_4 . The small red spheres are square planar copper atoms ; the larger green spheres represent linear oxygen link atoms ; and the large aqua spheres stand for neodymium (Nd^{3+}) cations , which are multicoordinated by oxygens . The heavy black lines represent covalent Cu-O bonds , while the dashed black lines are meant only to outline the tetragonal structure of the compound (it is rather unlikely there are any Cu-Nd or Nd-Nd bonds in this material) . The model was based on Figure 15 on p. 318 of Goodenough's review article (ref. 89 , page 404) .

The Zintl description of Nd_2CuO_4 is quite simple . We must first recognize that it is a "composite" of two phases , the copper oxide layer , $-CuO_2$ -, and the neodymium oxide layer , $-Nd_2O_2$ -, which is entirely ionic in nature . In

the copper oxide layer , there are four Cu-O covalent bonds per formula unit of "-CuO₂-" , which require eight valence electrons for completion . Copper(II) will donate two electrons , and the two linear oxygen links will provide two each , or four more from both . The neodymiums will transfer their valence electrons to the structure , three each or six from both . Of the six Nd(0) electrons donated , two will go to the Cu-O covalent skeleton , and the other four will be transferred to the two "-NdO₂-" oxygens , to make them oxide anions $[O^0 + 2e^- = O^{2-}]$. That completes the four Cu-O covalent bonds , and also creates the Nd-O ionic layer in this compound .

Poole , Datta , and Farach (ref. 12 , page 391 , their p. 82) say that"This structure [the tetragonal Nd₂CuO₄ form] tends to be unstable relative to its K₂NiF₄ counterpart [La₂CuO₄] , and is not known to superconduct" . They present side-by-side illustrations of La₂CuO₄ and Nd₂CuO₄ in Fig. VI-5 , p. 83 , in which the square planar copper atoms in the neodymium compound are clearly shown . I wonder , though : has Nd₂CuO₄ really been examined carefully with regard to modifying it into a high T_c superconductor ?

First, there is the matter of its magnetic susceptibility versus temperature behavior. Arjomand and Machin carried out a wide-ranging study of ternary copper(I), (II), and (III) compounds in the mid 1970s (ref. 102, page 406). Of the fifteen compounds they investigated with respect to magnetic susceptibility – which they measured at room temperature and at liquid nitrogen temperature – only La_2CuO_4 showed extraordinarily low values at both temperatures : 0.69 BM at 300 K, and 0.34 BM at 80 K (see their Table 3, "Summary of Magnetic Data", p. 1062). There are two implications here : first , La_2CuO_4 is strongly antiferromagnetic , with its T_N lying well above ambient temperature ; and second , other copper(II) compounds may not be very antiferromagnetic, if they are at all. That is, selection of La₂CuO₄ to experiment with may have just been a very lucky occurrence for Bednorz and Müller, who didn't cite Arjomand and Machin's paper in their references in their seminal report on the Ba-La-Cu-O system with $T_c = 30$ K; presumably they were unaware of the strongly antiferromagnetic nature of the precursor La_2CuO_4 .

I checked briefly in the literature for any studies carried out on the magnetic

susceptibility of Nd₂CuO₄ versus its temperature , over a reasonably wide range of temperatures , since this compound wasn't prepared or investigated by Arjomand and Machin . Naturally , it would be both of great interest and importance to learn of the magnetic nature of Nd₂CuO₄ before any chemical modification of it is undertaken . If the compound had only the "standard" Curie paramagnetism sort of magnetic susceptibility at room temperature (about 1.73 BM , spin only) , with little change at lower temperatures , the researcher might become discouraged at the prospects for modifying it into a high temperature superconductor .

At least one study had indeed been carried out on the magnetic susceptibility versus temperature of certain rare earth Ln_2CuO_4 compounds, where "Ln" was La, Pr, Nd, and Sm (ref. 103, page 406). They were studied over a temperature range of 4 - 700 K. The abstract of their paper stated, "All these solids show deviations from the Curie-Weiss law due to short-range interactions". Presumably, then, Nd₂CuO₄ is also antiferromagnetic, and so could be a suitable candidate precursor for a high T_c superconductor.

In another study the electrical conductivities versus temperature of several Ln_2CuO_4 compounds – including La_2CuO_4 and Nd_2CuO_4 – were measured (ref. 104, page 406). The behavior in this regard of La_2CuO_4 was exceptional, in that its conductivity remained almost unchanged over a wide temperature range : about 1.6 ohm⁻¹cm⁻¹ from 350 – 1250 K. The conductivity of Nd_2CuO_4 and the other rare earth cuprates examined corresponded to the characteristics of pseudometals ; that is , they had a direct temperature-conductivity relationship. The conductivity of Nd_2CuO_4 varied from 0.1 - 10 ohm⁻¹cm⁻¹ over the experimental temperature range .

The authors of this latter paper attributed the difference in electrical conductivity between La₂CuO₄ and Nd₂CuO₄ (and the other lanthanide cuprates) to the presence of 4f electrons in the neodymium compound and a lack of them in the lanthanum ; Nd³⁺ has a 4f³ electronic configuration in its valence shell , while lanthanum is 4f⁰. The neodymium 4f electrons would have to be more mobile than the copper 4p_z¹ electron . One of them might have been promoted to a higher energy level frontier orbital when the neodymium cation is coordinated by the oxide anions . See page 65 for a
comment on possible hybrid orbitals such as d^3fsp^3 and d^3f^4s that might involve f native orbitals .

The conductivities and semiconducting characteristics of neodymium copper(II) oxide would become irrelevant if we can find some way of activating the pi XO Cu-O metallic bond in the material without altering its original structure of flat, unkinked planes of copper oxide. Our thoughts now turn to possible ways of doping the precursor Nd_2CuO_4 so as to activate the Cu-O bilayer metallic bond in the solid.

At least two methods of doping Nd₂CuO₄ have been tried , having the objective of converting it into a high temperature superconductor , but with only mediocre results . Cation doping has been attempted , using Ce(IV) to replace some of the Nd(III) (ref. 105 , page 406) . Anion doping has also been investigated , replacing some of the oxides with fluorides (ref. 106 , page 407) . These are somewhat surprising in light of our experience with YBCO , which contains , in a formal sense , the powerful oxidizer cation Cu(III) [because YBCO is a Robin-Day Class II mixed-valent compound , the "blended valence" of the copper cations in it is really +2.33] . Doping of neodymium cuprate with cerium(IV) , and retaining the overall crystal structure of the compound , should induce the transformation of an equivalent quantity of copper(II) into copper(I) , not copper(III) . Similarly , replacing some of the oxides with fluorides should force the same transformation with an equivalent quantity of copper(II) cations .

In the latter case with the partial replacement of oxide with fluoride , some research had already been done in this area , with results that proved to be both hard to reproduce and somewhat controversial . Ovshinsky and coworkers had claimed to detect superconducting transitions , peaking at 155 K , in samples of fluorocuprates such as $YBa_2Cu_3F_2O_y$; I'm not sure what the value of "y" was (ref. 107 , page 407) . A few months later , a Chinese research group reported a maximum superconducting transition temperature of 148.5 K in Y-Ba-Cu-O compounds that had been bombarded with fluoride anions in an accelerator : a novel preparative technique , to be sure (ref. 108 , page 407) ! Japanese chemists claimed improved results with a fluorinated YBCO system they investigated in 1989 (ref. 109 , page 407) .

For example , the fluorocuprate $YBa_2Cu_3O_{7-\delta}F_{0.1}$ had an optimized T_c of about 90 K , which wasn't really an improvement on the performance of unfluorinated YBCO itself ($T_c = 93$ K). I suppose YBCO can tolerate some fluoride substitution without serious degradation in its performance as a high T_c superconductor .

In the neodymium cuprate system Chen and co-workers found evidence of superconductivity at 10 K (27 K onset) in the compound Nd₂CuO_{3.77}F_{0.3} (ref. 106, page 407). Taking the valences of Nd, O, and F as invariable at 3+, 2–, and 1– respectively, the blended valence of the copper is calculated to be 1.84+. If we partition this latter valence between "pure" copper(I) and copper(II), we will have Cu(1.84+) \rightarrow Cu(I)_{0.16} + Cu(II)_{0.84}, from the algebraic relationship, Cu¹⁺_x + Cu²⁺_{1-x} = Cu^{1.84+}, then solving for "x". There does indeed seem to be a small mole fraction of copper(I) induced in the compound by fluoride substitution in its lattice.

Naturally , the questions arise : how can we have copper(I) in the compound when its structure is unaltered (since a square planar coordination is unknown for copper(I) species) ? And wouldn't this violate Verwey' Rule concerning the coordination geometry of the active metal cations in electrically conductive solids (referred to on page 183) ? The answer to both questions might be provided by referring back to the sketch on page 193 of the proposed electronic structure of the copper(II) cations of the "diamonds" in YBCO . For the "copper(I)" cations , we merely add a second electron to the $4p_z$ native orbital . What we are doing in reality , though – because of the metallic bond in the material – is adding a few extra electrons to the overall lattice structure , into the Cu-O pi XO , and not to any one specific copper .

An analogy to this is the intercalation of certain alkali metal atoms (potassium, rubidium, and cesium) into the lattice of graphite. The valence electrons of the highly reactive, reducing metals are donated to the graphite's 2p pi XO electron "cloud", while the corresponding inert alkali metal cations are sandwiched between the sheets of graphite. We can formally think of these metal valence electrons being assigned to the $2p_z$ native orbitals on the carbon atoms, which already have a carbon valence electron, from the sp² trigonal planar hybridization : $\sigma_a^{-1} \sigma_b^{-1} \sigma_c^{-1} 2p_z^{-1}$. Thus , a carbanion will be formed by the acceptance of the metal electron by the carbon atom . However , the 2p pi XO metallic bond in graphite will "blend" these anionic charges into the XO , so that in reality the metal electrons are being donated to the entire system rather than resting on any one specific carbon atom . The same sort of blending should occur in the fluoride-substituted neodymium cuprate compounds , so that no distinguishable copper(I) cations are apparent . The partially fluorinated neodymium cuprate will be a functional Robin-Day Class II mixed-valent compound , and a Class 3 metallic solid [true metal – mixed-valent – Class II] .



Figure 41 : an M3D representation of the pi XO electrons in the partially reduced (i.e. with some Cu(I) present) Cu-O flat sheets , such as in the Nd-Cu-O-F system . Small red spheres : copper atoms ; larger green spheres : oxygen atoms ; pairs of small aqua dots : electron pairs , mostly in the oxygen $2p_z$ native AOs [one electron pair has been placed in a copper $4p_z$ AO , making it formally Cu(I)] ; and small silver spheres : singlet electrons in the formally Cu(II) $4p_z$ AOs . The oxygen $2p_z$ AOs and the copper $4p_z$ AOs have the correct size , shape , symmetry , and spatial orientation for overlapping continuously in the crystal lattice , thus forming a pi XO . Since the coppers' $4p_z$ AOs are at a higher energy level than the oxygens' $2p_z$ AOs , they will "float" over them in the bilayer metallic bond so formed .

In this orbital picture of the Cu-O pi XO in the doped neodymium cuprates , we can understand how electrons can be added to the XO in a reductive manner , reducing a small amount of Cu(II) to Cu(I) in a formal sense . Since the coordination geometry of all the copper atoms remains identical , Verwey's Rule holds true for this system , even though a square planar coordination for copper(I) is generally unknown and would not normally even be predicted by VB theory [the coordination of copper(I) by oxygens is universally linear sp ; I am unaware of any exceptions].

The other reductive approach to doping neodymium cuprate was taken by several teams of researchers in 1989 (ref. 105, page 406). This was also an example of Verwey's controlled valence technique, in that by substituting some cerium(IV) for neodymium(III), the equivalent amount of copper(I) was induced in the Cu-O lattice. But was it, really ? If we look at the following redox equation, we see right away that Ce(IV) and Cu(I) cannot co-exist in the same crystal lattice that contains a metallic bond, which will provide a pathway for the transfer of the valence electrons from Cu(I) to Ce(IV) :

Cu(I) + Ce(IV) $\xrightarrow{\text{thermodynamically}}$ Cu(II) + Ce(III) ; $E_T^{0} = 1.567 \text{ V}$. spontaneous at STP

That is, Ce(IV) - quite a powerful oxidizer, at 1.72 V to Ce(III) - will oxidize Cu(I) to Cu(II), at -0.153 V, with lots of "juice" (1.567 V, the cell potential) remaining.

A typical sample produced in this study of cerium-doped neodymium cuprate was $Nd_{1.85}Ce_{0.15}CuO_{3.93}$, which had a superconductor transition temperature of 24 K (Tokura et al.). We note the slight deficit in the oxygen content of the material ; this will have the effect of converting some of its Cu(II) into Cu(I), without modifying its overall crystal structure. Let's do some valence-counting arithmetic on this formula. We will assume that all the ceriums are trivalent ; if the calculation shows that there is some Cu(I) in the lattice , then our assumption will be correct , according to the above redox equation.

Total positive charge per unit formula is $2 \times 3^+ = 6^+$, plus that of the copper atom, which is to be calculated. The negative charge will be that of the oxygens, that is, $3.93 \times 2^- = 7.86^-$. The difference will be the positive charge on the copper atom : $7.86 - 6.00 = 1.86^+$. This can be partitioned between copper(II) and copper(I) as shown earlier on page 218 :

$$Cu(I)_{x} + Cu(II)_{1-x} \longrightarrow Cu(1.86+) ; \text{ then },$$

$$x + 2 - 2x = 1.86 ; \text{ thus },$$

$$x = 0.14+ \text{ for } Cu(I), \text{ and } 1-x = 0.86+, \text{ for } Cu(II).$$

So the formula can now be written : $Nd_{1.85}^{3+}Ce_{0.15}^{3+}Cu_{0.86}^{2+}Cu_{0.14}^{1+}O_{3.93}^{2-}$.

I conclude that yes, there is a small mole fraction of Cu(I) in the ceriumdoped neodymium cuprate; all the cerium must be present only as Ce(III), despite the statement of Tranquada et al. (cited in ref. 105, page 406) to the contrary [".... the average valence of Ce substituted into Nd₂CuO₄ is ~3.5+ rather than the formal valence of 4+]; and that this Nd-Ce-Cu-O system is a Robin-Day Class II mixed-valent compound and a Class 3 metallic solid.

There was a flurry of excitement when the preparation and analyses of these cerium-doped neodymium cuprates were published in 1989. Hall effect tests seemed to indicate that the charge carriers in them were indeed bona fide electrons, and not the "holes" thought to be the charge carriers for the other high temperature superconductors. Personally, I have always wondered if it was wise to describe the behavior of superconductors in semiconductor terms, and I have always avoided the concept of holes as charge carriers in my study of superconductors. Rather than adopt such ideas that make me a little uneasy, I have stuck throughout this presentation to the "tried-and-true" : just plain, simple, straightforward electrons as the charge carriers in all metallic solids, although they are "formatted" differently in different classes of metallic solids, to borrow a computer term.

Thus, in terms of VB, orbital picture, and redox, the Nd-Ce-Cu-O system is very easy to understand, and further experimentation in it is suggested.

Arjomand and Machin (ref. 102, page 406) described the conversion of copper(II) to copper(I) by prolonged heating at a rather high temperature :

CuO +
$$\frac{1}{2}$$
 Al₂O₃ $\xrightarrow{1100 \circ C}$, CuAlO₂ + $\frac{1}{4}$ O₂ (g)
5 days

As noted above , copper(II) is a mild oxidizer , at 0.153 V to Cu(I) , but I suppose that when heated to very high temperatures , this standard reduction potential – applicable at STP – rises steadily to the point where it is high enough to permit the copper(II) to oxidize even the formidable oxygens , which are converted to oxygen(0) and pop out of the lattice as oxygen molecules . It might be similarly possible to convert the copper(II) in Nd₂CuO₄ to Cu(I) by prolonged heating at this temperature , with the added experimental advantage of sweeping any oxygen gas by-product out of the reaction mass by a stream of flowing inert gas such as argon . This latter feature illustrates Le Chatelier's Principle of driving a reaction to completion by continuously removing from it a reaction product or by-product :

Nd₂CuO₄
heat to ca. 1100 °C,
Nd₂CuO_{3.5} +
$$\frac{1}{4}$$
O₂(g).

Assuming that the copper(I) product $Nd_2CuO_{3.5}$ is pure and has the Nd_2CuO_4 crystal structure, it could then be doped into pure Nd_2CuO_4 to produce the desired mixed-valent compound with different mole ratio values :

 $x Nd_2CuO_4 + (1-x) Nd_2CuO_{3.5} \longrightarrow Nd_2CuO_{3.5+0.5x}$.

The mole fraction "x" could be taken experimentally from zero (pure $Nd_2CuO_{3.5}$) to unity (pure Nd_2CuO_4) in as many steps as considered practical by the researcher .

In a second set of experiments , the copper(I) dopant $NdMCuO_4$ could be prepared , where "M" is a quadrivalent metal species , and the material

has the Nd₂CuO₄ crystal structure . One possibility for "M" might be uranium(IV), with a Shannon-Prewitt crystal ionic radius of 1.03 Å (compared to that of Nd³⁺, at 1.123 Å); also the uranium atom, from the actinide family of elements, prefers to have a very high coordination number when bonded to oxygen, so it should fit into the ionic -UO₂- layer quite well . A possible preparation for this dopant might involve the following reaction :

 $\frac{1}{2}$ Nd₂O₃ + UO₂ + $\frac{1}{2}$ Cu₂O $\xrightarrow{}$ NdUCuO₄ .

"Shake-n-bake" is the solid state chemist's informal term for the reaction of refractory materials to form a new product . It usually involves the intimate mixing together of the components by grinding them in a mortar with a pestle – a good, old-fashioned medieval alchemist's procedure ! – forming cylindrical pellets in a high pressure press, then calcining the pellets in a furnace at a high temperature to achieve a superficial sintering of the reactant particles (this temperature may range from perhaps 800 – 1100 °C). The pellets are cooled to room temperature and are ground to a fine powder again . A reactive atmosphere such as oxygen, or an inert atmosphere such as argon, may be used in the furnace ; it may be static, or dynamic (a flowing stream). Usually x-ray diffraction (XRD) analysis is used to determine the purity of the product, which may be subjected to additional pelletizing-heating-cooling-regrinding cycles until the desired degree of uniformity and purity for it is reached.

The copper(I) dopant can then be doped into the pure Nd_2CuO_4 substrate in a series of compounds with varying values of the mole fraction "x", taken again from zero (NdUCuO₄) to unity (Nd₂CuO₄) :

x Nd₂CuO₄ + (1-x) NdUCuO₄
$$\xrightarrow{\text{oxygen}}$$
 Nd_{1+x}U_{1-x}CuO₄.

A static atmosphere of oxygen in the furnace during the shake-n-bake calcination step is suggested to retard the slight deoxygenation that

could occur at this time in the procedure.

It might even be possible to use Sn(IV) to make a copper(I) dopant for neodymium cuprate, since Nd³⁺Sn⁴⁺Cu¹⁺O₄⁸⁻ should be redox stable. This would be an interesting dopant, since the weakly oxidizing Sn(IV) [0.151 V to Sn(II)] should be able to polarize the Cu-O pi XO metallic bond better than U(IV), and the resulting superconductor candidate compounds, Nd_{1+x}Sn_{1-x}CuO₄, might have a respectable transition temperature.

The compound $SrCuO_2$ was first synthesized by Arjomand and Machin back in 1975, and was second only to La_2CuO_4 in the strength of its antiferromagnetism among the copper compounds they examined in this context, (ref. 102, page 406, Table 3, "Summary of Magnetic Data", p. 1062). However, its Néel temperature must be much lower than that of La_2CuO_4 , probably not too much higher than 300 K or so. The crystal structure of $SrCuO_2$ is remarkably simple, consisting of flat Cu-O sheets with strontium cations sandwiched in between :



Figure 42 : the M3D model of strontium copper(II) oxide , $SrCuO_2$. The small red spheres are square planar coordinated copper(II) atoms ; the larger green spheres represent linear oxygen atom links ; and the large aqua spheres stand for the intercalated strontium cations , which are ionically bonded to the Cu-O anionic layers . This model was based on the sketch of $Ca_{0.86}Sr_{0.14}CuO_2$ presented in Figure 1 , p. 232 , in the article by Siegrist et al. (ref. 110 , page 407) . Pure $SrCuO_2$ has an identical structure .

Arjomand and Machin claimed to have synthesized pure $CaCuO_2$, but later research showed that it cannot be produced in bulk by the usual shake-nbake technique. By doping up to 0.14 mole fraction of strontium into the lattice of $CaCuO_2$, the compound $Ca_{0.86}Sr_{0.14}CuO_2$ can indeed be made in a bulk preparation under ambient pressure, with the crystal structure shown above . Under high pressure , or by using sophisticated single crystal thin film (epitaxial) growth techniques , cuprate compounds with variable strontium and calcium mole ratios can be made . For example , a typical thin film compound prepared and examined was $Ca_{0.3}Sr_{0.7}CuO_2$; it was found to be a semiconductor with a direct temperature-conductivity relationship , and an ambient electrical conductivity of 1 ohm⁻¹cm⁻¹ (ref. 111 , page 407) .

Azuma et al. prepared a cation-deficient version of $Ca_xSr_{1-x}CuO_2$ and found it to be a fair superconductor. For example, their product $(Sr_{0.7}Ca_{0.3})_{0.9}CuO_2$ had a T_c of about 40 K, with an onset T_c of 110 K (ref. 112, page 407). By simple valence counting we discover that the copper atoms in this compound have the NIOS valence of 2.2+, which indicates a blend of copper(II) and copper(III). Partitioning this valence into its "pure" constituents :

$$Cu_{x}^{2+} + Cu_{1-x}^{3+} = Cu_{1}^{2.2+}$$
; then, $2x + 3 - 3x = 2.2$, and $x = 0.8$.

The compound's formula can now be written out fully as,

$$Sr^{2+}_{0.63}Ca^{2+}_{0.27}Cu^{2+}_{0.8}Cu^{3+}_{0.2}O^{4-}_{2}$$

Unlike the previous cuprate superconductors with mixed-valent copper(I) and (II), this material is a copper(II,III) Robin-Day Class II mixed-valent compound and Class 3 metallic solid.

A research team at the University of Texas , Austin , reported in June , 1991 having successfully doped SrCuO₂ with neodymium , to produce a superconductor with an onset transition temperature of about 40 K , with the full effect at around 25 K or so (ref. 113 , page 407) . Let's examine a typical compound they prepared with these properties , Sr_{0.86}Nd_{0.14}CuO₂ (their Figure 4 , p. 550) . The cationic charge on the copper atoms in this material will be 1.86+ , which partitions to x = 0.14 and 1 - x = 0.86. The

compound's formula can be written out in full as :

 $Sr^{2+}_{0.86}Nd^{3+}_{0.14}Cu^{2+}_{0.86}Cu^{1+}_{0.14}O^{4-}_{2}$.

We see that the strontium "controls" the quantity of Cu(II) present in the compound, from the substrate $SrCuO_2$; and the neodymium controls the amount of Cu(I) in the doped material, from the hypothetical dopant used in the experiment, NdCuO₂. I don't know if this latter compound actually exists or not. On page 222 I suggested trying to deoxygenate Nd₂CuO₄, a well-known material, to the copper(I) derivative, Nd₂CuO_{3.5}.

In any case, neodymium-doped strontium copper(II) oxide is readily understood as a copper(I,II) Robin-Day Class II mixed-valent compound and a Class 3 metallic solid . At least, it seems to be so below the onset T_c. Above 50 K the resistance-temperature curve dips steadily downward (Figure 4, p. 550), or , conversely, the conductivity-temperature curve climbs upward as the temperature rises : a direct relationship, which is generally indicative of a semiconductor ! How can a semiconductor, whose ambient conductivity is about 50 ohm⁻¹cm⁻¹, falling to around 20 ohm⁻¹cm⁻¹ at 50 K (the onset temperature), suddenly become a superconductor ? Perhaps 50 K represents a Verwey transition temperature for the doped strontium cuprate, rather like what magnetite has at 120 K (page 48). The material might be "shifting gears", orbitally speaking, at this temperature, changing from a nodal XO to a nodeless XO. I don't know if there is a change of crystal structure at 50 K in the solid, but if there was, it might account for this unusual electronic behavior. I'm unwilling to discard Krebs's Theorem (page 30) based on this information ; rather, I think it would be quite interesting to revisit this particular cuprate system, with the emphasis on examining its electrical and magnetic properties over a wide temperature range, and its crystal structure below and above 50 K.

A Japanese research team , also in 1991 , reported the doping of $SrCuO_2$ with lanthanum(III) to produce the series of $Sr_{1-x}La_xCuO_2$ compounds (ref. 114 , page 407) . For example , a T_c of 43 K in the material was measured with x = 0.1. Its formula can be written as : $Sr^{2+}_{0.9}La^{3+}_{0.1}Cu^{2+}_{0.9}Cu^{1+}_{0.1}O^{4-}_2$. Again , we see that the cuprate has mixed-valent Cu(I,II) , and could be thought of as a "blend" of $(SrCuO_2)_{0.9} + (LaCuO_2)_{0.1}$. It was interesting to note that the usual shake-n-bake technique failed to produce the doped

compound directly, yielding only SrCuO₂ plus unreacted La₂O₃ and CuO. These intermediate components had to be subjected to high pressure (3-5 Gpa) and temperatures (450-1000 °C) to complete the preparation and produce the desired doped cuprate.

I wonder if a gentler method of making such a material might be achieved by a **metathesis** reaction, exchanging "softer" halide anions, such a chlorides, for "harder" oxide anions :

$$x \operatorname{SrCl}_{2} + (1-x) \operatorname{LaCl}_{3} + x \operatorname{CuCl}_{2} + (1-x) \operatorname{CuCl} \xrightarrow{\text{melt together}}$$

$$Sr_{x}\operatorname{La}_{1-x}\operatorname{Cu}^{2+}_{x}\operatorname{Cu}^{1+}_{1-x}\operatorname{Cl}_{4}^{4-} \xrightarrow{2 \operatorname{Li}_{2}\operatorname{O}}, \qquad Sr_{x}\operatorname{La}_{1-x}\operatorname{Cu}^{2+}_{x}\operatorname{Cu}^{1+}_{1-x}\operatorname{O}_{2}^{4-} \xrightarrow{-4 \operatorname{LiCl}}$$

In the last couple of decades new techniques of preparative inorganic chemistry have been devised as alternatives to the rather brutal shake-n-bake method of synthesizing solid state materials with infinite atomic lattices (i.e. non-molecular solids). The new procedures, especially those in aqueous solution or at or near room temperature are sometimes called by their French name, chimie douce (ref. 115, page 408). For example, in the above chloride route, the chloride salts are all water-soluble, except for the copper(I) chloride. Even the CuCl might dissolve, by complexation as the $[CuCl_4]^{3-}$ anion, in the aqueous solution of the other reactant salts (ammonium chloride added to the solution might be helpful in dissolving the CuCl). Then, the chloride salt solution would be poured, with vigorous stirring, into a second water solution of (say) sodium hydroxide, carbonate, or oxalate to completely precipitate all the polyvalent metal cations present. The precipitate would be digested, cooled, filtered, washed, and calcined in flowing air or nitrogen to (say) 800–1000 °C to (hopefully) yield the desired lanthanum-doped strontium copper(II) oxide .

In reading the literature of superconductor chemistry it seems to me that the analytical technique of **thermal analysis** has been underutilized by researchers in the field . The three types of thermal analysis of the most practical use to preparative solid state chemists are differential thermal analysis (dta ; measuring reaction energies : exotherms and endotherms) ;

thermogravimetry (TG; gains and losses of reactant mass with increasing reaction temperature); and derivative thermogravimetry (DTG; the rate of gain or loss of reactant mass with change of temperature). The latter procedure can provide an accurate measurement of the mass change, since integration of the area under the curve "peak" will yield the mass gain or loss (the instrumental rationale is similar to that of peak measurement in gas chromatography and in NMR spectrophotometry in organic chemistry, for example). A.R. West, in <u>Basic Solid State Chemistry</u> (ref. 34, page 395), pp. 196-205, provides a nice overview of thermal analysis techniques.

In the above example of the calcining of the polyvalent cation precipitate of $Sr_xLa_{1-x}Cu^{2+}_xCu^{1+}_{1-x}O^{4-}_2$, TG/DTG – the two analyses are usually carried out simultaneously – would be very helpful in guiding the researcher in the calcination step , helping to ensure that the residue isn't "overcooked" and that partial deoxygenation doesn't occur ; in other words , helping to determine the optimum temperature and time for the calcining .

In the reaction shown on the middle of page 222 to produce the hypothetical copper(I) dopant $Nd_2CuO_{3.5}$, TG/DTG again would be helpful in monitoring the reaction to give the researcher an idea of when , and under what conditions , the deoxygenation reaction was successfully concluded .

The extremely powerful oxidizer copper(III) is capable of oxidizing oxide anions to oxygen atoms , which exit the crystal lattice as oxygen molecules , at the high temperatures used to prepare , sinter , and anneal the superconductor candidate compounds . YBCO is well known to undergo deoxygenation at temperatures as low as 500 °C in a nitrogen atmosphere , and thereby lose its superconductive properties . This decomposition can be followed by TG/DTG (West , Figure 7.8 , p. 293) . The unintentional partial deoxygenation of cuprates can lead to the formation of samples with a "witches brew" sort of composition , containing mixtures of copper (II) and (III) , and copper(I) and (II) in multiple phases within the same sintered reaction pellet . TG/DTG can help to avoid such irreproducible mixtures by monitoring mass loss with increasing temperature .

Thermal analysis has shown the effect, attributable to Le Chatelier's

Principle , of flowing atmospheres of different gases over heated reactants . For example , an atmosphere of carbon dioxide over calcium carbonate will retard its pyrolysis (to $CO_2 + CaO$) relative to that in air , while a vacuum will accelerate its decomposition (West , Figure 4.30 , p. 198) . A dynamic (flowing) atmosphere over a pyrolysing sample will also speed up its decomposition , as reaction by-product gases are swept out of the reaction mass . The chemist can use these "tricks" , and monitor them by thermal analysis , in designing more efficient and effective reaction schemes in the preparation of new solid state materials . Thermal analysis methods , because they typically utilize only very small quantities of reactants (20-50 mg for dta , and several hundred milligrams to a few grams for TG/DTG) , can also be used as "pilot experiments" in determining optimum reaction conditions for future full-scale preparative reactions .

As mentioned , derivative thermogravimetry (DTG) provides "peaks" on the recording chart as the pyrolysis proceeds to higher temperatures with the loss of volatile by-products (sometimes a reactant will gain in mass if it is heated in a reactive atmosphere , eg. oxidation in air or pure oxygen , and nitriding in nitrogen or ammonia) . The peaks' areas represent the mass gain or loss over the temperature range of that particular peak . The peaks are obtained mathematically in the thermal analysis (TG/DTG) electronic controller by an onboard computer that continuously calculates the rate of change of mass with time , $\delta m/\delta t$.

I wonder if it would be possible to have such a time-based differentiation analysis with other physical measurements taken over a wide range of temperatures . For example , is it possible to have a continuous measurement of the electrical conductivity of a metallic solid over a temperature range ? If so , it might be possible to write a small computer program to continuously provide a calculation of the **rate** of change of the conductivity with time , with an unfolding graphic display of the resulting curve , with its peaks , either (or both) on a monitor screen or on graph paper . Unlike the gentle curves usually obtained for conductivity-temperature measurements , and whose analyses are often open to some subjective interpretation , the peaks obtained by the time-based differentiation analysis are usually quite distinct in shape , even dramatic at times (at least , in some of the DTG curves I have examined). Superconductor transitions should be easier to pinpoint.

Another example would be that of the measurement of the magnetic susceptibility of a solid over a wide temperature range . Using such data we can see if a material of interest displays colligative magnetic properties such as ferromagnetism , antiferromagnetism , ferrimagnetism , and so on . I believe that the critical temperatures associated with electrical conductivity and magnetic susceptibility measurements , such as the superconductor transition temperature , Verwey transition temperature , Curie temperature , and Néel temperature , would be displayed graphically more clearly in the peaks than in the present curves . They could then be analyzed more accurately than is conventionally possible [I don't know what , if anything , the peak areas for the conductivity and susceptibility analyses would represent , though] .

Ideally, it would be of great value to solid state chemists to have commercially available equipment for the simple yet accurate measurement of the electrical conductivity and magnetic susceptibility of solids on a continuous basis over a wide range of temperatures, with provision of the output data both as "direct" data (curves), and as the time-based derivative data (peaks). Just place the sample in the holder properly, activate the apparatus to start the furnace or cryostat (refrigerator) and the electronic measuring unit, and away you go ! The reader will of course by now readily understand my particular fondness for these electrical and magnetic measurements. I wish there was some way of making them fast, simple, informative, cheap, accessible and standardized, so that they would become a routine part of analyzing newly synthesized solids. Such continuous data feedback would, I am sure, become very important in solid state chemistry investigations.

Most of the doping experiments described above concerning Nd₂CuO₄ and SrCuO₂ involved copper(I,II) mixed-valent compounds . Copper(II,III) compounds should be more efficient at producing high T_c superconductor candidate compounds , because the base copper(III) cation is such a powerful oxidizer (2.4 V to Cu²⁺) compared to copper(II) [0.153 V to Cu¹⁺]. It should thus be able to polarize the pi XO metallic bond in the lattice more

strongly than with copper(I,II), and hopefully thereby raise the material's electrical conductivity accordingly, as occurs in the polarized pi XO metallic bond in graphite doped with the electrophilic SbF_5 (page 151).

Arjomand and Machin prepared several copper(III) ternary oxides , for example $YCuO_3$, using very forcing conditions to oxidize Cu(II) to Cu(III) :

$$\frac{1}{2} Y_2 O_3 + CuO + \frac{1}{4} O_2(g) = \frac{400 \text{ atm. } O_2(g)}{800 \text{ }^\circ \text{C}, 40 \text{ hrs}} YCuO_3 = \frac{1}{2} YCuO_3$$

In the same study, they also reported preparing and characterizing the compound $BaCuO_2$, which – incredibly ! – seemed to have ferromagnetic properties [YCuO₃ was strongly Curie paramagnetic]. Consider the following hypothetical "thought" experiment :

$$YCuO_3 + 2 BaCuO_2 \xrightarrow{(1) \text{ grind together , press}} YBa_2Cu_3O_7 .$$

$$(2) \text{ sinter in pure } O_2 \text{ atm.}$$

$$at ca. 800-900 \text{ °C };$$

$$(3) \text{ cool to ambient under}$$

$$pure O_2 \text{ ; regrind ; repelletize}$$

Arjomand and Machin were one experiment away from a liquid nitrogen range superconductor, and possibly a Nobel Prize in chemistry. But in truth they were interested in preparing only homovalent ("pure" copper I, II, or III) compounds and not mixed-valent compounds; they prepared ternary and not quaternary compounds; and they never did any electrical conductivity measurements on their products. Still so near, but yet so far !

For preparing copper(II,III) mixed-valent derivatives of neodymium copper(II) oxide while retaining the Nd_2CuO_4 crystal structure, we should first prepare a pure copper(III) compound with that structure, then dope it in increments into pure Nd_2CuO_4 as the substrate. Such a copper(III) candidate compound might be $NdSrCuO_4$, which would likely require rather forcing

conditions for its preparation :

 $\frac{1}{2}$ Nd₂O₃ + SrO + CuO + $\frac{1}{4}$ O₂ (g) high O₂ pressure NdSrCuO₄.

Assuming NdSrCuO₄ can be prepared in a pure , well characterized form , it would then be doped into Nd₂CuO₄ in increments , to produce a series of Cu(II,III) mixed-valent compounds for electrical testing :

 $x Nd_2CuO_4 + (1-x) NdSrCuO_4 \longrightarrow Nd_{1+x}Sr_{1-x}CuO_4$.

In these experiments , the mole fraction "x" could be increased experimentally from zero (pure $NdSrCuO_4$) to unity (pure Nd_2CuO_4).

It is interesting to note in all the preparations with neodymium compounds being fashioned into high temperature superconductors , that Nd^{3+} is a paramagnetic cation (4f³) . Neodymium(III) oxide is described as a blue powder , and the chloride salt , NdCl₃.6H₂O , is a purple crystalline solid . Clearly , this sort of paramagnetism has little if any effect on the appearance of superconductivity in the neodymium cuprate compounds mentioned here . This is undoubtedly so because the metallic bond is over the copper-oxide covalent framework , and excludes the nested neodymium cations , whose paramagnetic singlet 4f electrons cannot uncouple the Cooper pairs in the metallic bond .

For doping $SrCuO_2$ with a copper(III) compound to produce a copper(II,III) mixed-valent compound for electrical testing, we could try a $MCuO_2$ compound in which "M" is an alkali metal cation. The compound $KCuO_2$ has been known for over fifty years, and as expected – because it is a simple copper(III) composition – somewhat forcing conditions are required for its synthesis:

$$KO_2 + CuO = \frac{400 - 450 \text{ °C}}{O_2 \text{ atm.}, 24 \text{ hrs}} KCuO_2 + \frac{1}{2}O_2(g) .$$

It has been described as a "crystalline, steel-blue, non-magnetic powder thermolabile above 500 °C" (ref. 116, page 408).

The crystal structure of $KCuO_2$ isn't quite like that of $SrCuO_2$ (refer back to Figure 42 on page 224); it consists of infinite ribbons of Cu-O, stacked parallel to each other in the crystal, with the potassium cations intercalated between them, and electrostatically bonded to the anionic ribbons:



Figure 43 : the M3D model of potassium copper(III) oxide , $KCuO_2$. The small red spheres are square planar coordinated copper(III) cations ; the larger green spheres represent oxygen atom links ; and the large aqua spheres stand for potassium cations intercalated between the Cu-O ribbons . This model was based on the drawing of $KCuO_2$ in the excellent review article on metal cuprates by H. Müller-Buschbaum (ref. 117, page 408, his p. 733).

The two-coordinate oxygen linking atoms may use a trigonal planar hybrid AO (sp²) for their Cu-O covalent bonds : $\sigma_a^{\ 1} \sigma_b^{\ 1} \sigma_{lp}^{\ 2} 2p_z^{\ 2}$. If this is so, then the electron pairs in the $2p_z$ native AOs could overlap with the copper $4p_z$ AOs. They are empty in KCuO₂, but each has a promoted valence electron in the SrCuO₂ copper(II) substrate . KCuO₂ is a Zintl-type compound . Each copper atom , per formula unit , has four covalent bonds , which require

eight valence electrons for completion . The copper(III) cation contributes three ; the two oxygen links each contribute two bonding electrons , or four from them ; and the potassium(0) atom donates its valence electron to the covalent framework . That's a total of eight valence electrons per formula unit , to complete the covalent skeleton of KCuO₂ , with the inert potassium cations nested in between the anionic Cu-O ribbons .

The copper(II) substrate $SrCuO_2$ would be doped with increasing mole fractions of the copper(III) dopant , $KCuO_2$:

x SrCuO₂ + (1-x) KCuO₂ $\xrightarrow{\text{pure O}_2 \text{ atm.}}$ Sr_xK_{1-x}CuO₂ , where "x" is a mole fraction taken experimentally from zero to unity .

It's probably a good idea to conduct the heating and cooling down phases of all doping trials with copper(III) compounds under an atmosphere of pure oxygen gas; and if a gaseous by-product such as water vapor or carbon dioxide is expelled from the reactants, a flowing oxygen atmosphere should be used to sweep away the by-product gases to help drive the reaction to completion, and at the same time retard the inevitable deoxygenation that occurs with heated copper(III) or copper(II,III) compounds.

The crystal ionic radius of Sr^{2+} , per Shannon-Prewitt , is 1.32 Å (sixcoordinated) ; that of K^{1+} is 1.52 Å , and the next smallest alkali metal cation is that of Na^{1+} , at 1.16 Å . The compound $\mathrm{NaCuO_2}$ is known , and its crystal structure (shown at the top of the next page) is much like that of $\mathrm{KCuO_2}$, the difference essentially being in the coordination of the alkali metal cations by the oxygen linking atoms in the Cu-O ribbons . It might also be tried as a copper(III) dopant for $\mathrm{SrCuO_2}$. The known compound $\mathrm{Ca}_{0.86}\mathrm{Sr}_{0.14}\mathrm{CuO_2}$, referred to above on page 225 , and Arjomand and Machin's compound , BaCuO₂ , might also be tried as substrates in these doping experiments .

The copper(II) ternary compound with lithium cations , Li_2CuO_2 , has been known for some time , and its crystal structure (shown on the following page in Figure 45) , with ribbons of Cu-O , is somewhat similar to that of NaCuO₂ and KCuO₂ . It too might be used as a substrate for doping with copper(III) .



Figure 44 : the M3D model of sodium copper(III) oxide , $NaCuO_2$. The small red spheres are square-planar coordinated copper(III) cations ; the larger green spheres represent oxygen linking atoms ; and the large aqua spheres represent sodium cations intercalated between the Cu-O ribbons . This model was based on H. Müller-Buschbaum's sketch of $NaCuO_2$ (ref. 117, page 408, his p. 733).



Figure 45 : the M3D model of lithium copper(II) oxide , Li_2CuO_2 , where the small red spheres are copper(II) cations , the larger green spheres are oxygen linking atoms , and the small blue spheres represent lithium cations intercalated between the Cu-O ribbons . The lithium cations have a tetrahedral coordination by the oxygens . This model was also based on a sketch of Li_2CuO_2 in H. Müller-Buschbaum's review article (see above) .

An "all-alkali metal cation" cuprate system might be prepared as follows :

x $Li_2CuO_2 + (1-x) NaCuO_2 \longrightarrow Li_{2x}Na_{1-x}CuO_2$, where "x" is an experimental mole fraction between zero and unity.

The doped copper(II,III) composite should retain the Cu-O ribbon structure of the precursor substrate and dopant compounds .

By way of summarizing for this section, the following table lists the copper(II) substrates we have been looking at, with planar sheet or ribbon copper oxide assemblies, in between which are sandwiched either cations or cationic layers of metal oxides. Dopants are suggested for them, which might activate their metallic bond and permit them to become superconducting at a lowered temperature :

Summary of Suggested Cuprate Doping Experiments			
Copper(II) Substrate	Copper(I) or (III) Dopant		
Nd ₂ CuO ₄	$Nd_{2}CuO_{3.5}$ (I) (1)		
SrCuO ₂	NdUCuO ₄ (I) (1)		
BaCuO ₂	NdSnCuO ₄ (I) (1)		
$Ca_{0.86}Sr_{0.14}CuO_2$	NdCuO ₂ (I) (1,2)		
Li ₂ CuO ₂	NdSrCuO ₄ (III) (1)		
	KCuO ₂ (III)		
	NaCuO ₂ (III)		

Notes: (1) Apparently as yet unknown compound .

(2) Briefly alluded to in the text ; not discussed in detail .

The "CuO₄" materials should be considered as separate from the "CuO₂" substrates and dopants . Even in the latter cases , the Cu-O planes and ribbons might not be too compatible at higher mole fractions , "x" ; quite possibly a ribbon dopant such as KCuO₂ would blend into a plane substrate such as SrCuO₂ only at relatively low mole fractions (I'm guessing maybe not higher than x = 0.2). With higher values for "x" , multiphase products might be produced . In any case , these systems , which I believe are all novel , would be most interesting and potentially fruitful to investigate .

My approach to these doped cuprates is a very cautious, conservative one; rather than try to make a doped material from a complex mixture of reagents that may produce only a multiphase "witches brew", it is more prudent to use a two step procedure. First, prepare the substrate and dopant in a pure, well characterized state ; be very sure you know exactly what you are starting out with, before the second step – the syntheses of the doped products – is attempted. The substrate and dopant for the target system should have the same sort of crystal structure, if at all possible, in accordance with Verwey's Rule . This wasn't possible , for example , with SrCuO₂ [Cu-O planes] and KCuO₂ [Cu-O ribbons], but at least in them, the critical Cu-O assemblies have the same square planar coordinated copper atoms we hypothesize are the important feature for high temperature cuprate superconductors. I recommend this cautious, careful two step method for exploratory work in the new systems outlined in this report; once a successful or otherwise interesting system has been discovered by it, the chemist should be able to devise a simpler, faster, more economical one step route to the desired material, to produce it in larger quantities for an expanded research and development program.

Redox Activated High Temperature Cuprate Superconductors

There have been three major advances in high temperature superconductivity since 1986. The first was Bednorz and Müller's groundbreaking discovery of the La-Ba-Cu-O superconductor with $T_c = 30$ K, quickly followed by the second breakthrough in this field, the synthesis of YBCO with $T_c = 93$ K by

Chu, Wu, and co-workers in 1987. YBCO was, of course, the first liquid nitrogen range superconductor, and as such was considered to be a material with a bright economic potential.

The third significant advance in high temperature superconductors – and I am referring here to their materials chemistry aspect – was the discovery of the bismuth , thallium , and mercury cuprates as high T_c superconductors . Not only did these materials prove to have remarkably high transition temperatures ($T_c = 110$, 122, and 133 K, respectively, for optimized formulations), they also were homovalent copper(II) compounds without the benefit of mixed valency to activate the Cu-O pi XO metallic bond .

The bismuth and thallium cuprates were described in 1988, with the latter compounds probably receiving more attention than the former ones . Sheng and Hermann prepared and characterized a series of Tl-Ba(Ca)-Cu-O compounds with varying stoichiometries ; all their products had transition temperatures ranging from 90-122 K (ref. 118, page 408). Apparently their rationale for using thallium(III) in the formulations was to examine the effect of replacing yttrium (crystal ionic radius = 1.04 Å) in the YBCO-like structures with another small trivalent cation . The crystal ionic radius of thallium(III) – which is more covalent in nature than ionic – is 1.025 Å, almost identical in size to that of Y^{3+} . Let's look at three of their thallium cuprates in some detail . We have , for example :

 $\begin{array}{rll} Tl_2Ba_2CuO_6\ ,\ T_c=90\ K\ :\ (Tl^{3+})_2(Ba^{2+})_2Cu^{2+}O_6^{-12-}\ ;\\ Tl_2Ba_2CaCu_2O_8\ ,\ T_c=110\ K\ :\ (Tl^{3+})_2(Ba^{2+})_2Ca^{2+}(Cu^{2+})_2O_8^{-16-}\ ;\ and\ ,\\ Tl_2Ba_2Ca_2Cu_3O_{10}\ ,\ T_c=122\ K\ :\ (Tl^{3+})_2(Ba^{2+})_2(Ca^{2+})_2(Cu^{2+})_3O_{10}^{-20-}\ .\end{array}$

Assuming that the oxygen formula contents are indeed exactly 6, 8, and 10 in the three compounds, respectively, we see that these thallium cuprates contain entirely homovalent copper(II) as the "active ingredient", which together with the oxygens, comprise the Zintl covalent skeleton for the structures, over which a metallic bond has formed. The superconductivity, and "ordinary" conductivity above T_c , occur in this Cu-O pi XO [according to our VB/MO picture of the metallic bond], as has been discussed earlier with the La-Sr-Cu-O and YBCO systems.

The thallium cuprates have a "sandwich" structure consisting of layers of planar copper oxide bonded to layers of thallium(III) oxide , with the inert spectator cations (barium and calcium) nested in interlayer cavities . The copper atoms in these compounds have the usual coordinations by oxygen linking atoms : square planar (dsp²) ; square pyramid (dsp³) ; and 4+2 distorted octahedral (dsp² + sp) . We see that as the coordination number of the copper atoms decreases , the transition temperature of the compound rises . For example , in Tl₂Ba₂CuO₆ the copper atoms all have the six-coordinate 4+2 distorted octahedral [tetragonal] coordination by oxygens . It nevertheless has a quite respectable transition temperature of 90 K :



Figure 46 : the M3D model of thallium(III) barium copper(II) oxide , $Tl_2Ba_2CuO_6$ ($T_c = 90$ K). The small red spheres are copper(II) cations with the 4+2 distorted octahedral coordination ; the larger green spheres are linking oxygen atoms ; the aqua spheres are octahedrally coordinated thallium(III) atoms ; and the large violet spheres represent barium cations . This model was based on the sketch of $Tl_2Ba_2CuO_6$ in Figure 5 , p. 1522 , of A.W. Sleight's comprehensive review of the chemistry of high temperature superconductors (ref. 119 , page 408). In the compound $Tl_2Ba_2CaCu_2O_8$, with $T_c = 110$ K, the copper atoms all have a square pyramid coordination with the oxygen linking atoms :



Figure 47 : the M3D model of thallium(III) barium calcium copper(II) oxide , $Tl_2Ba_2CaCu_2O_8$ ($T_c = 110$ K) . Red spheres : copper ; green spheres : oxygen ; yellow spheres : calcium ; aqua spheres : thallium ; and violet spheres : barium . From Sleight's Figure 5 , p. 1522 , ref. 119 , page 408 .

In the compound $Tl_2Ba_2Ca_2Cu_3O_{10}$, with $T_c = 122$ K (the highest of the series), there is a central layer of square planar coordinated copper atoms (Figure 48, at the top of the next page), sandwiched between an upper and a lower layer of copper(II) atoms which are square pyramid coordinated with oxygen atoms. As speculated near the bottom of page 194 and on page 195, the Cu-O "diamonds" with the square planar coordinated copper(II) cations will likely be the best pathway for the superconductivity and "normal" electrical conductivity, simply because there is less oxygen atom hindrance



Figure 48 : the M3D model of thallium(III) barium calcium copper(II) oxide , $Tl_2Ba_2Ca_2Cu_3O_{10}$ ($T_c = 122$ K) . Red spheres : copper ; green spheres : oxygen ; yellow spheres : calcium ; aqua spheres : thallium ; and violet spheres : barium . From Sleight's Figure 5 , p. 1522 , ref. 119 , page 408 .

to the formation and stability of the Cu-O pi XO . Since the oxygen linking atoms have pendant electron pairs in $2p_{y,z}$ orbitals , which are quite repellent toward the itinerant electrons in the metallic bond , the fewer such oxygens there are clustering around the copper atoms the denser and stronger will be the metallic bond , in this case the Cu $4p_z - O 2p_z XO$. This is why I have recommended that researchers try to incorporate such planar Cu-O planes (or possibly even ribbons , as we saw earlier with the alkali metal cuprates) in any future high T_c superconductor candidate compounds they design and synthesize .

Discovery of the bismuth cuprates was announced by a Japanese research team in early 1988 (ref. 120, page 408), at about the same time as the publication of the American report on the thallium cuprates. An optimized formulation had a crystal structure fairly similar to them, with a planar

Cu-O sheet between an upper and lower layer of Cu-O with square pyramid coordinated copper(II) cations . Above and below this trilayer Cu-O structure were bonded bismuth-oxygen layers .

The idealized formula for this compound, with a transition temperature of 110 K (ref. 121, page 408), was $Bi_2Sr_2Ca_2Cu_3O_{10+y}$. If y = 0, then the valence-counting formula can be written $(Bi^{3+})_2(Sr^{2+})_2(Ca^{2+})_2(Cu^{2+})_3O_{10}^{20-}$. I believe that the value of "y" is critical to the success of the bismuth cuprate as a high temperature superconductor. It must be greater than zero in order for superconductivity to be observed in the material.

By increasing the value of "y" above zero, we will increase the degree of oxidation of bismuth in the compound :

$$Bi^{3+}Bi^{3+}...O_{10} \longrightarrow Bi^{3+}Bi^{5+}...O_{11} \longrightarrow Bi^{5+}Bi^{5+}...O_{12}$$

Note that the copper(II) cations in the lattice will be unaffected by the additional oxidation, since it is far more difficult to oxidize copper(II) to copper(III) -2.4 V - than it is to oxidize bismuth(III) to bismuth(V), 1.759 V.

This latter redox potential is quite high , indicating that bismuth(V) is a powerful oxidizing agent . Even if "y" is a small value , meaning that only a small mole fraction of Bi(III) had been oxidized to Bi(V) , that small amount of Bi(V) in the lattice would be sufficient to polarize the Cu-O pi XO metallic bond in the cuprate , thus making it an excellent electrical conductor and superconductor candidate . Then , an antiferromagnetic ordering in the copper(II) cations' $4p_z$ singlet "ninth" valence electrons , which have now been promoted above the Fermi level in the bilayer XO , would permit them to readily condense together into Cooper pairs at a relatively high T_c (about 110 K).

Bismuth(V) is thus the key ingredient in releasing the normally "frozen" (pinned) copper(II) $4p_z$ "ninth" valence electrons, permitting them to

become itinerant in the metallic bond XO. One way they might do this is to form a **resonant system** with the copper(II) "ninth" valence electrons :

$$\underline{Bi(V)} + 2 \underline{Cu(II)} \xrightarrow{[0.641 V]} Bi(III) + 2 Cu(III)$$

Of course , the equilibrium in the above reversible equation will lie well to the left , as I have tried to indicate by the boldface font and underlining . The potential of 0.641 V in square brackets is the absolute difference between the two standard reduction potentials of 2.4 V for Cu(III) and 1.759 V for Bi(V). Although this potential difference is substantial , the copper(II) "ninth" electrons should resonate to a certain extent between the copper(III) base kernels and the bismuth(V) atoms , and freed from their pinning , they can become itinerant in the Cu-O pi XO.

The question immediately arises : if some oxidation of Bi(III) to Bi(V) in this system has occurred, then might the superconductivity in it be attributed to mixed-valent bismuth, and not to the copper "ninth" valence electrons? The metallic bond would then have to be located in the bismuth oxide layer, and not necessarily in the copper oxide layers.

In fact, the synthesis and characterization of a "pure" mixed-valent bismuth superconductor compound was reported in 1988 by a research group at AT&T Bell Laboratories (ref. 122, page 409). Because Bi(V), a powerful oxidizer, was involved in the formulation, rather forcing conditions were necessary in the preparation of the bismuth compound (actually, one of a series of such materials):

The bismuth in this latter composite would have a NIOS valence of 4.4+, which can be partitioned between Bi(III) and Bi(V) so as to provide the valence-counting formula , $Ba^{2+}_{0.6}K^{1+}_{0.4}Bi^{3+}_{0.3}Bi^{5+}_{0.7}O_3^{6-}$.

The optimized product of the series , $Ba_{0.6}K_{0.4}BiO_3$, was found by X-ray diffraction to be a single phase material with a cubic symmetry perovskite crystal structure (Figure 26 , page 154) . As in the bismuth cuprates , the bismuth atoms in the Bell Labs' compound have an octahedral coordination by linear oxygen linking atoms . Since bismuth is a post-transition element , it will tend to favor s and p orbitals , and disfavor d native orbitals , in hybrid AO formation . It will probably be using the sp³ds hybrid orbital (page 157) to form the BiO₃ "supercube cage" in whose cavities the spectator barium and potassium cations are embedded .

The "base kernel" of the bismuthate compound is Bi(V). We can think of Bi(0) forming the octahedral sp³ds hybrid AO, then filling five of its six sigma-type lobes with its five valence electrons $(6s^2 6p^3)$. The potassium(0) atom donates its valence electron to fill the sixth lobe. The bismuths and linear oxygen atom links (page 147) then polymerize together to form the BiO₃ perovskite skeleton, with the inert potassium cations filling the cube cavities. We then dope the KBiO₃ substrate with the dopant $BaBiO_3$, whose bismuth atoms can be thought of as half Bi(III) and the other half Bi(V). This doping procedure adds "extra" valence electrons into the frontier orbitals of the BiO₃ cage. Since the 7s AO is used in the hybrid AO, the extra electrons from the Bi(III) dopant will have to enter the $7p_{x,y,z}$ AOs; however, the $7p_x$ AO will by default be destabilized by the linear oxygen links that occupy its volume . No problem : the "extra" dopant electrons will end up in the $7p_{y,z}$ AOs , which can overlap continuously in the lattice with the oxygen links' $2p_{y,z}$ AOs to form the Bi-O pi XO metallic bond in the crystal. This XO will be activated by mixed-valency and polarization by the oxidizing Bi(V) to permit the bismuth "extra" $7p_{v,z}$ electrons to become itinerant above the Fermi level in the XO.

However, the compound $Ba_{0.6}K_{0.4}BiO_3$ has a superconductivity onset transition temperature of 29.8 K, which is of course far below the T_c (110 K) of the other bismuth superconductor, $Bi_2Sr_2Ca_2Cu_3O_{10+y}$. This suggests that the "pure" bismuthates such as $Ba_{0.6}K_{0.4}BiO_3$ aren't very antiferromagnetic, if they are at all (Bi_2O_3 is diamagnetic), and are therefore relying on the "classic" BCS mechanism – phonon-assisted electron coupling – to form the Cooper pairs in the superconducting state.

I conclude that it is the copper(II) "ninth" valence electrons in the high T_c bismuth cuprates , which apparently are assisted by antiferromagnetism , that are condensing into Cooper pairs in the superconducting state in the material . It is the strongly oxidizing bismuth(V) in the compound , though , that is activating the metallic bond XO in it by polarization or by redoxinduced resonant exchange of the XO free electrons between the copper(III) and bismuth(V) kernels .

I was wondering about the synthetic strategy employed by the Bell Labs' research teams (ref. 122, page 409) in their design and preparation of the Ba-K-Bi-O series of compounds . They studied , in essence , a blend of two bismuth components , KBiO₃ and BaBiO₃ , which formed the composite material , $Ba_xK_{1-x}BiO_3$, under investigation . Normally we would expect KBiO₃ , with "empty" Bi(V) , to be either an insulator or a poor semiconductor at best . However , there is the interesting example of barium plumbate , BaPbO₃ , with "empty" Pb(IV) , that is a true metal (its electrical conductivity at room temperature is 3448 ohm⁻¹cm⁻¹ , and at liquid helium temperature , 4 K , is 13,514 ohm⁻¹cm⁻¹ ; see Table II , p. 636 of ref. 123 , page 409) . Lead(IV) and Bi(V) are 5d¹⁰ electronically , and the 5d orbitals are at roughly the same energy level as the 6 s-p AOs (Figure 4 , page 35) that form the sp³ds hybrid AO for the PbO₃ and BiO₃ skeletons .

Suppose this sp³ds AO used one of the 5d native orbitals in its formation , including its two contained electrons : $(5d_x^{2}{}_{-y}^{2})^2 + 6s^2 + 6p_x^{2} + 6p_y^{0} + 6p_z^{0} + 7s^{0} = (sp^3ds)^6$, recalling that lead(0) is $6s^2 6p^2$ electronically . Polymerizing this hybrid AO with the linear oxygen atom links would form the covalent PbO₃ skeleton . When we add Ba(0) to the PbO₃ , or K(0) to the BiO₃ , the extra electrons must go into frontier orbitals around the skeleton , and the inert Ba²⁺ or K¹⁺ cations are nested in the supercube cavities in the structure . Since the 7s AOs are used for the hybrid AO , and the 7p_x AOs are energetically destabilized by the oxygen links occupying their volumes , the extra electrons from the Ba(0) or K(0) will enter the 7p_{y,z} native orbitals on the lead and bismuth atoms . These can overlap continuously with the 2p_{y,z} AOs on the oxygen links to form the pi XO metallic bond in BaPbO₃ and – possibly – in KBiO₃ . This pi XO will be polarized by the strongly oxidizing Pb(IV) [1.69 V to Pb(II)] , permitting the solid to have a

respectable electrical conductivity , and to be a true metal as well . The same considerations will also apply to $KBiO_3$, which is isoelectronic with $BaPbO_3$; it too could conceivably be a fair electrical conductor and true metal .

The suggested electronic structure of the lead atoms in barium plumbate is summarized in the following sketch :





 \underline{Note} : the $7p_{x}$ orbital is destabilized by the oxygen ligands . .

The compound BaBiO₃, the other component of $Ba_xK_{1-x}BiO_3$, has been synthesized in a pure form (ref. 124, page 409). It was described as "bronze colored crystals", which were semiconducting over a wide temperature range (4 – 970 K; its electrical conductivity at room temperature was found to be about 0.1 ohm⁻¹cm⁻¹). Its crystal structure was determined to be that of a perovskite with orthorhombic symmetry. Unfortunately, no magnetic susceptibility information was reported for BaBiO₃. The bismuth valence in it is an even 4+, but this is "unnatural" for bismuth , whose normal valences are 3+ and 5+ (more correctly, (III) and (V), indicating their covalent nature). Clearly, BaBiO₃ isn't at all like the highly metallic SnP (page 160) with its "unnatural" valence – for tin – of 3+. If BaBiO₃ had genuine Bi(IV) in its lattice, we would expect some sort of paramagnetism in it, either of the Curie variety (pinned singlet electrons), or Pauli paramagnetism, from delocalized itinerant electrons in a metallic bond.

The compound isn't like BaPbO₃, either . It has one additional electron to fit into an orbital somewhere , and possibly has some undefined difficulty locating this third extra electron in the $7p_{y,z}$ native orbitals . The distorted symmetry of its perovskite structure hints at a possible "inert pair effect" (refer back to page 69), in which two of the promoted electrons are located in a nonbonding orbital . Another possibility might be that the singlet "seventh" electrons in BaBiO₃ [two from Ba(0) + five from Bi(0)] might dimerize in pairs throughout the solid to form covalent bonds that introduce periodic distortions in the lattice structure . This troublesome electronic behavior may be deleterious to the compound's application in prospective high temperature superconductor candidates , and suggests that bismuth may not be the ideal element to try to forge into high T_c superconductors .

Way back in 1975 a compound in the BaPb_{1-x}Bi_xO₃ system , BaPb_{0.7}Bi_{0.3}O₃ , was found to have a transition temperature of 13 K (ref. 124 , page 409) . These lead-bismuth composites were solid solutions of varying mole ratios of BaPbO₃ and BaBiO₃ . The color of the Ba-Pb-Bi-O compounds was black up to x = 0.3, and bronze at higher values of "x" . The black compounds were found to be metallic , and the bronze materials were semiconductors . Clearly , higher bismuth contents were ruining the composites , with respect to their performance as electrical conductors . Curiously , superconductivity in the system was optimized at the changeover point [black⇔bronze] , at x = 0.3. Note that BaPbO₃ alone never became superconducting (although it was tested only to liquid helium temperature , 4 K).

So it seems that BaBiO₃ might not be the best component to include in the design of new composites as high T_c superconductor candidate compounds. The problem is that the Bi(V) in KBiO₃ is already "tanked up" with frontier orbital electrons, a counterintuitive conclusion derived from the VB/MO description of the electronic structure of the substance. We really want a hole-generating dopant for it, such as the hypothetical (-)BiO₃ ["(-)" represents a cation vacancy in the structure], with the impossible Bi(VI).

Failing that , a heteroatomic dopant (not having bismuth) for $KBiO_3$, such as tungsten(VI) oxide , WO_3 , which is somewhat similar to "BiO₃", might be investigated :

x KBiO₃ + (1-x) WO₃ \longrightarrow K_xW_{1-x}Bi_xO₃, with "x" ranging from zero to unity.

In this event , the WO₃ would use its empty $6p_{y,z}$ frontier orbitals to "blend into" the Bi-O pi XO metallic bond . That would have the effect of introducing holes into the XO . Assuming that there are no untoward redox effects between the Bi(V) and the W(VI) – for example , pinning of the itinerant electrons on the tungsten kernels – a serviceable series of superconductor candidates might be produced for investigation .

Returning briefly to the thallium cuprates , we can credit the same sort of polarization mechanism as in the bismuth cuprates to explain their functioning as high temperature superconductors . Thallium(III) , which is found in all the thallium cuprates , is a fairly strong oxidizer , with its $E^{0}_{red} = 1.252 \text{ V}$. As before , polarization of the Cu-O pi XO metallic bond might be accomplished by a resonance of the itinerant electrons between the thallium(III) and copper(III) kernels , with the latter very powerful oxidizer (2.4 V) winning the tug-of-war :

 $2 \underline{Cu(II)} + \underline{Tl(III)} \xrightarrow{[1.148 V]} 2 Cu(III) + Tl(I) .$

The resonance equilibrium will favor the copper(II) and thallium(III), which are presented in bold font and underlined, on the left side of the equation. In effect, the Cu(II)/Tl(III) couple acts somewhat like an inefficient mixed-valent copper system, since with the true mixed-valent system Cu(II)/Cu(III) the absolute potential difference value, [V], will always be zero. The copper-thallium resonance should serve to unpin the copper(II) "ninth" valence electrons from their $4p_z$ orbitals.

In 1993, a Swiss group reported the synthesis and characterization of a series of mercury cuprates having crystal structures fairly similar to those

of the thallium and bismuth cuprates (ref. 125, page 409). The most successful compound in the series, "Hg-1223", had a transition temperature of 133 K under ambient pressure. Its formula was HgBa₂Ca₂Cu₃O_x, with the value for the oxygen content, "x", being about 8. With mercury having a valence of 2+, the valence-counting formula for this high T_c cuprate would be Hg²⁺(Ba²⁺)₂(Ca²⁺)₂(Cu²⁺)₃O₈¹⁶⁻. Again, homovalent copper(II) seems to be the electronically active component in the material. Mercury(II) is a relatively mild oxidizer at 0.851 V [to Hg(0)], but it seems to be strong enough to induce the resonance in the copper(II) "ninth" valence electrons in order to activate the Cu-O pi XO metallic bond :

$$2 \underline{Cu(II)} + \underline{Hg(II)} \xrightarrow{[1.549 V]} 2 Cu(III) + Hg(0) .$$

Its crystal structure resembled that of the thallium cuprate illustrated in Figure 48, page 241. A central layer of planar Cu-O was sandwiched between an upper and a lower layer of square pyramidal Cu-O, with a layer of Hg-O on each side of the trilayer Cu-O section.

Two years after this significant achievement , another research group "tweaked" the composition of the mercury cuprate slightly , substituting some thallium for the mercury content (ref. 126 , page 409) . The resulting composite had the general formula $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\gamma}$. When the mole fraction $\gamma = 0.33$, the compound had a transition temperature of 138 K , the highest T_c yet measured for any superconductor under ambient pressure . I believe that this record is still standing today . The valence-counting formula for the optimized material is [with the mixed-valence charges partitioned between copper(II) and copper(III)] :

 $(Hg^{2+})_{0.8}(Tl^{3+})_{0.2}(Ba^{2+})_2(Ca^{2+})_2(Cu^{2+})_{2.55}(Cu^{3+})_{0.45}(O^{2-})_{8.33}$. This compound is a "witches brew", with Hg^{2+} , Tl^{3+} , and even some Cu^{3+} to activate the metallic bond. All that for an increase in T_c of a few kelvins !

Comparing the three redox-activated high T_c cuprates with respect to their oxidizing component and resultant transition temperatures , we see that there is an inverse relationship between the standard reduction potentials of the oxidizers and the T_c of the material activated by that particular oxidizer :

Oxidizer	Standard Red. Pot.	Trans.Temp.	
Hg(II)	0.851 V	133 K	
Tl(III)	1.252	122	
Bi(III)	1.759	110	
Cu(III)	2.4	93	

The addition of copper(III) to the list may be a little unfair , because the T_c involved (93 K) belongs to YBCO , which has a somewhat different crystal structure than the other three compounds referred to . Also , it is involved in a homoatomic mixed-valence system – with copper(II) – while the other oxidizers are combined with foreign elements in heteroatomic pseudo mixed-valent systems .

Consideration of this list suggests that we might fruitfully investigate other oxidizing species combined with the planar copper(II) systems we looked at earlier, such as Nd_2CuO_4 , $SrCuO_2$, $KCuO_2$, and Li_2CuO_2 . For example, could the compound Tl_2CuO_4 , with the Nd_2CuO_4 structure, be prepared?

 $Tl_2O_3 + CuO \longrightarrow Tl_2CuO_4$.

I am somewhat loath to recommend the preparation or manipulation of thallium compounds , which are notoriously toxic . Thallium(III) oxide , in particular , is very volatile – because of its covalent nature – at the high temperatures used in shake-n-bake syntheses , and eventually permeates the workplace environment , much to the detriment of any researchers in the vicinity , unless suitable precautions are taken . Perhaps a chimie douce route to the target product might be preferable , to avoid the use of Tl_2O_3 :

2 $Tl(NO_3)_3$. 3 H_2O + $Cu(NO_3)_2$. 3 H_2O \longrightarrow Tl_2CuO_4 . (1) dissolve in water (2) pour into excess aqueous NaOH or Na₂CO₃ (3) digest, cool, filter, wash, dry, calcine

Table of Oxidizers

<u>Oxidizer</u>	Ē	<u>radius</u>	<u>oxide</u>	<u>m.p. or dec.</u>
U(VI) / U(V)	0.062 V	0.87 A (VI)	UΟ ₃	n/a
Sn(IV) / Sn(II)	0.151	0.83 (IV)	SnO ₂	1630 C
Cu(II) / Cu(I)	0.153	0.71 (II) (sq)	CuO	1326
W(VI) / W(V)	0.26	0.74 (VI)	WO₃	1473
Re(VI) / Re(IV)	0.400	ca. 0.65 (VI)	${\rm ReO}_3$	400 (dec.)
Sb(V) / Sb(III)	0.671 (O ^{2·})	0.74 (V)	$\mathbf{Sb}_{2}\mathbf{O}_{3}$	380 (dec.)
Mo(VI) / Mo(V)	0.700	0.73 (VI)	MoO ₃	795
Fe(III) / Fe(II)	0.771	0.785 (III)	$\mathbf{Fe}_{2}\mathbf{O}_{3}$	1565
Ag(l) / Ag(0)	0.7996	1.29 (I)	Ag_2O	230 (dec.)
Hg(II) / Hg(0)	0.851	1.16 (II)	HgO	500 (dec.)
V(V) / V(IV)	0.957 (H ⁺)	0.68 (V)	V_2O_5	690
Ni(III) / Ni(II)	1.17	0.74 (III)	NiO	1984
Mn(IV) / Mn(II)	1.224 (H⁺)	0.67 (IV)	MnO ₂	535 (dec.)
TI(III) / TI(I)	1.252	1.025 (III)	$\mathbf{TI}_{2}\mathbf{O}_{3}$	717 (subl.)
Cr(VI) / Cr(III)	1.350 (H⁺)	0.58 (VI)	CrO₃	195
Mn(III) / Mn(II)	1.5415	0.785 (III)	Mn_2O_3	1080 (dec.)
Pb(IV) / Pb(II)	1.6913 (H⁺)	0.915 (IV)	PbO_2	290 (dec.)
Ce(IV) / Ce(III)	1.72	1.01 (IV)	CeO_2	2600
Bi(V) / Bi(III)	1.759	0.90 (V)	Bi ₂ O ₅	150 (dec.)
Co(III) / Co(II)	1.92	0.685 (III)	Co ₂ O ₃	900 (dec.)
Cu(III) / Cu(II)	2.4	0.68 (III)	n/a	n/a

Assuming Tl_2CuO_4 could be prepared in a pure state, it might also be tried as a dopant for Nd_2CuO_4 in a series of doping trials :

 $x Nd_2CuO_4 + (1-x) Tl_2CuO_4 \longrightarrow Nd_{2x}Tl_{2-2x}CuO_4 .$

Perusing the Table of Oxidizers on the previous page , we can select several interesting oxidizing oxides listed there to try to replace some or all of the Nd₂O₃ in Nd₂CuO₄ . For the moment , these replacement oxides should have diamagnetic metal cation components , like the Tl(III) in Tl₂O₃ . Since the two neodymium cations in Nd₂CuO₄ are (Nd³⁺Nd³⁺) , we might try to replace them with other 3,3 combinations , or 1,5 combinations , or 2,4 combinations . I have already suggested the Nd(III)/Tl(III) combination , for example . Here are a few other suggestions :

 $\begin{array}{cccc} \underline{3,3} & \underline{1,5} & \underline{2,4} \\ \hline & & \\ \hline & & \\ &$

We could also try low energy 2,3,4, and 5 cations with oxidizer cations . For example , Al(III)/Tl(III) , K(I)/Bi(V) , etc. , Ba(II)/Pb(IV) etc. , and Hg(II)/Ti(IV) , combined with CuO , could be studied .

Direct, simple combinations of the oxidizer oxides with copper(II) oxide might also be examined. These could open a new route to novel high temperature superconductors with simple formulas and structures and open up a new area of inorganic chemistry research. Here are several suggestions that follow from consideration of the Table of Oxidizers :

HgO + CuO \longrightarrow HgCuO₂ (cf. SrCuO₂) ;

 $CeO_2 + CuO \longrightarrow CeCuO_3$;
$$2 \text{ AgNO}_{3} + \text{Cu(NO}_{3})_{2} \cdot 3 \text{ H}_{2}\text{O} \xrightarrow{(1) \text{ dissolve in water}} \text{ Ag}_{2}\text{CuO}_{2};$$

$$(2) \text{ pour into NaOH or (cf. Li_{2}\text{CuO}_{2})} \text{ Na}_{2}\text{CO}_{3} (aq)$$

$$(3) \text{ digest ppt.}, \text{ filter}, \text{ wash}, \text{ dry}, \text{ calcine}$$

$$\text{CuO} + \text{PbO}_{2} \xrightarrow{} \text{CuPbO}_{3} ;$$

$$\text{V}_{2}\text{O}_{5} + \text{CuO} \xrightarrow{} \text{V}_{2}\text{CuO}_{6} [\text{or Cu(VO}_{3})_{2}?];$$

$$\text{CuO} + \text{CrO}_{3} \xrightarrow{} \text{CuCrO}_{4} ;$$

But is this latter compound molecular in nature ? Could it be prepared by,

The chromium(IV) in this latter compound , $CuCrO_3$, is also oxidizing, and should be able to activate the Cu-O pi XO in the material, assuming such a metallic bond can actually form in it.

It might be possible to combine copper(II) oxide with an insoluble chromate salt, such as lead(II) chromate, $PbCrO_4$ ("chrome yellow" paint pigment). This would hopefully insert alternating layers of chromate between layers of Cu-O, which would be physically flattened out and chemically activated by the oxidizing Cr(VI) atoms :

Calcining this latter product could yield $(Pb^{2+}Cr^{4+})(Cu^{2+})O_4^{8-}$, which might have the Nd_2CuO_4 crystal structure and activating Cr(IV) atoms .

I commented on page 232 about the fact that while Nd^{3+} is paramagnetic , it doesn't seem to disrupt the superconductivity in the various neodymium compounds the phenomenon occurs in . This is probably because the metallic bond – where the superconductivity occurs – is in the Cu-O planes , and doesn't include the neodymium cations nested in the oxide layers between them .

It would be quite interesting to test this hypothesis, and it should be simple and relatively inexpensive (at least, in chemical costs) to do so:

 $Fe_2O_3 + CuO \longrightarrow Fe_2CuO_4$. [I see that Fe_2CuO_4 is offered commercially, eg. by Alfa Aesar.]

If this compound , Fe_2CuO_4 , had the Nd_2CuO_4 structure , the iron(III) cations would be in a Fe-O layer sandwiched between Cu-O planes . Iron(III) is a mild oxidizer (0.771 V) , roughly comparable to mercury(II) at 0.851 V , so we could reasonably expect activation of the Cu-O pi XO using this oxidizing oxide component . If superconductivity was confined to the Cu-O planes , the hypothetical compound Fe_2CuO_4 might actually have a measurable transition temperature , despite the presence in the material of the Curie paramagnetic iron(III) cations . That would be quite an achievement indeed , given iron's notoriety in destroying superconductivity in a sample of solid , even when Fe(III) is present in trace quantities in it .

What I think would probably happen in reality is that Fe_2CuO_4 might be semiconducting or even metallic , but probably not superconducting at any temperature . This is because of the resonance of the copper(II) "ninth" valence electrons between the iron(III) and copper(III) kernels. That mechanism would extend the Cu-O metallic bond over the Fe(III) cations , and thereby prevent the Cooper pairs from forming in the first place . The iron atoms would probably ruin the Cu-O antiferromagnetic ordering that is the essential mechanism of high temperature superconductivity (according to this VB/MO picture of the metallic bond and superconductivity) . In any case , the compound Fe_2CuO_4 would be most interesting to prepare and study , and might provide some illuminating results . <u>Added note :</u> I haven't done a literature survey to see if the electrical and magnetic properties of Fe_2CuO_4 have been studied before . This might be a long shot, but recalling that SbF₅ was able to form a charge transfer compound with graphite , and boost its electrical conductivity from a modest 25,000 ohm⁻¹cm⁻¹ to around a million ohm⁻¹cm⁻¹, an interesting experiment might be to mechanically mix SbF₅ (b.p. 150 °C) – "Liquid Oxidizer in a Bottle", so to speak – in small aliquots with copper(II) oxide powder , mulling the liquid and solid together in a mortar with a pestle so as to achieve a well-ground paste . Ideally , the mix should be treated , possibly by gentle warming , so as to obtain a free-flowing powder , as with the 75% by weight SbF₅-graphite reaction mixture . Of course , CuO doesn't have a lamellar structure like graphite , although – contemplating its crystal structure in Figure 38 , page 208 – there may be some space in the solid for small molecules to creep in . Certainly , some SbF₅ could adsorb on the surface of the copper oxide .

At 0.82 V (halide environment), the standard reduction potential of Sb(V) is slightly less than that of mercury(II), at 0.851 V, so we might hope for some activation of the Cu-Cu sigma XO metallic bond by the additive. There is always the proven track record of SbF₅ with graphite to encourage us in this experiment. The Sb(V) can't oxidize either the copper(II) to copper(III), or the oxygen links, but as with graphite, a charge transfer complex between the adsorbed SbF₅ and the Cu-Cu bonds is quite possible. This charge transfer would distort and polarize the Cu-Cu XO, as it does to the pi XO in graphite. The hope is that the bond polarization will boost the conductivity of CuO into the metallic range. Copper(II) oxide might thus be converted into a copper-based synthetic metal (Class 2). Note that the tetrahedral oxygen links in CuO can't form a Cu-O bilayer XO, because their valence shell electrons are entirely involved in the covalent structure.

Antimony(V) fluoride is one of a host of covalent Lewis acid halides that might also be investigated as possible activators of the dormant metallic bond in CuO. Most of the ones I've listed in the table on the following page have low energy metal atom centers, and so aren't oxidizing. However, as halides, their metal atom centers are all quite electrophilic, and so will have a pronounced bonding affinity with the electronegative $4p_z$ singlet electrons on the copper(II) atoms. This electrophile \rightarrow Cu(II) atom coordination may provide a useful mechanism for polarizing the Cu-Cu sigma XO in CuO.

Table of Lewis Acids

Fluoride	<u>B.P.</u> (* <u>M.P.</u>)	<u>Chloride</u>	<u>B.P.</u> (* <u>M.P.</u>)
		AICI ₃	190 C *
AsF_{3}	63 C	AsCl₃	130
\mathbf{BF}_{3}	- 101	\mathbf{BCI}_3	13
		BiCl ₃	230 *
NbF_{5}	72 *	NbCl₅	208 *
\mathbf{PF}_3	-102	\mathbf{PCI}_3	76
\mathbf{PF}_{5}	-75	\mathbf{PCI}_{5}	162 * (subl)
${\rm SbF}_{\scriptscriptstyle 3}$	292 *	\mathbf{SbCl}_{3}	73 *
$\mathbf{SbF}_{\mathrm{s}}$	150	SbCl ₅	79 (22 mm)
		SiCl4	58
		SnCl ₄	114
TaF₅	97 *	TaCl ₅	216 *
		TiCl4	136
		$ZnCl_2$	283 *

At the top of the following page I have listed more interesting electrophilic materials that may also be able to activate the Cu-Cu sigma XO metallic bond in copper(II) oxide . Most of these latter compounds contain oxidizing metal centers that might be able to activate the Cu-Cu bond via a resonance mechanism . The compact crystal structure of copper(II) oxide may preclude admission of any significant amounts of these molecular species into its interatomic spaces . The best we may hope for , then , is a strong surface adsorption of these electrophilic Lewis acids and oxidizers onto the CuO

surfaces, which is why the reaction mixtures should be as finely ground as possible, to maximize the surface area of the adsorbing solid.

Reagent	<u>B.P.</u> (<u>M.P.*</u>)	Ē	<u>Comments</u>
AgF	435 C *	0.7996 V	very soluble in water
			and organic solvents
AgNO₃	212 *	0.7996	
FeCl ₃	306 *	0.771	Lewis acid , Friedel-Crafts
			catalyst , paramagnetic
	277 *	0.851	b.p. 302 C ; volatile
\mathbf{POF}_{3}	- 40		
POCI ₃	105		
Pb(CH ₃ COO ⁻) ₄	175 *	1.6913	soluble in organic solvents
TI(CF ₃ COO ⁻) ₃	169 *	1.252	soluble in organic solvents
VF_4	325 *	0.337	V(IV) is paramagnetic
VCI ₄	149	0.337	
VOCI ₃	127	0.957	
\mathbf{WF}_{6}	17	0.260	
WCI ₆	275 *	0.260	

Miscellaneous Potential Cu-O Activators

As can be readily guessed by the gaseous and liquid states of these adsorbent compounds, and by the relatively low melting points of the solids listed, they are all essentially covalent in nature. Adsorption of the reagents onto the CuO surfaces as pure gases, or diluted in an inert carrier gas such as

nitrogen or argon , by neat liquid-solid mulling in a mortar , or from solution in an inert organic solvent are various experimental possibilities .

If encouraging results were obtained in trials of the Lewis acids and electrophilic oxidizers with CuO, other copper(II) oxide systems whose crystal structures are primarily comprised of flat Cu-O planes or ribbons could be investigated with these reagents. Compounds such as Nd_2CuO_4 , $SrCuO_2$, and Li_2CuO_2 come to mind in this regard. In these cases activation of the Cu-O pi XO metallic bond is a distinct and intriguing possibility, with possible induction of high T_c superconductivity in the treated samples.

Other Resonance Activated Metallic Systems

On page 243 I introduced the concept of the resonant system as a possible mechanism to activate the Cu-O pi XO metallic bond in copper(II) oxide and related crystal structures with planes or ribbons of Cu-O. The alert reader may have noticed hints of the generality of this idea , for example in the bismuth perovskite KBiO₃ doped with WO₃ on page 248. Why stop at activated copper(II) oxide and ternary oxides ? Can we activate the metallic bond by resonance in other systems that don't contain copper(II) ? Before examining possible experimental systems , we should first review four important conditions that must be taken into consideration with respect to these **heteroatomic redox couples**.

First , since it's always fun and exciting to produce a new superconductor , we should try to ensure that one component of the couple can act as the base cation with the higher positive charge . This base cation should have an even number of valence electrons in its outer shell , and it should be low spin and diamagnetic . For example , in YBCO the mixed-valent copper cations are $Cu^{2+}-Cu^{3+}-Cu^{2+}$; the base cation is Cu^{3+} : $Cu^{3+}-Cu^{3+}-Cu^{3+}$ (2e⁻); and in YBCO the Cu^{3+} is 3d⁸ electronically , with an even number of electrons . These copper(III) base cations are all spin paired (low spin) , at least below the transition temperature , and would correspond to a diamagnetic condition without the "ninth" valence electrons [as the copper(III) in KCuO₂ is, for example]. The reason for these requirements should be obvious : the diamagnetic cation base is an essential condition for the appearance of superconductivity in the material. The "extra" electrons are promoted to frontier orbitals, where they create the metallic bond, and can condense – if the conditions are favorable – into Cooper pairs. At the transition temperature the Pauli paramagnetism of the metallic bond electrons disappears, and the sample becomes entirely diamagnetic with the appearance of superconductivity in it.

Second, it is anticipated (although as yet unproven) that metallic properties may become more pronounced with a decrease in the absolute potential difference, [V], volts, between the redox potentials of the two different components of the couples. This should occur because as [V] decreases, the couple will behave electronically more and more like a **homoatomic** mixed-valent system, for example like the Cu(II,III) in YBCO, in which [V] = 0. As we have seen above (page 250), superconductivity seems to be as quirky as ever in this regard, and actually appears to strengthen as [V] increases; but probably only to a point, after which the extra electrons become more and more pinned on their respective kernels, and the material becomes distressingly insulating:

Oxidizer Couple	[V]	Tc
Cu(II)/Hg(II)	1.549 V	133 K
Cu(II)/Tl(III)	1.148	122
Cu(II)/Bi(V)	0.641	110
Cu(II)/Cu(III)	0	93

This puzzle remains to be explored and resolved .

Third, there remains the mystery of antiferromagnetism in solids. Although we may be able to design and synthesize new metallic solids utilizing resonance as their operating mechanism, these new materials may show no sign whatsoever of antiferromagnetism at any temperature ; they may remain only Pauli paramagnetic over a wide temperature range. If that is the case, they will never become superconducting at any temperature, even close to absolute zero . Referring back to page 206 to the table of antiferromagnetic compounds , we see that antiferromagnetism occurs most strongly in those materials containing one or other of the transition elements in the skeleton of the structure , so we would have the best chance of producing a new superconductor incorporating one of those elements (Fe , Co , Ni , and Cu) in the couple . Apart from that , it would be difficult to predict or induce antiferromagnetism in compounds forged from elements outside the block of transition elements . Antiferromagnetism is pretty much out of our hands ; unfortunately so , since we need it to produce high temperature superconductors .

Fourth , although many permutations and combinations will be possible of redox-active metal cations , we must always keep in mind the "practical chemistry" underlying them . They are never isolated species ; they are always accompanied by anions , and usually have preferential coordination geometries . Ideally , Verwey's Rule concerning cation coordination in electronically active solids should always be observed , if possible .

With these considerations in mind , let's look at a few possible heteroatomic resonance systems that might produce new metallic solids – at least – and in some cases possibly even a novel superconductor . Scanning the Table of Oxidizers on page 251 , we can select various redox couples for experimental evaluation . Of particular interest will be combinations with iron , cobalt , and nickel (copper has already been covered in the earlier discussion) , since we know that these transition elements , with oxygen , can produce potent antiferromagnetic lattices .

On page 179 we looked at one of Verwey's controlled valence products , nickel(II) oxide doped with lithium oxide , $Li_xNi_{1-x}O$, and observed how the insulating NiO was converted into a semiconductor in the doping process . It would be interesting to dope NiO with another oxidizing dopant , to confirm that heteroatomic resonance can activate a metallic bond in the substrate (recall that in Verwey's experiment , Ni(III) , a potent oxidizer , was generated in the NiO lattice by the lithium substitution , but this was a homoatomic system) . We could try using mercury(II) , with $E^0 = 0.851$ V ,

going head-to-head with nickel(II)'s standard oxidation potential $E_{ox}^{0} = -1.17 \text{ V}$ (to Ni³⁺) :

$$2 \underline{\text{Ni(II)}} + \underline{\text{Hg(II)}} \xrightarrow{[0.319 \text{ V}]} 2 \underline{\text{Ni(III)}} + \underline{\text{Hg(0)}}$$

The resonance equilibrium favors the original Ni(II) and Hg(II), but the absolute potential difference, [V], is a relatively modest 0.319 V, suggesting that mercury(II) might produce a respectable resonance in the lattice, and so be able to activate the Ni-O metallic bond in the solid.

Chemically, NiO (rocksalt structure, m.p. 1984 °C) and HgO (linear chain structure, m.p. 500 °C dec.) are quite dissimilar substances, so the simple shake-n-bake preparation of HgO + NiO \rightarrow HgNiO₂ might not be applicable in this situation. Perhaps a chimie douce method would be more successful (and safer, given the volatility of mercury and many of its compounds, and of their high toxicity):

$$HgCl_{2} + NiCl_{2} \cdot 6 H_{2}O \xrightarrow{(1) \text{ dissolve in water}} HgNiO_{2} \cdot (2) \text{ add to NaOH / } H_{2}O \xrightarrow{(3) \text{ digest , cool , filter , wash , dry , calcine}}$$

The crystal structure of the hypothetical compound $HgNiO_2$ is problematic . When nickel(II) is bonded with oxide anions , it almost always prefers to have an octahedral coordination (as in NiO itself) , and the nickel cations are inevitably in a high spin condition exhibiting Curie paramagnetism or (as with NiO) antiferromagnetism . However , mercury(II) bonded with oxygen links prefers a linear coordination with the sp hybrid AO being used for the Hg-O covalent bonds . An interesting crystal structure which could accommodate both of these coordination preferences simultaneously in HgNiO₂ is the delafossite structure , an M3D model of which is shown at the top of the following page . Delafossite is the mineral CuFeO₂ , with linear Cu(I) and octahedral Fe(III) , and lends its name to the general crystal structure of which CuFeO₂ is typical , and whose chemical formula is



Figure 49 : the M3D model of the delafossite crystal structure , for example of the compound $CuFeO_2$. The small red spheres are octahedrally coordinated iron(III) cations , the larger green spheres represent oxygen linking atoms , and the yellow spheres stand for linearly coordinated copper(I) atoms . This model is based on the sketch of delafossite presented in Figure 8.1 , p. 126 , in Wold and Dwight's textbook , ref. 24, page 394 .

The nickel(II) and mercury(II) atoms are connected by oxygen bridges, requiring the resonance to occur via a superexchange mechanism. The question is, what might the metallic bond XO in HgNiO₂ with such a crystal structure be? The nickel atoms $(3d^8)$ will almost certainly be in a high spin condition, $3d_{xy}^2 d_{xz}^2 d_{yz}^2 \dots (d_x^{2-2})^1 (d_z^2)^1$, and as mentioned on page 181, the $3d_z^2$ native AO could conceivably form a linear Ni-O sigma XO with the oxygen links' $2sp_z$, which in turn overlaps with the mercurys' $6sp_z$ linear hybrid AOs. Such a sigma XO would be nodal in nature, and HgNiO₂ should be semiconducting as a result. The "temporary storage" orbitals on the mercury atoms for the nickels' $(3d_z^2)^1$ valence electron would be the vacant $6p_{y,z}$ native AOs, but resonance will be unfavorable for this location.

In the above example , Verwey's Rule wasn't followed , the XO is nodal , and the nickel atoms are undoubtedly in a high spin condition , making the compound Curie paramagnetic . I think it's a safe bet to predict that $HgNiO_2$ won't be a superconductor at any temperature !

Another heteroatomic resonance system of possible interest would be Tl(I) / Sb(V):

 $\underline{\mathbf{Tl}(\mathbf{I})} + \underline{\mathbf{Sb}(\mathbf{V})} \xrightarrow{[0.581 \text{ V}]} \mathbf{Tl}(\mathbf{III}) + \mathbf{Sb}(\mathbf{III}) .$

A perovskite might be formed from these two components :

 \longrightarrow TlSbO₃ + 6 LiCl .

The crystal ionic radii involved are : Tl(I), 1.64 Å; Sb(V), 0.74 Å; and the oxygen linking atom , 1.26 Å. Assuming $TlSbO_3$ actually has the perovskite structure (Figure 26, page 154), we can obtain an idea of its degree of distortion from the following formula (the "Goldschmidt equation"),

$$t = \frac{r(A) + r(X)}{2^{\frac{1}{2}} [r(M) + r(X)]}$$

,

where "t" is the tolerance factor for the distortion ; "r" is the crystal ionic radius (per Shannon and Prewitt) of the atom ; A is the large central cation , M is the small "framework" cation , and X is the anion in the AMX₃ perovskite unit formula (Müller , p. 200 , ref. 23 , page 394) . If the value of "t" lies between 0.80 and 0.89 , a distorted crystal structure is usually noted

(often it is an ilmenite structure) ; between 0.89 and 1.00 a perovskite with a cubic symmetry is generally obtained . If the tolerance factor exceeds 1.00, the crystal begins to distort again . In the case of our hypothetical perovskite TlSbO₃, t = 1.025, so some distortion in its crystal structure would be anticipated .

The electronic structure of this compound would be quite interesting . The Sb(V) would use an octahedral sp³ds hybrid orbital to form the Sb-O covalent framework with the linear (sp_x) oxygen linking atoms , using its five valence electrons and that one of thallium(0) . We could postulate an Sb-O pi XO metallic bond , bilayered and polarized by the mild Sb(V) oxidizer , from the combination of the empty $6p_{y,z}$ native orbitals (the $6p_x$ AO would be destabilized by the oxygen link in its space) with the neighboring $2p_{y,z}$ AOs on the oxygens . The thallium(I) cation trapped in the supercube center is formally $6s^2$ electronically , but the s native orbital has the wrong symmetry for overlapping with the pi XO . However , the $6s^2$ could easily leak electrons into the $6p_{x,y,z}$ native orbitals , which could successfully overlap with the pi XO surrounding the TI(I) on all sides .

Cox (p. 149, ref. 18, page 393) has given an example of a large, posttransition metal cation, Bi(III), interacting electronically with a framework to produce a metallic solid :

"Post-transition B metals [in perovskites , ABO_3] have s orbitals , which may be filled , in the same energy range as the d band . Interaction between the two cations [A and B], either by direct overlap or indirectly via an anion , can broaden the d band . Thus in $Y_2Ru_2O_7$ the Ru(IV) has a localized 4d⁴ configuration , but Bi₂Ru₂O₇ is metallic , and PES [photoelectron spectroscopy] measurements suggest that this is due to some involvement of the 6s electrons present in Bi(III)".

VB/MOT suggests that the electronic interaction in $TlSbO_3$ (and possibly also in $Bi_2Ru_2O_7$) is between the pi XO (band) and not the d band of the transition metal atom , "B". Note that d orbitals also have the wrong symmetry to overlap successfully with s orbitals ; at least , to produce a functional metallic bond . This might be achieved , though , with pi

orbital overlap . The Tl^{1+} cation might leak enough of its electrons into its 6p orbitals , and through them into the Sb-O pi XO , to reduce its crystal ionic radius enough (and simultaneously increase the size of the Sb-O framework) to minimize the mechanical strain in the lattice . The tolerance factor , "t", might be reduced from its value of 1.025 (distorted) to below 1.00 (cubic symmetry , lowered strain) . This effect should become more noticeable as the temperature of the compound falls toward absolute zero . The Sb-O lattice will shrink when it is cooled , and expand when it is warmed . However , the thallium(I) cation will stay the same size at all temperatures . Thus , as it cools , the shrinking Sb-O supercube lattice will press around the large Tl^{1+} cation , squeezing the $6s^2$ electrons into the Sb-O pi XO like toothpaste out of a tube . An anomalously elevated electrical conductivity for TlSbO₃ with falling temperature would thus be predicted .

Some charge transfer from the thallium(I) cation to the Sb-O pi XO is possible from the Tl⇔Sb redox resonance . If the antimony(V) atom uses its $(4d_x^2)^2$ native orbital for the sp³ds hybrid AO, as with the lead(IV) atoms in BaPbO₃ (page 246), two of the Sb valence electrons will be promoted to its $6p_{y,z}$ frontier orbitals, so TlSbO₃ could be metallic in the same sense as BaPbO₃. What might the effect be, if any, of the Tl⇔Sb redox resonance on the electrical conductivity in the Sb-O pi XO metallic bond ? W.A. Little's theory of ambient superconductivity (ref. 2, page 390) proposed an "exciton pumping mechanism" to induce the formation of stable Cooper pairs at high temperatures . Would the Tl⇔Sb redox resonance promote this excitonic pumping of the Sb-O pi XO electrons ? We can only speculate .

I suppose that many odd new couples could be predicted from the Table of Oxidizers on page 251. The left member of the couples listed there is the higher energy oxidizer; the right member is its lower energy conjugate. What we can do is select any oxidizer on the list, then choose a suitable conjugate higher on the list to team it up with. Generally, the oxidizers are "empty", and will accept an electron (or two) into an empty orbital. Copper(II) is an exception to the rule; its "ninth" valence electron is a singlet, usually located in the copper's $4p_z$ orbital. We combined it, a mild oxidizer, with mercury(II), a stronger oxidizer, to try to form HgCuO₂ (refer back to near the bottom of page 252). The ninth valence electron

would then hopefully resonate between the copper and mercury atoms, activating the Cu-O pi XO metallic bond in the lattice.

Note that if you try to combine an oxidizer with a conjugate lower (in reduction potential) on the list, it will cleanly oxidize it, with the production of the converse couple. For example, let's combine Tl(III) with Ni(II), lower on the list:

$$Tl(III) + 2 Ni(II) \xrightarrow{[0.082 V]} \underline{Tl(I)} + 2 \underline{Ni(III)}$$

This is the same as selecting Ni(III) from the oxidizers, then trying to couple it with the conjugate Tl(I) higher on the list. You could design your experiment around either Tl(III) plus Ni(II), or Tl(I) plus Ni(III). Chemically, they should both work. Now, let's combine Tl(III) with Pb(II), higher on the list:

$$\underline{\mathbf{Tl(III)}} + \underline{\mathbf{Pb(II)}} \qquad \underbrace{ \begin{bmatrix} 0.4393 \text{ V} \end{bmatrix}}_{\longleftarrow} \qquad \mathbf{Tl(I)} + \underline{\mathbf{Pb(IV)}}$$

The interpretation of this is that thallium(III) isn't strong enough an oxidizer to cleanly oxidize lead(II) to lead(IV), but it sure tries hard; and as it does so, it sets up a resonance equilibrium in the lattice that activates the metallic bond XO between the thallium and lead atoms.

On page 248 I briefly discussed the doping of $KBiO_3$ with the "empty" dopant WO_3 . The heteroatomic couple involved here is :

$$\underline{Bi(V)} + 2 \underline{W(VI)} \xrightarrow{[n-0.26 V]} "Bi(VII)" + 2 W(V)$$

This equilibrium assures us that the "extra" itinerant electrons will remain in the Bi-O pi XO, and not be displaced to any great extent, or localized, onto the tungsten atoms. What would happen, I wonder, if we were to try a more strongly oxidizing MO_3 dopant in KBiO₃ [the standard reduction

potential for W(VI) \rightarrow W(V) is $E_{red}^{0} = 0.26$ V]? For example, it would be interesting to dope KBiO₃ with the powerful oxidizer, chromium trioxide :

$$3 \underline{Bi(V)} + 2 \underline{Cr(VI)} \xrightarrow{[n-1.35 V]} 3 "Bi(VII)" + 2 Cr(III) .$$

$$x \text{ KBiO}_3 + (1-x) \text{ CrO}_3 \xrightarrow{} \text{ K}_x \text{Cr}_{1-x} \text{Bi}_x \text{O}_3 .$$

$$m.p. 195 \text{ °C}$$

The resonance of the free electrons in the Bi-O pi XO with the chromium atoms in the CrO_3 -doped composite should be much stronger than with the tungstens, using WO₃ as the dopant. The K-Bi-Cr-O system would be driven closer to localization than the K-Bi-W-O system. It is interesting to note in this regard that the Ba-Pb-Bi-O system became superconducting near its localization point (page 247).

Molybdenum(VI) is a mild oxidizer, at $E_{red}^{0} = 0.700 \text{ V} (\text{H}^{+}, \text{Cl}^{-}$ environment); "n" is the unknown E_{ox}^{0} of Bi(V) to "Bi(VII)":

$$\underline{Bi(V)} + 2 \underline{Mo(VI)} \xrightarrow{[n-0.7 V]} "Bi(VII)" + 2 Mo(V) .$$

$$x \text{ KBiO}_3 + (1-x) \text{ MoO}_3 \xrightarrow{} K_x \ _{1-x}\text{Mo}_{1-x}\text{Bi}_x\text{O}_3 ,$$

$$m.p. \ 795 \ ^{\circ}\text{C}$$

where the symbol "" refers to a vacancy in the Bi-O supercube center . Presumably these vacancies would be randomly dispersed in the lattice together with the other occupants of the supercube centers , the potassium cations . I haven't put the vacancy symbol in the formulas of the other compounds in this doping series for the sake of simplicity .

Doping KBiO₃ with a weak (WO₃, 0.26 V), medium (MoO₃, 0.700 V), and strong oxidizer (CrO₃, 1.350 V) would produce a series of compounds whose metallic nature could be modified in different ways. Using a constant baseline (KBiO₃), the oxidizer variable could be changed in type and degree of doping. The results would help us better understand this interesting

chemistry . Note carefully I am assuming that $KBiO_3$, which is isoelectronic with $BaPbO_3$, is a metallic solid like the latter compound (page 245). It may not be . If it isn't, then the experiments I have outlined could be tried with $BaPbO_3$. This might be a good opportunity to test the picture of the electronic structure of $BaPbO_3$ I presented on page 246. By reducing the electron population of the $7p_{y,z}$ native orbitals and driving the material toward electron localization, we might actually be able to make it superconducting. If that was observed experimentally, the simple picture I proposed for $BaPbO_3$ would have received some valuable support.

Redox Resonance with Chemical Reducers

It should similarly be possible to activate a metallic bond in a solid using redox resonance in a chemically reducing system. In such systems low valent cations are generally involved, with ionic rather than covalent bonding in the solid. There is no polarization of the XO, unless small, highly charged cations are present in the lattice.

A Table of Reducers is presented on the next page . It is organized by an increasing standard oxidation potential, descending the table, as with the Table of Oxidizers on page 251. These are all chemically reducing systems, with the reducer being the left member of the couple, and the low energy conjugate being its right member. As with the oxidizers, a lower strength reducer can be combined with a higher strength conjugate , which it can't cleanly reduce, but might be able to form a redox resonance system with, if the couple can be linked up with a suitable XO which will carry the resonant valence electrons, hence electrical current, in the lattice.

Of course , in reality these redox couples have to be installed in the appropriate solid state crystal structures , and that's where the real challenge to the chemist arises . Still , with a little creativity and ingenuity we might be able to devise some interesting new compounds – "designer electronic materials" , so to speak – for investigation . How practical they are remains to be seen , but research with them would be fascinating !

Reducer	<u></u> E ⁰	<u>radius</u>	<u>oxide</u>	<u>m.p. or dec.</u>
Ti(III)/Ti(IV)	0.09 V	0.81 A (III)	Ti ₂ O ₃	2130 C (dec)
Pb(0)/Pb(II)	0.1262	1.33 (II)	PbO	886
Sn(0)/Sn(II)	0.1375	1.22 (II)	SnO	1080 (dec)
V(II)/V(III)	0.255	0.93 (II)	vo	n/a
Ni(0)/Ni(II)	0.257	0.63 (II)	NiO	1984
Co(0)/Co(II)	0.28	0.79 (II)	CoO	1935
TI(0) <i>I</i> TI(l)	0.336	1.64 (l)	[Tl ₂ CO ₃]	273
Eu(II)/Eu(III)	0.36	1.31 (II)	[Eu ₂ 0 ₃]	2291
Cd(0)/Cd(II)	0.403	1.09 (II)	CdO	1430
Cr(II)/Cr(III)	0.407	0.87 (II)	[Cr ₂ O ₃]	2435
ln(l)/ln(lll)	0.443	0.94 (III)	[ln ₂ 0 ₃]	850
Fe(0)/Fe(II)	0.447	0.75 (II)	FeO	1369
U(III)/U(IV)	0.607	1.03 (IV)	[UO ₂]	2500
Ga(I)/Ga(III)	0.67	0.76 (III)	[Ga ₂ O ₃]	1900
Zn(0)/Zn(II)	0.7618	0.88 (II)	ZnO	1975
Yb(II)/Yb(III)	1.15	1.16 (II)	[Yb ₂ O ₃]	2227
Sm(II)/Sm(III)	1.55	1.41 (II)	[Sm ₂ O ₃]	2300

Table of Reducers

This is certainly a diverse collection of materials, about half of which consists of rather rare and costly elements. Nevertheless, despite the narrower scope presented to the chemist by these reducers than the redox couples in the Table of Oxidizers, I'll propose several "real world" materials based on the species listed above, incorporating reducers coupled with higher energy conjugates. A series of indium-based perovskites with iron(II) might be prepared by the following reactions :

InCl + FeCl₂
$$\longrightarrow$$
 InFeCl₃ ;
m.p. 225 °C 674 °C
InBr + FeBr₂ \longrightarrow InFeBr₃ ;
220 °C 684 °C (dec)
InI + Fel₂ \longrightarrow InFeI₃ .
351 °C

All the reagents cited above are commercially available, eg. from Alfa-Aesar. Note that indium(I) compounds are somewhat unstable, being subject to disproportionation to In(0) and In(III) [ref. 127, page 409].

The absolute potential difference, [V], between the indium and iron(II) redox couples is virtually nil :

$$\underline{In(I)} + \underline{Fe(II)} \xrightarrow{[0.004 V]} In(III) + Fe(0)$$

This suggests that there should be a strong valence electron resonance between the indium "A" cation and the iron(II) "B" cation in the perovskite lattice , assuming that the InFeX₃ compounds actually have such a structure . However , the In(III) / Fe(0) couple would be sterically unfavorable , because Fe(0) has a large metallic radius (1.26 Å) which would drastically distort and disrupt the perovskite structure . Nevertheless , these compounds should still present some interesting electronic properties for study .

Another synthetic approach to the $InMX_3$ compounds that could be tried is the reproportionation of In(0) – the metal – with the stabler (and somewhat cheaper) In(III) salts :

 $2/3 \text{ In}^0 + 1/3 \text{ In}\text{Br}_3 + \text{Fe}\text{Br}_2 \longrightarrow \text{In}\text{Fe}\text{Br}_3$. m.p. 156 °C 436 °C 684 °C (dec) A third method , possibly the simplest experimentally , would be a direct reaction of the "A" or "B" metal with the corresponding MX_3 salt :

$$In^{0} + FeBr_{3} \longrightarrow InFeBr_{3}$$
;
 $Fe^{0} + InBr_{3} \longrightarrow InFeBr_{3}$.

Indium is a mildly reducing metal $(0.14 \text{ V to In}^{1+})$, and iron(III) is a mild oxidizer $(0.771 \text{ V to Fe}^{2+})$, so the first reaction is not recommended for investigation, unless the researcher takes special precautions to avoid a strong exotherm. The solid state reactions of mixtures of reducers and oxidizers is always potentially hazardous, as a gunpowder-like detonation may result upon their combination.

The second reaction between finely powdered iron and indium(III) bromide should be safer and hopefully more fruitful, as In(III) is an innocuous low energy species. As a variation in this reaction, the zerovalent iron compound pentacarbonyl iron(V), $Fe(CO)_5$ might be used as the iron source with the indium tribromide. Iron pentacarbonyl is an oily orange liquid, b.p. 103 °C; it is commercially available and relatively inexpensive. It is air sensitive, and should be handled and reacted under an inert atmosphere such as nitrogen or argon.

Referring to the Table of Reducers on page 269, another interesting redox couple that might be fashioned into a perovskite is U(III) / Ga(III); the former component is the reducer, and the second one is the higher energy conjugate :

$$2 \underline{U(III)} + \underline{Ga(III)} \qquad \boxed{[V] = 0.063 V} \\ \boxed{2 U(IV) + Ga(I)} \qquad \boxed{2 U(IV) + Ga(I)}$$

Since uranium(III) oxide , U_2O_3 , seems to be commercially unavailable , it might be prepared in situ by means of a reproportionation reaction of the available (Alfa Aesar) uranium metal and uranium(IV) oxide , UO_2 . As it is formed it would react with the gallium(III) oxide in the mixture to produce the compound UGaO₃ , which is another candidate for the perovskite crystal structure :

Given the refractory nature of the three reactants in this experiment, a conventional muffle-type furnace might not be hot enough to accomplish the sintering of the mixture particles. Use of an arc furnace, as in the synthesis of niobium monoxide (page 125), would certainly provide a hot enough environment for fusion of the mixture into a button, but very few laboratories have such an exotic apparatus available for high temperature reactions.

I'm guessing the crystal ionic radius of U(III) to be about 1.17 Å; that of Ga(III) is 0.76 Å, and the radius of the oxides is 1.26 Å. The tolerance factor "t" (page 263) for UGaO₃ would be 0.85, which suggests that this compound could have a slightly distorted perovskite structure.

The electronic configuration (valence shell) of uranium(0) is $5f^3 6s^1 7s^2$; that of U(III) will therefore be $5f^3$. Can the f native orbitals, with their strange shapes and symmetries (ref. 128, page 409), overlap successfully with the Ga-O pi XO, thus permitting redox resonance to occur? If not, the 5f AOs would have to leak electrons into the empty uranium 7p AOs, and from them into the pi XO, in order for the resonance to occur.

The U(III) / Ga(III) redox couple might also be incorporated into a rocksalt crystal structure :

 $x UN + (1-x) GaN \longrightarrow U_x Ga_{1-x} N$.

Gallium(III) nitride is commercially available, and I understand is being investigated for its interesting property of emitting blue laser light when electronically stimulated. It has the wurtzite crystal structure. Uranium(III) nitride is a known material, having the rocksalt structure.

Another similar interesting system to look at would be EuO - FeO, whose separate components both have the rocksalt structure. The Eu(II) cannot

cleanly reduce Fe(II) to Fe(0):

$$2 \underline{Eu(II)} + \underline{Fe(II)} \xrightarrow{[V] = 0.087 V} 2 Eu(III) + Fe(0) .$$

x/3 Eu⁰ + x/3 Eu₂O₃ + (1-x) FeO \longrightarrow Eu_x Fe_{1-x} O ;
Also, Eu₂O₃ + Fe⁰ \longrightarrow (Eu²⁺ Eu²⁺ Fe²⁺) O₃⁶⁻ .

Europium(II) oxide has a pronounced ferromagnetic ordering in its $4f^7$ valence electrons (ref . 129, page 410). It is thought that some of these 4f electrons can leak into the empty 5d AOs, and that hopping of the promoted electrons can take place via oxide superexchange. Europium(II) oxide can be doped with Eu⁰ to partially fill the 5d AOs, producing an electrically conductive metallic solid.

Iron(II) oxide also has a rocksalt structure – slightly distorted – in which the iron(II) cations have a $3d^6$ electronic configuration (the material is actually antiferromagnetic). This suggests that redox resonance might occur to some extent in the Eu(II)-Fe(II) redox couple between the Eu 5d and the Fe 3d native orbitals.

Since cadmium oxide , CdO , has the rocksalt structure , a similar sort of rocksalt composite might be formed from the Eu(II) / Cd(II) redox couple :

$$2 \underline{Eu(II)} + \underline{Cd(II)} \xrightarrow{[V] = 0.043 V} 2 Eu(III) + Cd(0) .$$

x/3 Eu⁰ + x/3 Eu₂O₃ + (1-x) CdO \longrightarrow Eu_x Cd_{1-x} O ;
Also, Eu₂O₃ + Cd⁰ \longrightarrow (Eu²⁺Eu²⁺Cd²⁺)O₃⁶⁻.

The crystal ionic radius of Cd(II), 1.09 Å, is closer to that of Eu(II) – 1.31 Å – than to the radius of Fe(II), which is 0.75 Å. However, Cd(II) has a full 4d shell (4d¹⁰), compared to the partly filled iron(II) valence shell, 3d⁶. That may make the magnetic properties of Eu-Cd-O quite different than

those of the Eu-Fe-O composite material.

As a final suggestion in this area of reducing redox couples , we have the Ga(I) / Zn(II) combination :

Similarly for the other halide analogues .

Insertion of Metal Atoms Into Host Lattices

The reader will have observed that in the Tables of Oxidizers and Reducers I have listed zerovalent metal atoms in several of the redox couples . For example, in the oxidizers section, we have the possible couple Fe(III) / Ag(0):

 $\underline{Fe(III)} + \underline{Ag(0)} \qquad \boxed{[V] = 0.0286 V} \\ \overline{} \qquad Fe(II) + Ag(I) .$

Experimentally, $Ag^0 + FeF_3 \longrightarrow AgFeF_3$.

Let's assume that the product , $AgFeF_3$, has the perovskite structure , yet the "A" atom , silver , remains zerovalent . The metallic radius of silver(0) is 1.44 Å ; the crystal ionic radii of Fe(III) – high spin six-coordinate – and fluoride anion are 0.785 Å and 1.19 Å , respectively . The tolerance ratio "t" for Ag^0FeF_3 is then 0.94 , which suggests that its perovskite lattice would be comfortably cubic in symmetry .

If , on the other hand , the charge distribution results in the formula , $Ag^{1+}Fe^{2+}F_3^{3-}$, its presumed perovskite structure probably won't be cubic in symmetry . The crystal ionic radius of Ag(I) is 1.29 Å , and that of Fe(II) [high spin , six coordinate] is 0.92 Å . With fluoride's radius remaining at 1.19 Å , the tolerance factor "t" for this latter composition is calculated to be 0.83 , suggesting that its perovskite structure will indeed be distorted .

Presumably, $Ag^{0}FeF_{3}$ with the more comfortably fitting atoms tightly packed into the rather compact perovskite structure will be more stable than the twisted $Ag^{1+}FeF_{3}$; and in any case, the redox equilibrium shown above slightly favors the Ag(0) / Fe(III) couple over the Ag(I) / Fe(II) couple.

It should also be possible to insert silver(0) into other MX_3 host lattices to produce more perovskites . The "M" atom of the host could possibly be low energy in its redox nature , for example the Al(III) cation :

 $Ag^0 + AlF_3 \longrightarrow Ag^0AlF_3 (t = 1.00)$. m.p. 961 °C 1291 °C (subl.)

In this case , there would be no question of the zerovalency of the silver "A" atoms in the AMX_3 perovskite structure .

The preparation of the related perovskite , $Ag^{1+}ZnF_3$ (cubic symmetry , a = 3.98 Å) was described in 1953 by DeVries and Roy (ref. 130 , page 410) :

 $AgF + ZnF_3 \longrightarrow AgZnF_3 (t = 0.85)$. m.p. 435 °C 872 °C

These authors noted that silver fluoride was sensitive to light, and tended to decompose to silver when heated (most, if not all silver compounds share these characteristics; the light-sensitive nature of silver bromide, for example, is the basis of classic black-and-white photography). A chemie douce preparation of $AgZnF_3$, shielded from ambient light, would be desirable. The preparation and characterization of a series of fluoride perovskites, KMF₃, where "M" is Mn, Fe, Co, Ni, Cu, and Zn, have been described (ref. 131, page 410). These are simple experiments

suitable for student instruction , being carried out in water solution at room temperature ; the KMF_3 compounds , which are all perovskites , are insoluble , and immediately precipitate from the solution :

ZnO + 2 HCl (aq)
$$\longrightarrow$$
 [ZnCl₂] $\xrightarrow{add to KF (aq)}$,
(not isolated) 3 drops HNO₃

Several variations to this student experiment could be tried with silver salts . Noting that silver(I) fluoride is very water-soluble (1820 g/l), it might be substituted for the KF used for the KMF₃ compounds, to produce AgZnF₃. The water-soluble silver and zinc nitrates might also undergo a simultaneous metathesis with sodium or potassium fluoride in water solution.

Assuming we have secured pure samples of Ag^0AlF_3 and $Ag^{1+}ZnF_3$ by whatever routes (and hopefully they are both cubic perovskites), the former substrate could be doped with gradually increasing mole fractions "x" of the latter dopant, to obtain composites containing mixed-valent silver atoms in the "A" position of the AMX₃ perovskite :

$$x Ag^{0}AlF_{3} + (1-x) Ag^{1+}ZnF_{3} \xrightarrow{x = 1 \rightarrow 0} Ag^{(1-x)+}Al_{x}Zn_{1-x}F_{3} .$$

Referring to Figure 27 on page 155, illustrating the B type of perovskite unit cell, would it be possible for the "A" cations – silver in this case – to communicate directly with each other, without having to superexchange their $5s^1$ valence electrons through the intervening fluoride anions? The s native orbitals are very voluminous, and this might actually be possible. My M3D models are "exploded structures", but in reality the atoms, especially in the remarkably compact perovskites, are closely packed together. If such a direct Ag-Ag interaction was feasible in these mixed-valent silver doped composites, we might expect them to behave electronically somewhat like the synthetic metal silver subfluoride (page 108), in which the sigma XO metallic bond is formed by the direct overlapping of the silver atoms' $5s^0$ and $5s^1$ native AOs in the lattice.

In fact – come to think of it – the compound Ag^0AIF_3 itself might be a Robin-Day Class IIIB synthetic metal , since the silvers' $5s^1$ sigma XO metallic bond [valence band] would be only half occupied with valence shell electrons . I will later propose (on page 302) a highly utilitarian application for these new materials with formally zerovalent atoms nesting in host crystal structures .

Another such interesting perovskite system might be the following :

In this case , the thalliums' $6s^2$ orbitals are filled , and their $6p^1$ native AOs are only partly filled . Since the native p orbitals are smaller and more directional than are the corresponding s AOs , will mixed-valent resonance occur between the thallium atoms in the "A" position of the perovskite ? Note that we might also expect some redox resonance between the thallium(0,1) , europium(III) and cadmium(II) atoms . Would the redox resonance **enhance** the electronic activity between the thallium atoms ? I think this would be a fascinating system to study , providing it could actually be synthesized (and we shouldn't disregard the toxic nature of the thallium and cadmium components , either) .

In general , we might be able to synthesize , characterize , and study a wide range of new perovskites in which there is a formally zerovalent "A" atom in the center of an MX_3 supercube lattice . These interesting materials might be prepared from the direct reaction of the "A" atom with an MX_3 host crystal . In the following two pages I have presented tabulations of suggested "A" atoms and MX_3 host crystals as possible reagents for metal atom insertion .

<u>Metal Atom</u>	Ē	<u>conjugate</u>	<u>radius</u>	<u>atomic wt.</u>	<u>m.p.</u>	<u>notes</u>
Gold	-1.692 V	Au(l)	1.44 A	196.967 g/mol	1063 0	2
Mercury	- 0.851	Hg(II)	1.55	200.59	357 (I	b.p.)
Silver	- 0.7996	Ag(I)	1.44	107.868	961	
Copper	- 0.521	Cu(l)	1.28	63.546	1083	
Bismuth	- 0.308	Bi(III)	1.82	208.98	271	
Tungsten	- 0.1	W(III)	1.41	183.84	169	as W(CO) $_{\rm 6}$
Lead	0.1262	Pb(II)	1.75	207.2	327	
Tin	0.1375	Sn(II)	1.58	118.71	232	
Indium	0.14	ln(l)	1.67	114.813	156	
Gallium	0.2	Ga(I)	1.53	69.723	30	
Molybdenum	0.200	Mo(III)	1.41	95.94	150	as Mo(CO) ₆
Nickel	0.257	Ni(II)	1.25	58.693	43	(b.p.)
						as Ni(CO) ₄
Cobalt	0.28	Co(II)	1.25	58.933	51	as Co ₂ (CO) ₈
Thallium	0.336	TI(I)	1.71	204.383	303	
Cadmium	0.403	Cd(II)	1.52	112.40	321	
Iron	0.447	Fe(II)	1.26	55.845	103	(b.p.)
						as Fe(CO) ₅
Zinc	0.7618	Zn(II)	1.37	65.39	420	
Chromium	0.913	Cr(II)	1.29	51.996	154	as Cr(CO) ₆
Aluminum	1.662	AI(III)	1.43	26.982	660	

The transition metals are too refractory for a direct metal-host insertion ; their corresponding zerovalent metal carbonyls might be tried instead . These are low melting (or boiling) covalent solids and liquids that when heated should decompose to , and release , the metal atoms into the host lattice . These transition metal carbonyls are all commercially available (eg. Alfa Aesar , Strem , etc.) . In the table , those elements listed with negative standard oxidation potentials E^0 are noble metals ; those with positive potentials are generally considered to be base metals . [Note 5 , page 378].

<u>Host</u>	Ē	<u>conjugate</u>	<u>radius</u>	<u>m.p.</u>	<u>F.W.</u>
UO₃	0.062 V	U(V)	0.087 A	dec.	286.03 g/mol
$\mathbf{WO}_{_{3}}$	0.26	W(V)	0.74	1473 C	231.84
${\rm ReO}_3$	0.400	Re(IV)	ca. 0.65	400 (dec.)	236.20
MoO ₃	0.700	Mo(∨)	0.73	795	143.94
TiF_3	- 0.24	Ti(IV)	0.81	1200	104.86
$\mathbf{SbF}_{\scriptscriptstyle 3}$	0.212 (H⁺)	Sb(0)	0.94	292	178.76
BiF_3	0.308	Bi(0)	1.17	727	265.98
\mathbf{FeF}_{3}	0.771	Fe(II)	0.785	1027	112.84
AIF_3	[1.662]	[AI(0)]	0.675	1291 (subl.)	83.98
\mathbf{CrF}_{3}	[0.407]	[Cr(II)]	0.755	1100	108.99
\mathbf{EuF}_{3}	[0.36]	[Eu(II)]	1.087	1390	208.96
\mathbf{GaF}_{3}	[0.67]	[Ga(l)]	0.76	800 (subl.)) 126.72
$\ln\!\mathbf{F}_{\scriptscriptstyle 3}$	[0.443]	[ln(l)]	0.94	ca. 1170	171.81
LaF ₃	[2.379]	[La(0)]	1.172	1493	195.90
$V\!F_{_3}$	[0.255]	[V(II)]	0.78	ca. 1406	107.94
YF_3	[2.372]	[Y(0)]	1.04	1387	145.90

Suggested MX₃ Host Structures for Metal Atom Insertion

In this table , the "M" atoms of the MX_3 hosts that are listed with positive standard reduction potentials E^0 are natural oxidizers ; one "M" atom , the Ti(III) of TiF₃ , is a natural reducer with a negative potential ; and those MX_3 hosts with bracketed [] potentials are generally considered as low

energy atoms, being neither naturally oxidizing nor reducing in their chemical behavior. As metal cations they can, of course, be forcibly reduced by chemical or electrochemical means; hence their standard reduction potentials have been bracketed.

The redox properties of the reagents and tolerance factors of the products should be considered when selecting pairs of "A" atoms and MX_3 hosts for possible investigation. Thus, the oxidizing hosts will cleanly oxidize all the base metals and several of the noble metals; for example,

$$Cu^{0} + MoO_{3} \longrightarrow Cu^{1+}Mo^{5+}O_{3}$$
, or $Cu^{2+}Mo^{4+}O_{3}$;
 $Tl^{0} + UO_{3} \longrightarrow Tl^{1+}U^{5+}O_{3}$.

The idea behind inserting zerovalent atoms into host crystals , and ensuring that those atoms stay zerovalent after insertion , is that the resulting compounds are expected to be metallic solids , which of course are what this study is all about . As discussed earlier , even those compounds with polyvalent cation components , like the $Cu^{2+}Mo^{4+}O_3$ and $Tl^{1+}U^{5+}O_3$ mentioned above , may have interesting electronic activity because of electron resonance between the two redox-active cation species in them .

I have included data for the crystal ionic radii , per Shannon and Prewitt , of the "A" and "M" atoms , which can be used for calculating the tolerances of the AMX₃ products . The radii of the "A" atoms on page 261 are their metallic radii , from Rodgers' textbook (ref. 36 , page 395 , his p. 164) ; these are the radii of the atoms in the bulk elementary metal , which I hope will be appropriate and acceptable for use in this context as well . A perovskite product with a cubic symmetry (t = $0.89 \rightarrow 1.00$) is preferable .

Perovskites are of special interest in this regard, because first they are remarkably compact crystal structures, generally having short unit cell dimensions, at least with oxide and fluoride anions. Second, their "A" and "M" cations permit the researcher to take advantage of Verwey's controlled valence to synthesize compounds with variable, and even NIOS valences. I pointed out two possible mixed-valent "A" cation systems above, the silver one on page 276 and the thallium system on page 277.

The following are a few interesting examples of metal atom insertion experiments that have been selected from a perusal of the tables above :

$$Hg^{0} + FeF_{3} \xrightarrow{[V = 0.080 V]} Hg^{0}FeF_{3} (t = 0.98) ;$$

$$Hg^{0} + SbF_{3} \xrightarrow{[V = 0.639 V]} Hg^{0}SbF_{3} (t = 0.91) ;$$

$$Zn^{0} + AlF_{3} \xrightarrow{[V = 0.9002 V]} Zn^{0}AlF_{3} (t = 0.97) ;$$

 $Al^0 + AlF_3 \longrightarrow Al^0AlF_3$ (t = 0.99); This would probably be a Robin-Day Class I mixed-valent compound with respect to the Al(0) and Al(III), but it could be Class IIIB with respect to the Al(0) "A" atoms themselves; that is, an aluminum-based synthetic metal. I'm assuming that it remains in the stable perovskite crystal structure, and doesn't rearrange to another structure, eg. Al₂F₃ (corundum?).

$$\begin{array}{rcl} Fe(CO)_{5} &+ & AlF_{3} & & \hline & & Fe^{0}AlF_{3} &+ & 5 & CO & (g) &; \\ b.p. & 103 \ ^{\circ}C & & & & & \\ Cd^{0} &+ & CrF_{3} & & \hline & & & Cd^{0}CrF_{3} & (t=0.99) &; & and , \\ Ag^{0} &+ & MoO_{3} & & & \hline & & Ag^{0}MoO_{3} & (t=0.96) &. \end{array}$$

As pointed out earlier, all the base metals would transfer electrons to the oxidizing MX_3 hosts, and so could maintain their zerovalent condition only with low energy hosts (and even then, some of them might be oxidized; so the researcher should do a little redox arithmetic before experimenting). Some of the noble metals could be combined with certain of the oxidizing MX_3 hosts, as I have indicated with Ag^0FeF_3 and Ag^0MoO_3 . One really fascinating combination would be of the noble metals copper, silver, gold,

and mercury with rhenium trioxide, ReO_3 . You will recall that rhenium trioxide is an extraordinary metallic solid (page 144), whose ambient electrical conductivity, 149,300 ohm⁻¹cm⁻¹, is comparable to that of several metallurgical metals. What effect would insertion of these noble metal atoms into ReO_3 , to presumably obtain a perovskite product, have on the electrical properties of the host? Would its electrical conductivity be **enhanced** to the point where it might become superconducting? Note the possible redox resonance in the perovskite systems below :

b.p. 357 °C

In the last example , Hg^0ReO_3 might behave electronically somewhat like I thought TISbO₃ would (page 265) . That is , in order to reduce the strain in the lattice , indicated by the tolerance factor of 1.04 , the Hg(0) could inject some of its 6s² valence electrons into the partially filled Re-O $6p_{y,z}-2p_{y,z}$ pi XO metallic bond . That would simultaneously reduce the metallic radius of the mercury atoms from 1.55 Å , and increase the Re-O bond length , resulting in a lower tolerance factor and decreased strain in the lattice . Experimentally , mercury with its relatively low boiling point would likely present the least difficulties in its reaction with ReO₃ , which unfortunately disproportionates to ReO₂ and Re₂O₇ at about 400 °C . Mercury atoms might be inserted into the ReO₃ lattice by heating equimolar quantities of the two

reagents together in a sealed tube , capsule , or autoclave to a temperature safely below 400 $^{\circ}\rm C$, say 300 $^{\circ}\rm C$.

Novel experimental techniques would have to be devised for the synthesis of the other noble metal analogue adducts with ReO_3 . For example, with copper, the more stable rhenium(IV) oxide could be tried as the rhenium source :

CuO + ReO₂
$$\longrightarrow$$
 [Cu²⁺Re⁴⁺O₃⁶⁻] \longrightarrow Cu⁰Re⁶⁺O₃⁶⁻.

May I again remind the reader of the great usefulness of thermal analysis techniques (page 227) in the monitoring of these high temperature reactions, in order to discover the optimum conditions for carrying them out . In cases where there is no reagent gas absorption or emission , and no change in total reaction mass weight , thermogravimetry (TG) and derivative thermogravimetry (DTG) wouldn't be helpful ; however , differential thermal analysis (dta) might prove quite useful , as it should provide energy "spikes" (exotherms and endotherms) at reactant melting points , changes in crystal structure , and chemical reactions , such as the formation of the stable perovskite structure . Hence , "overcooking" the reaction mix could be avoided , and neat clean , efficient solid state reactions could be developed for desired materials .

Another "practical" note : most if not all of the standard redox potentials cited in this study were derived either from theoretical calculations or from experimental measurements , the latter usually made in aqueous media under controlled conditions . The more covalent species are inevitably bonded to oxygen ligands to various degrees , and require either alkaline or acidic environments in order for the electrochemical valence changes to be observed . The potentials are also highly sensitive to the presence of bonding ligands in the media (for example , cyanide anion can strongly bond to transition metal cations , and dramatically affect their electrochemical properties) . Thus , these redox potentials are very conditional , and may apply only approximately to those metal cations embedded in solid state matrices . So I must strongly advise the reader : **caveat emptor** ! (buyer

beware) . In some cases , I'm not even sure what redox potential may actually apply . Copper , for example , may be oxidized to either copper(I) or (II) cations :

$$Cu^{0} - e^{-}$$
 — Cu^{1+} ; $E_{ox}^{0} = -0.521 V$; and,
 $Cu^{0} - 2e^{-}$ — Cu^{2+} ; $E_{ox}^{0} = -0.3419 V$.

So in the above insertion of Cu^0 into ReO_3 , we could very well end up with the product of lesser interest, $Cu^{2+}Re^{4+}O_3^{6-}$ (which would have a layered structure, rather than that of a perovskite, because of the strong Jahn-Teller effect with Cu^{2+} compounds). On the other hand, the standard reduction potential of 0.400 V for Re(VI) \rightarrow Re(IV) may not be very accurate when applied in a solid state environment, either, so who knows? Chemistry is full of surprises !

I have also been listing fluorides as MX_3 candidates, and not the other halides, because the tolerance factors decrease from fluoride to iodide in any given system. The following table illustrates this effect for a series of Ag^0AlX_3 products:

<u>Halide</u>	<u>Form. Wt.</u>	<u>M.P. (B.P.)</u>	<u>Ag⁰Compound</u>	<u>Tol. Factor</u>
AIF_3	83.976 g/mol	1291 C (subl.)	$Ag^{o}AIF_{3}$	1.00
AICI ₃	133.341	178 (subl.)	Ag⁰AICI₃	0.94
AlBr₃	266.694	98 (b.p. 263 C)	AgºAlBr ₃	0.92
AII_3	407.694	191 (b.p. 360 C)	Ag⁰All₃	0.90
(Ag ⁰)	(107.868)	(961 C)		

Aluminum Halides as Hosts for Metal Atoms

In this particular case, it turns out that the entire series of aluminum halides might be able to form cubic symmetry perovskites when silver atoms are inserted into their lattices in an equimolar ratio. This may or may not be the case for other metal atom / host crystal systems , however . Experimentally , in the example above , Ag^0 is more physically compatible with the higher melting AlF₃ than with the other lower melting (or subliming) aluminum halides . Its insertion compound with AlF₃ should be easier to make than with the higher formula weight analogues . On the other hand , from an industrial aspect , the AlCl₃ product contains a lower percentage of the expensive silver reagent (44.7%) than the fluoride analogue (56.2%) . Aluminum chloride is a relatively cheap industrial chemical , while the fluoride , bromide , and iodide are expensive specialty reagents . If these materials ever found a widespread practical application , and assuming equal performances from all four products , Ag^0AlCl_3 would be the material of choice for large-scale development from the economic point of view .

There is, however, another consideration concerning the anions in these perovskites, and presumably, in other solid state compounds. Apparently the higher the atomic weight of the anion, the more a metallic bond can be supported in the lattice. Indeed, of all the halogen elements, iodine is the only one that exhibits metallic properties, albeit under elevated pressure. Salts of certain polyiodide anions, such as triiodide, pentaiodide, and heptaiodide, have a brilliant, colored metallic luster (ref. 132, page 410), although no mention was made of their electrical conductivities.

The effect of different halide anions on the metallic properties of perovskites is vividly illustrated by the cesium tin(II) trihalide series . These perovskites can be prepared by several routes, the simplest being the melting together of the reagent salts with the Cs(I) and Sn(II) cations (ref. 133, page 410) :

]	heat at 500 °C
CsBr +	SnBr ₂ —	$ CsSnBr_3$.
т.р. 636 °С	216 °C	450 °C
colorless salt	pale yellow	black, conductive

Cesium tin(II) tribromide is a semiconductor with an ambient electrical conductivity of 0.05 ohm⁻¹cm⁻¹. It is reported to show a "metallic-type behavior between -100 and 350 °C with no major change in resistance observed" (Scaife, Weller, and Fisher, ref. 134, their p. 313).

It is interesting to note that if the tolerance factor for CsSnBr₃ is calculated using the crystal ionic radius of Sn(II), 1.22 Å, it turns out rather low, at t = 0.84, but if the value for Sn(IV), 0.83 Å, is used in the Goldschmidt equation, it will be much higher (t = 0.97). The former low value would be indicative of a distorted perovskite, while the latter high factor would generally be associated with a perovskite of cubic symmetry. As CsSnBr₃ has a cubic symmetry from 19 °C and above, the implication is that the SnBr₃ supercube framework is indeed based on Sn(IV), with the tins' 5s² inert pair of valence electrons somehow promoted to a higher energy level frontier orbital, where they can interact with the bromide orbitals to form a functional XO metallic bond (conduction band).

Cesium tin(II) tribromide can be thought of as a Zintl compound in the general sense I have employed that term in this study . Tin uses an octahedral hybrid orbital to form the SnBr₃ supercube framework . There are six Sn-Br covalent bonds per unit formula of the compound , which require twelve valence electrons to fill . Tin donates two (its 5p² pair) ; cesium(0) donates one , its single 6s¹ valence electron ; and each bromine(0) ligand , which has seven valence electrons in a linear sp hybrid orbital , donates three electrons to the covalent framework $[4\sigma_a^{-1} 4\sigma_b^{-2} 4p_y^{-2} 4p_z^{-2}]$: 2 + 1 + 9 = 12 electrons , to form the SnBr₃ supercube skeleton . The depleted cesium cation then nests in the supercube center , to complete the Zintl structure .

A proposed electronic structure for the tin(II) atoms in CsSnBr₃ is presented at the top of the following page . It is really a rationalization for the dispersal of the 5s² pair of electrons into a conduction band . Presumably the $6p_{y,z}$ frontier orbitals with the promoted electrons would be able to overlap continuously with the corresponding $4p_{y,z}$ AOs on the bromine ligands to form a pi XO that could function as the metallic bond in CsSnBr₃ . The question remains : why are bromide and iodide relatively successful in cooperating with tin(II) in forming a metallic bond , while chloride (and presumably also fluoride , which wasn't reported on) apparently was a failure at this ?

A concise summary of the properties of several of the $CsSnX_3$ series of perovskites, including a couple of mixed-anion compounds, has been

Proposed Electronic Structure of the Tin(II) Atoms in CsSnBr₂



 \mathbf{y} = tin atoms' 5s² inert pair electrons promoted to the 6p_{vz} AOs

Note : the 6p_x orbital is destabilized by the bromine ligands. .

presented in Scaife , Weller , and Fisher's Table 1 , on p. 310 of their paper (cited in ref. 133 , page 410) . Chemie douce preparations under near ambient conditions yield white , monoclinic CsSnCl₃ ; black , cubic perovskite CsSnBr₃ ; and yellow , orthorhombic CsSnI₃ . When heated , the chloride converts to a yellow cubic perovskite at 117 °C ; and the iodide coverts to a black , conductive cubic perovskite at 152 °C . Interestingly , the intermediate product CsSnBr₂Cl is a **red** cubic perovskite . Clearly , in this system the chloride anion seems to inhibit the formation and/or functioning of a metallic bond in the perovskite crystal . Changes in the crystal habit of the compounds are probably related to the making and breaking of Sn-X covalent bonds , with the physical assistance of heating , to either force a lone pair into a new bond , or break an existing bond to recreate a lone pair :



We saw earlier (page 69) where such electron pairs – "lone" or "inert" – are quite voluminous and will occupy space in a crystal lattice just as an atom will . Since they aren't detected by X-rays , the presence of these electron

pairs in the solid will usually be indicated by open spaces in the structure , or by an exceptionally large spacing between planes of atoms in it . The existence of these lone , or inert , pairs of electrons is a clear indication of covalent bonding in the material , which is well described by VB theory . We saw the same effect in the cubic rocksalt and tetragonal tin(III) phosphides (page 164) . The Sn-P bonds were intact in the former structure , but one (of the six Sn-P bonds per formula unit) was broken in the tetragonal SnP , with the spatially bulging electron pair sitting on the tin atom as an inert pair . It is probably such inert pairs of electrons that are causing the distortion in the non-cubic forms of the CsSnX₃ compounds .

If the assignment of the tins' $5s^2$ inert pair to the $6p_{y,z}$ frontier orbitals is correct, possibly only the bromine $4p_{y,z}$ and iodine $5p_{y,z}$ AOs are at a sufficiently high energy level to overlap properly with them. We wouldn't expect any polarization of the pi XO in this low energy system, nor would there be any mixed-valence or redox resonance to cause any sort of electronic activity in Sn-Br pi XO. Maybe by opening up some holes in the XO by doping we might be able to increase activity in the metallic bond to a certain extent :

 $x \operatorname{CsSnX}_3 + (1-x) \operatorname{CsCdX}_3 \xrightarrow{x = 1 \to 0} \operatorname{CsSn}_x \operatorname{Cd}_{1-x} X_3 ,$ where "X" is a halide anion.

Cd(II) is $5s^0$ electronically , and so lacks the $5s^2$ inert pair of tin(II) . The compounds $CsCdF_3$, $CsCdCl_3$, and $CsCdBr_3$ are all known to be perovskites .

This experience with the $CsSnX_3$ perovskites could be an inducement for the researcher to include halide anions other than fluorides in his or her experimental design when investigating the redox resonance and A^0MX_3 systems outlined above . Of course , it would add considerably to the laboratory work load and project cost , but it would be a shame to have gone to a lot of trouble and expense synthesizing only fluoride and possibly chloride compounds , and finding them to be insulators or semiconductors ,
while the metallic bromides and iodides awaited discovery in the future . This is where "practical" concerns of funding , budget , and personnel will come into play .

A web site on the Internet , "Web Elements" , has provided a Periodic Table web page with links to other pages describing many properties of the elements and their simple , binary compounds . Excellent illustrations of the crystal structures of most of these solid state compounds are provided in linked web pages . For example , the crystal structure of aluminum fluoride , in the "polygon style" , can be viewed at the URL : http://www.webelements.com/webelements/compounds/text/Al/Al1F3-7784181.html .

Most of the new materials I have discussed above would have the AMX₃ perovskite structure (a few , like the $U_xGa_{1-x}N$, $Eu_xFe_{1-x}O$, and $Eu_xCd_{1-x}O$ series of compounds mentioned above , should have the rocksalt structure) . However , there is no theoretical impediment to inserting zerovalent metal atoms into a wide variety of host crystal structures , to obtain either well known "classical" structures , or even brand new crystal architectures .

Several years ago, when I was browsing in one of those "New Age" boutiques – it was called , in fact , "l'Age du Verseau" [The Age of Aquarius] - looking over their offering of "magic crystals" for the occultminded, I noticed an interesting quartz crystal that got me thinking about atom insertion. According to the attached card, the quartz, which was an attractive purple color, had been doped with gold atoms. Of course, gold is the noblest of metals, and won't transfer its 6s¹ valence electron to the silicon in the quartz. It will stay as zerovalent gold atoms, embedded in the silicon dioxide chains, coordinated by the oxygen $2p_{yz}$ lone pairs. I was wondering : this purple quartz probably contains only a few parts per million of gold, which causes its coloring. Would it be possible to combine gold with reagent silicon dioxide in a stoichiometric ratio, eg 1:1, to obtain a new metallic solid? If so, what kind of a structure would the new compound have ? Could we combine other noble metals with other host lattices to similarly produce a wide range of new electronically active materials ? Could we even use certain base metals this way, inserting their

atoms into host lattices that will resist their chemically reducing nature and leave them embedded in a zerovalent state? That was the origin of some of the ideas presented above . [You might think that after having been so inspired by the purple quartz, I would have purchased it as a souvenir, but alas, my magpie eye was diverted by a dazzling fist-sized chunk of fool's gold, with its brassy, yellow gleam. This mass of iron pyrite is now a paper weight here, a shiny, metallic-looking decoration. But even fool's gold has provided me with some food for thought. I'll comment later about its electronic structure and suggest an intriguing link to its possible use in new superconducting compounds (page 328)].

I should point out that many minerals found in Nature are colored by trace quantities of transition metal impurities . The purple quartz , amethyst , derives its color from iron(III) substituting for silicon(IV) . Doping the colorless alumina with low levels of chromium(III) , or iron(III) and titanium(IV) , will produce (as a gemstone crystal) ruby and sapphire , respectively . I have seen a beautiful mass of synthetic sapphire , still retaining the conical shape of the crucible it was formed in , synthesized by such a doping method . Even the colorless diamond can be tinted yellow or blue by trace quantities of impurities .

I haven't done a literature search into the "prior art" of zerovalent atom insertion into host lattices . However, I am aware of one such example, that of the compound $Cu^0Ti_2S_4$, which was prepared by French solid state chemists around 1980 (ref. 134, page 411). The host lattice, TiS_2 , has a graphite-like "two-dimensional" structure, resulting in its physically flaky morphology. Naturally, this has made it of considerable interest as a host for a number of intercalating reagents, just as graphite has been.

One such intercalating species was copper , possibly inspired by the successful insertion of lithium into TiS_2 . The host structure remained flaky and sheet-like up to a copper : TiS_2 ratio of 1:2, at which point the composite's structure changed to that of a normal spinel, $A_{tet}(B_{oct})_2X_4$. In this case, copper(0) atoms occupied the tetrahedral vacancies in the lattice, with Ti(IV) in the octahedral sites. $Cu^0Ti_2S_4$ was found to be "metallic conducting and temperature independent paramagnetic [t.i.p.]". Copper, as

a noble metal, was unable to reduce Ti(IV) to Ti(III):

$$\underline{Cu}^{0} + \underline{Ti(IV)} \xrightarrow{[V] = 0.611 \text{ V}} Cu(I) + Ti(III)$$

That is , Cu(I) is a natural oxidizer , and Ti(III) is a natural reducer , so the left-hand components will predominate , with copper(0) embedded in the lattice .

Copper(0) is normally $3d^{10} 4s^1$ electronically, but its tetrahedral coordination by the sulfides in $Cu^0Ti_2S_4$, informally by the VB hybrid orbital, sp^3 , will destabilize the 4 s-p orbitals. Given the chemically reducing environment of the spinel matrix – sulfide anions are reducers $(0.4763 \text{ V to } S^0)$ – the displaced copper $4s^1$ valence electron is unlikely to be relocated to the vacant 4d orbitals, which are closer to the kernel than are the 5s-p frontier orbitals; chemical reducers want to get rid of outer electrons, and push them away from the kernel. Oxidizing kernels pull the valence electrons inward, into closer [d] orbitals. The $4s^1$ "orphan" electron will likely be relocated to the 5s AO. The 5p orbitals will be unable to overlap with their neighbors in a tetrahedral geometry, so the metallic bond in $Cu^0Ti_2S_4$ will probably be a sigma XO. The coppers' 5s AOs may be able to overlap successfully with neighboring $3s^2$ AOs on the sulfides, or maybe with their empty $4s^0$ AOs [which were used in poly(sulfur nitride)].

The French researchers also prepared a series of copper(I) thiospinels , with the general formula $Cu^{1+}M^{3+}M^{*4+}S_4^{8-}$. M^{3+} and M^{*4+} were transition metal cations and Sn(IV) . These latter compounds were described as being "semiconducting and paramagnetic" . It would be interesting to prepare and study a series of mixed-valent thiospinels based on the two types of compounds , Cu(0) and Cu(I) , reported in this article . In deference to the possibility of preparing potential superconductor candidates , however , the dopants should be diamagnetic insulators .

In this latter category, diamagnetic trivalent cations such as Al^{3+} , Y^{3+} , and La^{3+} could be used in conjunction with diamagnetic tetravalent species such

Ti(IV), Zr(IV), and Th(IV). Oxidizing species such as Tl(III), Sn(IV), and Pb(IV) would be unsatisfactory. Illustrating a dopant synthesis with aluminum(III) and titanium(IV):

$$\frac{1}{2}$$
 Cu₂S + $\frac{1}{2}$ Al₂S₃ + TiS₂
 $\xrightarrow{\text{shake-n-bake}}$ Cu¹⁺Al³⁺Ti⁴⁺S₄⁸⁻
inert atmosphere

All the reagents cited are commercially available, eg. from Alfa Aesar.

The dopant is then incrementally doped into the metallic substrate $Cu^{0}Ti_{2}S_{4}$:

$$x \quad Cu^{0}Ti_{2}S_{4} + (1-x)Cu^{1+}AlTiS_{4} \xrightarrow{x = 1 \rightarrow 0} Cu^{(1-x)+}Al_{1-x}Ti_{1+x}S_{4} .$$

The resulting composite will have mixed-valent copper, and could even be a Robin-Day Class IIIB synthetic metal if the metallic bond is direct Cu-Cu, without participation of the intervening sulfide anions. If the sulfides do provide their $3s^2$ or $4s^0$ AOs to the sigma XO, the compound would then be a Class II mixed-valent compound. In either case, it should have some interesting electrical properties.

It might be possible to prepare other noble metal adducts with TiS_2 and related flaky transition metal dichalcogenides (MoS_2 , the industrial lubricant, most notably; also NbS_2 and TaS_2 , which have been studied as hosts for a number of intercalated reagents):

$$Hg^{0} + 2 MoS_{2} \xrightarrow{[V] = 0.751 V} Hg^{0}Mo_{2}S_{4} .$$
Note : Mo(IV) + e⁻ \longrightarrow Mo(III) ; $E_{red}^{0} = 0.100 V (H^{+})$

Mercury is known to have a powerful affinity for sulfur and sulfur compounds, so the mercury(0) atoms should be strongly bonded in the thiospinel lattice by the sulfide anions. The mercury's $6s^2$ electrons should be promoted into the 7s frontier orbital, with leakage of electron density

into the inactive 7p AOs . As with copper , a sigma XO is predicted to function as the metallic bond in this hypothetical compound . Silver and gold should behave similarly with the flaky disulfides . Even bismuth , which surprisingly seems to be noble (and I always thought it was a trashy metalloid !) , could be intercalated into them in a 1:2 ratio to provide a normal spinel :

Bi⁰ + 2 VS₂
$$\xrightarrow{[V] = 0.029 \text{ V}}$$
 Bi⁰V₂S₄ .
Note : V(IV) + e⁻ $\xrightarrow{}$ V(III) ; E_{red}⁰ = 0.337 V

I wonder if normal spinels with zerovalent "A" atoms could be made using halide anions rather than divalent anions such as oxide or sulfide :

 Cu^0 + 2 MX₂ \longrightarrow $Cu^0M_2X_4$,

where "M" could be the metal cation in a rutile or fluorite halide, such as MnF_2 , FeF_2 , CoF_2 , NiF_2 , MgF_2 , ZnF_2 , CaF_2 , SrF_2 , $SrCl_2$, BaF_2 , $BaCl_2$, CdF_2 , PbF_2 , and so on ; or from the CdI_2 or $CdCl_2$ structural families . Generally, almost any MX_2 compound (where M is a divalent metal cation, and X is a halide anion) could be combined this way with a noble metal atom , and in many cases even certain base metals could yield zerovalent "A" atom derivatives with selected MX_2 hosts , redox conditions permitting .

Note that a tetrahedral coordination of the base Cu(I) by halide anions (for example, as in CuCl) involving the sp³ hybrid orbital on the copper atoms is quite favorable, and the resulting spinel structure is a very stable one. While the usual anions found in spinels are oxides and sulfides, halides can also be used in their formation, correctly balanced with cationic charge.

Similarly, a rocksalt composite with an inserted zerovalent metal atom might be synthesized, taking care that the cations and anions are appropriately sized, and that the redox chemistry of the system permits such an insertion; for example,

$$x \text{ KCl} + (\underline{1-x}) \text{ Cd}^{0} + (\underline{1-x}) \text{ BaCl}_{2} \xrightarrow{X = 1 \rightarrow 0} K_{x} \text{Cd}_{\underline{1-x}} \text{Ba}_{\underline{1-x}} \text{Cl} .$$

Radii : $K^{1+} = 1.52 \text{ Å}$; $Cd^0 = 1.52 \text{ Å}$; $Ba^{2+} = 1.49 \text{ Å}$; and $Cl^{1-} = 1.67 \text{ Å}$.

The host, KCl, is a rocksalt; the dopant, $BaCl_2$, has the fluorite (8:4,4) structure. Pure KCl (x = 1) could be incrementally doped to x = 0 (the dubious $Cd_{0.5}^{0}Ba_{0.5}Cl$). In practice, there would probably be only a low percentage of $Cd^0/BaCl_2$ substituting for KCl in the host lattice in this system. Nevertheless, we might observe some interesting electrical effects with such a doped material.

Zerovalent metal atoms might also be inserted into host lattices to provide completely novel, "non-classical" structures. For example, copper(I) in oxide compounds prefers a linear (sp) coordination by covalent oxygen links or oxide anions. If copper(0) is inserted into an oxide host, we can be assured that it will have such a linear coordination, and the coppers' $4s^1$ valence electron will be relocated in the $4p_{y,z}$ native orbitals (the $4p_z$ AO is either used in covalent bonding for the sp_x hybrid orbital, or is energetically destabilized in ionic bonding environments by the oxide ligands on each side of the copper atom).

With this understanding, we can try to insert copper(0) into, say, zinc oxide in a 1:1 mole ratio:

 $Cu^{0} + ZnO \qquad \underbrace{ [V] = 1.2828 V}_{\text{shake-n-bake}} Cu^{0}ZnO .$ m.p. 1083 °C 1975 °C shake-n-bake , inert atmosphere

The high redox potential between Cu^0 and Zn^{2+} suggests that the former atom is incapable of reducing the latter cation to Zn^0 , even at a high temperature, where the zinc vapor (b.p. 907 °C) might distill out of the reaction mixture. Differential thermal analysis would be useful as a pilot experiment to see, first, if the compound Cu^0ZnO was actually made, and then second , what the optimum reaction conditions were for its synthesis .

The zinc oxide host has the wurtzite crystal structure , which is somewhat like the diamond structure (all atoms are tetrahedrally coordinated), but with alternating AX atoms . We can think of a simple ZnO_4 tetrahedron in a box :



With a 1:1 mole ratio stoichiometry of Cu^0 to ZnO, the copper atoms (red) can be placed at each corner of the box, then bonded linearly to the adjacent oxygens (green) to provide parallel linear –O-Cu-O-Cu-O – chains :



The zinc cation (blue) retains its tetrahedral coordination in between the

planes of Cu-O chains . Here's the M3D model of the hypothetical new compound , Cu^0ZnO :



Figure 50 : the M3D model of copper(0) zinc oxide . Small blue spheres : tetrahedrally coordinated zinc(II) cations ; small red spheres : linearly coordinated copper(0) atoms ; larger green spheres : octahedrally coordinating oxygen atoms . Heavy black lines are covalent bonds between the atoms . Dashed lines outline the original "boxes" containing the ZnO_4 tetrahedrons .

Continuous overlap along the Cu-O chains of the coppers' $4p_{y,z}^{1}$ AOs with the neighboring $2p_{y,z}^{2}$ AOs on the oxygens could produce a pi XO metallic bond. The base copper(I) cations are only mildly oxidizing (0.521 V), so there would be only weak polarization in this bilayer pi XO.

I'm just guessing that this could be the crystal structure of the hypothetical compound Cu^0ZnO ; the actual structure could be something entirely different. Note that in my proposed structure, the original zinc oxide's wurtzite framework remains intact, with the copper atoms nested into available vacancies. No radical rearrangement of the host lattice is required here, and the three atomic components are in their preferred coordinations. The oxygen atoms have additional coordinating ability in their tetrahedral conformation. They can still be octahedral, as in the oxide rocksalts (eg. magnesium oxide, MgO), or even eight-coordinate, as in the antifluorites (eg. lithium oxide, Li_2O).

Although the compound Cu⁰ZnO should be a metallic solid as I have drawn it, it is unlikely to be a superconductor at a transition temperature much

above absolute zero , if that . To improve its chances of exhibiting high temperature superconductivity , we might try doping it with a corresponding copper(I) compound . A series of $Cu^{1+}MO$ compounds has been prepared and characterized , for example $Cu^{1+}LiO$, whose lithium spectator cation has about the same crystal ionic radius (0.73 Å) as the zinc cation (0.74 Å ; both radii cited were for a tetrahedral coordination environment) :

[This product was described as "light greenand weakly paramagnetic", which it should not have been; all copper(I) compounds are diamagnetic. It might have been contaminated with some copper(II) oxide impurity].

As an alternate preparation of CuLiO, may I suggest the following solid state metathesis reaction :

 $\begin{array}{rcl} & & \text{melt together} \\ \text{CuCl} + \text{Li}_2\text{CO}_3 & & & \\ \text{m.p. 430 °C} & 723 °C & \text{inert atmosphere} & & 605 °C \\ \end{array}$

This latter reaction would take place at a lower temperature than the one immediately above , with the added advantage of melting the components together . The by-product LiCl could also serve as a flux (high temperature ionic "solvent") for the reactants . The copper(I) chloride reagent , which is highly sensitive to oxygen , would have to be protected under a blanket of inert gas such as nitrogen or argon . A dynamic atmosphere – flowing gas – would continuously expel by-product CO_2 and help drive the reaction to completion . TG/DTG could be used as a pilot experiment , monitoring the carbon dioxide evolution (mass loss) , to establish optimum experimental parameters . Solid state metathesis with molten reactants can sometimes be a spectacularly fast , and occasionally exothermic , type of reaction (ref. 136 , page 411) .

The crystal structure of CuLiO isn't exactly like the one I suggested for

CuZnO, but at least its copper(I) has a linear coordination :



Figure 51 : the M3D model for CuLiO , where the blue spheres are lithium cations , the red spheres are copper(I) cations , and the larger green spheres represent oxygen atoms . This model was based on H. Müller-Buschbaum's fig. 12 , p. 727 , in ref. 117 , page 408) .

The copper(I) dopant , CuLiO , would be incrementally doped into the substrate , the hypothetical CuZnO :

At low doping levels , the CuLiO rings would hopefully unzip and blend into the majority CuZnO structure as Cu-O chains .

I think the mixed-valent composite would have a better chance of displaying superconductivity than the CuZnO alone . Nevertheless , we must recognize that the composite's NIOS valence is much lower than that of YBCO , and that the latter material , because of the powerfully oxidizing nature of its copper atoms , has a strongly polarized metallic bond , which is expected to

significantly enhance its electrical conductivity . The low-valent copper composite , on the other hand , has only weakly oxidizing copper(I) atoms – formally – and so its metallic bond will be only slightly polarized . Still , low-valent , mixed-valent copper compounds would be both valuable and instructive to study .

Copper(0) might also be inserted into titanium dioxide in an equimolar ratio to provide an interesting new metallic solid :

 $\begin{array}{rl} Cu^{0} + TiO_{2} & \xrightarrow{\text{shake-n-bake (dta)}} & Cu^{0}TiO_{2} & .\\ \text{m.p. 1083 °C 1870 °C inert atmosphere} & \end{array}$

The inserted copper(0) atoms will have a linear coordination by oxides , and the titanium(IV) atoms will retain the octahedral coordinations they have in the host titania [rutile] structure . This hypothetical compound might therefore have the delafossite crystal structure (Figure 49 , page 262) . The copper atoms in this atomic arrangement will be "dead-ended" by titania layers . However , the $4p_{y,z}^{-1}$ AOs on the copper atoms should be able to overlap face-to-face with adjacent corresponding 4p AOs in the y and z planes to form Cu-Cu pi XOs in those planes . Thus , Cu⁰TiO₂ might turn out to be a copper-based synthetic metal (yes , I know it seems somewhat foolish to make a synthetic metal directly from a metallurgical metal , but scientists sometimes have to run the risk of looking silly in their pursuit of Nature's secrets . And synthetic metals are beautiful compounds !) .

As a copper(I) dopant for the hypothetical Cu^0TiO_2 , we recall (page 222) the compound $Cu^{1+}AIO_2$ prepared and studied (among others) by Arjomand and Machin back in the mid-1970s (ref. 102, page 406). Although these researchers didn't determine the structure of $CuAIO_2$, I think it's a fair bet that given its linear copper(I) and octahedral aluminum with an AMX_2 empirical formula, it too is in the delafossite family. Assuming this is the case, a series of doping trials could be carried out to prepare mixed-valent Cu(0,I) composites with Cu^0TiO_2 as the substrate and $Cu^{1+}AIO_2$ as the dopant :

$$x \quad Cu^{0}TiO_{2} + (1-x) \quad Cu^{1+}AlO_{2} \quad \longrightarrow \quad Cu^{(1-x)+}Al_{1-x}Ti_{x}O_{2}$$

Note that in the mixed-valent composite there should also be a Cu-Cu metallic bond, as with the original substrate Cu^0TiO_2 . That is, Cu^0TiO_2 would be a Class 2 metallic solid, while I would assign the mixed-valent composites to Class 4 (page 57). Alas, the composites still probably wouldn't be high temperature superconductors, and like the other "classical" synthetic metals would be superconducting only close to absolute zero, if at all, as befits their bronze metal nature.

Three other noble metals, silver, gold, and mercury, also exhibit a preference for sp linear coordination in some of their compounds, and so might form a similar sort of delafossite structure when inserted in a 1:1 molar ratio into titania. Platinum group metals can also apparently form delafossite compounds, eg. PdCoO₂ and PtCoO₂, in which the heavy metal has the linear coordination and the lighter one is octahedrally coordinated by the oxygens (Wold and Dwight, ref. 24, page 394, their p. 125 et seq.). In these two examples, the platinum or palladium is divalent, with divalent cobalt, but if they were inserted into TiO₂, they would be unable to reduce the Ti(IV) to Ti(III), and so should remain zerovalent :

$$\underline{\mathbf{Pd}^{0}} + 2 \quad \underline{\mathbf{Ti}(\mathbf{IV})} \quad \underbrace{[\mathbf{V}] = 1.191 \text{ V}}_{\longleftarrow} \quad \mathbf{Pd}(\mathbf{II}) + 2 \quad \mathbf{Ti}(\mathbf{III}) ;$$
Note: $\mathbf{Pd}^{0} - 2 e^{-} \quad \longrightarrow \quad \mathbf{Pd}^{2+} ; \quad \mathbf{E}_{ox}^{-0} = -0.951 \text{ V} ; \text{ and },$

$$\underline{\mathbf{Pt}^{0}} + 2 \quad \underline{\mathbf{Ti}(\mathbf{III})} \quad \underbrace{[\mathbf{V}] = 1.42 \text{ V}}_{\longleftarrow} \quad \mathbf{Pt}(\mathbf{II}) + 2 \quad \mathbf{Ti}(\mathbf{III}) ;$$
Note: $\mathbf{Pt}^{0} - 2e^{-} \quad \longrightarrow \quad \mathbf{Pt}^{2+} ; \quad \mathbf{E}_{ox}^{-0} = -1.18 \text{ V} .$

That is , Pd(II) and Pt(II) are strong natural oxidizers , and Ti(III) is a mild natural reducer , so the redox equilibrium will lie far to the left in both these examples , and the platinum and palladium atoms inserted into titania should remain in a zerovalent state in their delafossite compounds , Pt^0/Pd^0TiO_2 .

I haven't bothered discussing the chemistry of platinum group metals in this study, because of their horrendous cost (gold is rather impractical, too, for the same reason). Yes, I know true scientific endeavor is, or should be, oblivious to money considerations, but I'm trying to keep the discussion of chemistry in this work **practical**, both in term of cost factors, and also of experimental feasibility. I have tried to ensure that the reagents I cite for use in syntheses are either commercially available at a reasonable price (I have used the Alfa Aesar catalogue extensively for this), or could be prepared by the researcher according to procedures published in the chemical literature. However, judging from the extensive research effort with the platinum group metals (and gold) as evidenced in Chemical Abstracts, it would seem that cost considerations of these materials haven't deterred investigators from studying them and their compounds. The remarkable synthetic metals, the Krogmann Salts – of which KCP (page 87) is the outstanding example – are platinum compounds, and we are fortunate that they were synthesized and characterized, because of their invaluable contribution to our knowledge of the metallic bond and metallic solids.

Insertion of zerovalent metal atoms into host lattices could be a very general solid state chemistry reaction. Wells has listed the crystal structures of a number of metal oxides in his Table 83, p. 457, of ref. 21, page 394. Most of these crystal varieties would be suitable as hosts for metal atom insertion, with the possible exception of the antifluorite oxides, whose oxygens are eight-fold coordinating to the metal cation. They probably would have no coordinating power –"ligancy" – left in them at that stage.

Sulfides , nitrides , and halides (page 293) could also be examined for their hosting ability for zerovalent metal atoms . Their redox chemistry is quite different than that of the relatively inert oxides and fluorides , and their higher reactivity would have to be carefully considered beforehand by the researcher .

The electronic properties of the host lattice would undoubtedly be radically altered by the inclusion in it of zerovalent guest atoms, particularly if the valence shell electrons of the guest were capable of interacting with those of the lattice's cations (cf. $Bi_2Ru_2O_7$, page 264). These enhanced electronic

properties might find some practical – and potentially very valuable – industrial uses , one such possible application being in the field of solar electrical energy production .

A New Type of Photovoltaic Diode?

I must confess to being a novice in the areas of solar energy and photovoltaic diodes (PVDs), the devices that convert light into electricity. I have read only one book about these subjects : the broadbased overview, suitable for the layman, by Palz (ref. 137, page 411). It seems to me that solar energy has for decades remained a dream of the future, with researchers being unable to exceed the roughly 30% or so efficiency level achieved by conventional PVDs, the "best" of them apparently still the costly gallium arsenide diode. Despite considerable, and ongoing, research and development, solar energy conversion remains uncompetitive with other major electricity production technologies.

I wonder if the fundamental problem with conventional PVDs is that they are based on semiconductors, which are all poor electrical conductors. Conventional wisdom, as I understand it, says that PVDs can't be made from metals. Perhaps not from metallurgical metals, but how about from other classes of metallic solids (of the "true metal" variety, Classes 1 to 4; refer back to page 56) that we have been discussing earlier? In particular, I'll proceed to outline the construction and functioning of a new type of PVD utilizing the perovskite materials proposed on page 275 and following.

Most semiconductor materials these days are manufactured , now on a large scale , by the process of molecular beam epitaxy (MBE) , which in essence is "spray painting" atoms onto a substrate surface . An informative , readable account of MBE has been given by Amato (ref. 138 , page 411) . This has been developed into an extraordinarily precise method of atomic placement , such that semiconductor layers only a few atoms thick can be deposited onto the target substrate in the MBE apparatus , in a high vacuum . This sort of precision is required , for example , in the manufacture of light-emitting

diodes (LEDs), used in commercial electronics appliances such as the various sorts of laser writing devices. So, I'm confident that the technology actually exists to implement my proposal for a new PVD, should basic research verify its performance and efficiency.

The two layers of perovskite comprising the light capturing and transforming zone of the diode would be the A^0MX_3 compound, such as Ag^0AlF_3 (on the "outside" of the two layers, receiving the radiant energy), and the corresponding doped mixed-valent composite on the "inside" of the bilayer, covering the substrate's surface, in this case $Ag^{(1-x)+}Al_xZn_{1-x}F_3$ (page 276). Here is the situation with the two layers in the dark condition :



The "e-" on the $Ag^{e^{-}}$ atoms indicates the silvers' $5s^{1}$ valence electrons, which could be located in a sigma XO connecting the silver atoms directly (that is, $Ag^{0}AlF_{3}$ could conceivably be a synthetic metal, with a high electrical conductivity). The mixed-valent composite layer is coating the metal substrate. The doped composite could also be a synthetic metal, so the entire assembly envisaged here should have an excellent electrical conductivity, probably comparable to that of metallurgical metals. No electrical activity is anticipated in the diode when in the dark condition. When radiant energy such as sunlight falls on the diode , illuminating its outer Ag^0AlF_3 outer layer , some of the silvers' $5s^1$ electrons in the sigma XO could be energetically promoted into a higher energy , physically larger frontier orbital , that extends into the doped composite layer . The photoexcited 5s electrons can fall into , and occupy the vacant 5s orbitals on the silver(I) cations in the composite layer :



When this photo-induced electron transfer occurs, the electrical charges become unbalanced in the two layers because of the underlying perovskite chemistry, of course. This charge imbalance polarizes the two layers, with the outer one becoming positive in overall charge, and the inner composite layer acquiring a negative charge as it receives the excited 5s electrons from the outer layer.

It should be emphasized that this electron transfer occurs only in the illuminated condition . The instant the light source is removed and the diode is returned to its dark condition , the 5s electrons instantly flow back to the Ag^0AIF_3 outer layer to rebalance the assembly . Although quantum processes are usually credited with the photo-induced electron transfer – as in promotion of the 5s electrons to a higher energy , more voluminous frontier orbital – I wonder if we could look at the electron transfer process as

occurring under the **pressure** of the radiant energy . We know that radiant energy does exert a vanishingly small , yet finite pressure on surfaces it falls on . This phenomenon has been the basis , for example , of the science fiction-like scheme for solar-powered vessels traveling in outer space between the planets , sailing like ships of the past on oceans , using the pressure of the sunlight on enormous light-gathering sails extending far out beyond the spaceship . In the case of this new type of PVD , the light falling on the surface of the Ag^0AlF_3 could perhaps push under its pressure the $5s^1$ electrons in the readily deformable sigma XO metallic bond into the composite layer underneath . Actually , the metallic bond would be continuous throughout the assembly , and there would be no insulating interface between the two layers . The sunlight , or other radiant energy , would "push" the electron density from the outer to the inner layer , and in doing so would create the polarization between them .

This polarization would appear physically as a potential difference (p.d.), or voltage, between the two layers. By placing electrodes strategically on or in the two surfaces, we should be able to tap this p.d. to do useful work for us. An external circuit connected to the electrodes will permit the excited 5s electrons in the composite layer, **as long as the diode is still in the illuminated state**, to travel back to the outer Ag^0AIF_3 layer, and as they do so, they can do useful work, such as running an electric motor or causing a lightbulb to shine. And so the cycle continues, the 5s electrons moving around through the diode's layers and through the work circuit. The sunlight or other radiant energy will have been converted into electrical energy.

The success of this scheme will depend on the photochemistry of the Ag^0AIF_3 / composite system . Will sunlight actually energize the 5s electrons , and promote them into the composite layer to join up with the Ag(I) cations ? [Or alternately , will the sunlight be able to physically push under its pressure the 5s electrons through the metallic bond into the underlying composite layer ?] However you visualize the system , its success will hinge on its photochemistry . Other related systems could also be investigated in this regard , such as the $Tl^0EuF_3 / Tl^{(1-x)+}Eu_xCd_{1-x}F_3$ combination discussed on page 277 , in which I have predicted the additional interesting feature of redox resonance among its metal atom components .

We need not confine our search for new PVD materials to perovskites , either . The copper-based thiospinel system discussed on page 292 , for example , might also be looked at in this regard : $Cu^0Ti_2S_4$ acting as the donor layer , and the doped composite $Cu^{(1-x)+}Al_{1-x}Ti_{1+x}S_4$ forming the acceptor layer over the metal (or other) substrate . In general , the "electron rich" zerovalent compound would be the outer illuminated layer , while the "electron poor" (with "holes" in its XO , to receive the photoexcited electrons) composite , with its mixed-valent cations , would serve as the inner electron receiver . The creative solid state chemist could undoubtedly devise many more such candidate bilayer systems to be evaluated for their photochemical activity .

The latter half of the twentieth century has rightly been called the "Silicon Age" (ref. 139, page 411), from the revolutionary effect the transistor and its many descendants have had on daily life in modern society. Perhaps, though – at least where solar electrical energy is concerned – we should look outside the "semiconductor box" for new solutions to unlocking this largely untapped bountiful energy supply. The new metallic solids described in this study may offer such a novel approach to the economic and widespread production and distribution of solar electricity.

New Homoatomic Mixed-valent Systems

In this final section we will take a guided tour of the Periodic Table of the elements , stopping off here and there to visit interesting locales and see the sights . While the heteroatomic systems I discussed earlier may , with redox resonance , mimic the classical Robin-Day mixed valent systems (Classes II and IIIB) , in the following pages we'll look at a number of novel homovalent mixed-valent systems . Apart from being fascinating new solid state materials , they may also be superconductors at a lowered temperature . They should all be true metals , having a nodeless XO along at least one crystal axis as the metallic bond in the solid . Most of the materials to be discussed will be from the Class 3 metallic solids group (like YBCO , for example : Robin-Day Class II mixed-valent ; see page 57) . These will be the best candidate compounds to examine as high temperature superconductors .

The Alkali Metal Elements

I didn't include any of the alkali metals in the list of suggested elements for possible insertion into crystal hosts on page 278 because they are such powerful reducers that they would almost certainly react with , and radically alter , almost any lattice they were brought into contact with . Nevertheless , mixed-valent alkali metal compounds are known , such as the low-valent suboxide compounds (ref. 140 , page 411) . An interesting example of such a suboxide is tricesium oxide , Cs_3O , whose structure is comprised of stacks of triangular Cs_3 rings separated by oxygen atoms ; the columns are packed together side by side in the solid :



Figure 52 : the M3D model of tricesium oxide , Cs_3O . The large aqua spheres are cesium atoms ; the small red spheres represent oxygen atoms . This model was based on Figure 150 , p. 459 , in A.F. Well's textbook (ref. 21 , page 394) .

Tricesium oxide is a synthetic metal (Class 4 metallic solid, Robin-Day Class IIIB); it is soft and malleable like the alkali metals themselves, having the appearance of dark green crystals with a metallic luster (ref. 141, page 411). It is a fair electrical conductor, with an ambient conductivity of 14,000 ohm⁻¹cm⁻¹; that of the parent cesium metal is about 50,000 ohm⁻¹cm⁻¹. Both cesium and tricesium oxide have a weak Pauli paramagnetism, which is typical of most bronze metals.

Since the oxygen atoms in the compound are six-coordinating to the cesium atoms , we would expect them to be oxide anions . The trio of cesiums per formula unit would then be $(Cs_3)^{2+}$, each having a NIOS valence of 0.67+. Cesium cations are $6s^0 6p^0$ electronically , and they are two-coordinated by the oxides ; this would destabilize their $6p_{x,y}$ native orbitals (being ionically equivalent to the VB bent p^2 hybrid orbital). The metallic bond in Cs_3O is thus probably in the 6s AOs , as the sigma XO , with some leakage into the $6p_z$ AO , as the pi XO , both extending over the cesium layers .

The alkali metals (except lithium and sodium) intercalate in graphite and form discrete compounds with fullerenes, but in these cases they seem to cleanly reduce the carbon acceptors, and are present in them as their univalent cations, and not as the zerovalent atoms. The electrides are much more interesting, as they offer us the hope of preparing mixed-valent alkali metal compounds of the Robin-Day Class II (or maybe IIIB) variety.

The ammonia electrides have been known for a long time ; a number of review articles on the subject are listed in ref. 142, page 412. It is possible to dissolve quantities of the alkali metals in pure, anhydrous liquid ammonia to produce a solution of the electride, which is the ammoniated metal cation (probably tetrahedral tetrammine for Li^{1+} , and octahedral hexammine for the other alkali metal cations), closely associated with the displaced ns¹ valence electron. The latter is thought to be located in cavities in the solution of ammonia molecules ; in fact, these solvated electrons are theorized to possibly even form pairs in the cavities. Dilute solutions of electrides have an inky, blue-black appearance, while more concentrated solutions have a bronze color with a metallic luster.

Solubilities of the three more common alkali metals in liquid ammonia are presented in the following table :

Solubility of Selected Alkali Metals in Liquid Ammonia

<u>Alkali Metal</u>	<u>Atomic Wt.</u>	<u>Solubility (1)</u>	Solubility (2)	Solubility (3)
lithium	6.941 g/mol	0.2770 mol <i>i</i> mol	76.97 g/litre	11.089 mol/L
sodium	22.9898	0.1863	171.46	7.458
potassium	39.098	0.2055	321.65	8.227

Solubility (1) : mole of metal dissolved in one mole of liquid ammonia [an experimental value : see text for reference] . The M.W. of ammonia is 17.031 g/mol ; its liquid density at its b.p. (-33 C) at one atm. is 0.6818 g/mL ; its "molecular volume" is therefore 24.9795 mL/mol under these conditions .

Solubility (2) : mass of metal dissolved in one litre of liquid ammonia .

Solubility (3) : moles of metal dissolved in one litre of liquid ammonia .

The experimental data in the "Solubility (1)" column were from Kraus et al. (ref. 143, page 412). Substantial quantities of these metals will dissolve in liquid ammonia.

In order to form a Robin-Day Class II (or IIIB) mixed-valent compound from one of these electrides , we can consider the electride as the zerovalent component , M^0 , and dope it with the corresponding univalent component with the M^{1+} cation . The latter can be readily prepared by dissolving the pure , anhydrous alkali metal halide salt in liquid ammonia . It is then added to an appropriate quantity of the corresponding electride solution . As it turns out , the alkali metal halide salts are somewhat soluble in anhydrous liquid ammonia , perhaps not as soluble as they are in water , but sufficiently so for our purposes . The ammonia solubilities of a number of halide salts are presented in the table at the top of the following page . The fluoride and chloride salts are only sparingly soluble , while the bromide and iodide salts are substantially ammonia-soluble .

I haven't any data on the ammonia solubilities of lithium, rubidium, and cesium halide salts. However, lithium chloride is almost twice as soluble

Solubility of Selected Alkali Metal Halide Salts in Liquid Ammonia

<u>Alkali Metal Halide Salt</u>	<u>Formula Wt.</u>	<u>Solubility (1)</u>	<u>Solubility (2)</u>
sodium fluoride	41.988 g/mol	2.1 g/L	0.050 mol/L
sodium chloride	58.442	18.2	0.311
sodium bromide	102.894	833.2	8.098
sodium iodide	149.894	977.8	6.523
potassium chloride	74.551	0.24	0.0032
potassium bromide	119.002	81.5	0.685
potassium iodide	166.003	1099.2	6.622

Solubility (1) : mass of salt dissolved in one litre of liquid ammonia . This is an experimental value ; see the text for the reference .

Solubility (2) : mole(s) of salt dissolved in one litre of liquid ammonia .

The experimental data in the "Solubility (1)" column were from Table II in Hunt's paper (ref. 144, page 412).

in water as sodium chloride, and is also appreciably soluble in polar organic solvents, so it too might be fairly soluble in anhydrous liquid ammonia. Similarly, cesium fluoride is more than ten times water-soluble as sodium chloride, and has some solubility in polar organic solvents as well, so it too could be tried in these experiments.

The researcher could incrementally dope mole fractions of the substrate electride (calculated as the metal content) with the dopant halide salt solution :

$$x M^{0} + (1-x) M^{1+}(X)^{-} \longrightarrow M^{(1-x)+}(X_{1-x})^{-}$$

It is difficult in this case to predict beforehand what might happen experimentally as the two solutions are mixed together in the Dewar flask (in the fume hood !). The mixed-valent compound might immediately precipitate from solution as a fine, microcrystalline material; it might slowly crystallize from the ammonia in coarser-grained crystals ; or some or all of the ammonia solution might have to be evaporated in order to recover the solid reaction product .

It is similarly difficult to imagine what the crystal structure of the doped composite of electride-salt would be . Lacking such information , its electronic structure would be speculative as well . However , the electrides have been referred to as "expanded metals" ; that is , the ns¹ valence shell electrons have been promoted up into the (n+1)s orbitals by the ammonia ligands coordinating the underlying metal cations . The metallic bond in the doped composite is thus likely to be a sigma XO , formed from the continuous overlap in the solid of the (n+1)s orbitals . If the s AO overlap was direct metal-to-metal , the composite would be a synthetic metal (Robin-Day Class IIIB , Class 4 metallic solid) based on the original alkali metal element . If the halide anions' frontier orbitals were somehow involved as intermediaries in the XO formation , then the mixed-valent composite could be categorized as Robin-Day Class II (Class 3 metallic solid) .

The question arises as to whether the doped electride-salt composite would be a bronze or black metal . The answer is important , as the material might stand a fair chance of being a superconductor at some low temperature if it is the latter , but slim to none if it is a bronze . Interestingly – as mentioned – the concentrated electrides have a bronze , metallic appearance , which agrees with the "expanded metal" view of them . No doubt the pure electrides are indeed bronze metals like their parent alkali metals . Dilution of the concentrated electrides by additional liquid ammonia causes them to assume their typical inky , blue-black color , produced by the strong absorption of incident light by the paramagnetic singlet electrons in the solution . Intercalation of the corresponding univalent alkali metal cations in the solid electrides may radically alter the magnetic arrangement of the singlet valence electrons in the (n+1)s orbitals , with the imposition on them of an antiferromagnetic ordering . If this occurs , we could reasonably expect to detect superconductivity in the doped , mixed-valent composite material .

As mentioned on page 197, Ogg actually reported having observed

superconductivity (persistent currents) in samples of frozen electrides up to the melting point of the ammonia solvent, which is -77 °C, or 196 K (ref. 96, page 405), but his claims apparently could not be reproduced or otherwise confirmed, and later superconductivity researchers have tended to ignore or even deride his work. Since the pure electrides are almost certainly bronze metals, we wouldn't expect them to be high temperature superconductors. I wonder if Ogg's samples of frozen electrides might have been contaminated with hydroxide anion impurity, formed by the reaction of the electride with traces of moisture in the liquid ammonia :

 $(NH_3)_6Na^{1+}e_{-} + H_2O \longrightarrow (NH_3)_6Na^{1+}OH_{-} + \frac{1}{2}H_2(g)$.

The ammoniated sodium hydroxide product shown could act as a dopant for the parent "zerovalent" electride (the reactant in the equation). In fact, the alkali metal hydroxides, if they were pure and dry, and reasonably soluble in liquid ammonia, could also be tried as the univalent cation source for the dopant in preparing the mixed-valent composite. In any case, if such impurities were indeed present in Ogg's test samples, he may have inadvertently prepared slightly doped mixed-valent electride composites, which could then have given the readings of persistent currents. Later researchers trying to duplicate his findings might have used scrupulously anhydrous reagents and bone-dry liquid ammonia, to produce the pure, but bronze electrides, which yielded negative results for superconductivity.

If this conjecture proved to be factual , the mixed-valence electrides might have remarkably high transition temperatures of around 200 K ! Wouldn't it be delightful if we could use the very familiar and ordinary sodium chloride as a successful dopant in preparing such a high T_c superconductor ! In reality NaCl is only slightly soluble in liquid ammonia , and there is also the important question concerning the stability and undoubted high reactivity of the mixed-valent composite . Pure , solid ammonia electrides apparently are too reactive and unstable to be isolated and retained at room temperature . The mixed-valent electrides , which can be thought of as electrides "diluted" by intercalated salt , might be both stable and isolable – although probably highly reactive with atmospheric oxygen and water vapor – and so could be readily synthesized and studied by researchers under ambient conditions .

There is another way of preparing the low valent , mixed-valent alkali metal compounds containing $M^{(1-x)^+}$ cations (x = 0 \rightarrow 1). When irradiated with high energy radiation , crystals of alkali metal halide salts (and presumably other halide salts as well) will become strongly colored by halogen atom defects in the lattice , called "F centers" [F from "farben", German for "color"]. For example , a beam of X-rays directed through a colorless crystal of sodium chloride will color it brownish-orange , and will color KCl violet (there is a nice color photo of such irradiated salt crystals in <u>Van Nostrand's Scientific Encyclopedia</u>, fourth edition , 1968 , p. 374 . The F centers are described as follows :

"Certain crystals, such as the alkali halides, can be colored by the introduction of excess alkali metal into the lattice, or by irradiation with X-rays, energetic electrons, etc. Thus sodium chloride acquires a yellow color and potassium chloride a blue-violet color" (p. 384).

The X-rays knock an electron off the valence shell of the halide anion , converting it into the corresponding halide atom . As the neutral , diatomic halogen molecule , it can diffuse through the crystal , pop out of the lattice , and disappear into the atmosphere . The electron ejected from the halide anion rejoins the alkali metal cation to form the zerovalent metal atom . Presumably the resonance of these ex-halide electrons between the metal cations is responsible for the strong tinting of the crystal by the F centers . In effect , the high energy irradiation of the salt crystal has created a low concentration of the M^{(1-x)+} mixed-valent state in its alkali metal atoms .

The nice round color spots in the salt crystals shown in the scientific encyclopedia photograph were made by a beam of X-rays . Few laboratories would have an X-ray machine , though . However , I noted on a Web Page – now disappeared , alas – that F centers could be created rather easily by irradiating the salt , contained in a round-bottom glass flask , and under high vacuum to remove the ejected halogen gas , by a Tesla coil . This is a simple device used for verifying the degree of evacuation in a vacuum line , and indeed is usually called a "vacuum checker" . It is commercially available from scientific supply houses . It is also the "spark coil" in automobiles , by the way . Unfortunately I have no bibliographical references at hand concerning this method of producing F centers in halide salt crystals .

Large salt crystals are commercially available, for example, as the sodium chloride discs, used in infrared spectrophotometry (in my experience as an undergraduate student, there were always several broken pieces of such salt discs, still pure and clear, kept in glass desiccators near the IR equipment. Perhaps a friendly organic chemist would donate such a broken piece for your experiment). The researcher could also prepare clear salt discs, about the size of a small coin, in the KBr press, as the organic chemist does when making KBr discs containing organic compounds for IR analysis.

Such salt discs, after Tesla irradiation, should contain F centers with the $M^{(1-x)+}$ mixed-valent alkali metal (or other) cations. It would be most interesting to examine such irradiated salt discs to see if they show evidence of superconductivity at lowered temperatures. Obviously, since the F centers represent, in effect, only traces of the mixed-valent compound, and the irradiated salt discs are still insulators, we wouldn't expect to see full superconductivity in them. However, Meissner exclusion effects might be observed in the irradiated salt discs using highly sensitive detection equipment like the SQUID magnetometer, when the discs are cooled to a low temperature in a helium cryostat and are held in a strong magnetic field.

If , after some practice , the preparation of the irradiated salt discs became routine , many other halide salts with a wide variety of metal cations from across the Periodic Table could be similarly examined to see how they behaved after Tesla irradiation , with respect to producing Meissner exclusion signals at low temperatures . Samples giving positive results could be followed up with an investigation of the chemistry of their low valent , mixed-valent compounds . We would expect transition metal halide salts to yield negative results in these trials , because their Curie paramagnetic cations would inhibit Cooper pair formation in the F centers , just as they do in macroscopic , pure materials .

A third way of preparing at least low concentrations of $M^{(1-x)+}$ mixed-valent cations in alkali metal halide salts is to expose the pure salt to doping by the corresponding alkali metal vapor (I don't know what the actual experimental

conditions for this technique are). What are the limits, if any, to the insertion of the zerovalent metal atoms into the salt lattice? We recall the alkali metal suboxides such as tricesium oxide (page 307), in which the atoms of metal and oxygen can be combined in many different ratios. I would suggest that if the zerovalent atoms, cations, and anions can be combined together in ratios representing stable crystal structures, and in which the coordinations of the component atoms are electronically and sterically stable, then formation of a thermodynamically stable compound may be possible from those components under ambient conditions.

For example, let's combine – in a "thought experiment" – one equivalent of lithium metal with one equivalent of lithium chloride :

$$Li^0$$
 + $LiCl$ \longrightarrow Li_2Cl .
m.p. 181 °C 605 °C

A possible stable form for the hypothetical product Li_2Cl might be the antifluorite structure, the converse of the fluorite structure (page 99). In this case, the lithium atoms are tetrahedrally coordinated by the chloride anions, which have an eight-fold coordination. Tetrahedral coordination of lithium cations in many compounds is quite stable and well known, and eight-fold coordination of chloride anions is equally acceptable (as in the CsCl type of crystal structure). Lithium oxide, Li_2O , has this antifluorite structure.

Bonding in this compound would be ionic . Tetrahedral coordination of the lithiums would destabilize their 2 s-p orbitals (formally sp^3 in VB terms), causing the "extra" valence electrons to be promoted up into the 3s frontier orbitals . Taking sodium ($3s^1$) as a model , with a metallic radius of 1.91 Å, it might be possible to overlap these 3s AOs in the antifluorite lattice (the lithium atoms are in coplanar layers) to form a sigma XO as the metallic bond in the solid , isoelectronic with sodium metal .

It might also be possible to form a perovskite with mixed-valent lithium cations, by inserting barium(0) into the lattice of lithium nitride, Li_3N . Lithium nitride is commercially available (eg. from Alfa Aesar), but it can be synthesized by the researcher if desired from a direct reaction at about

450 °C from the elements (ref. 145 , page 413) . It is a stable , brownish-red crystalline material , with an odd sort of crystal structure :



Figure 53 : the M3D model of lithium nitride , Li_3N . The blue spheres are lithium atoms , and the red spheres represent nitrogen atoms . Two formula lithiums (in the planes) have a trigonal planar coordination ; one formula lithium , in between the planes , has a linear coordination . The nitrogens have an eight-fold coordination . The model was based on Figure 22 (ii) in Palmer's textbook (ref. 146 , page 413 , his p. 37) , and on the ball-and-stick model of Li_3N on the Internet web site , "Web Elements" , web page "Lithium Nitride" :

http://www.webelements.com/webelements/compounds/text/Li/Li3N1-26134623.html

Although Li_3N doesn't have the very simple ReO_3 "supercube" crystal structure (page 145), or its converse, the anti- ReO_3 structure, when the large barium atom is forced into it in an equimolar ratio, the atoms will hopefully rearrange to form the stable perovskite crystal structure :

$$Ba^{0} + Li_{3}N \longrightarrow Ba^{2+}[NLi_{3} (2e-)]$$

m.p. 725 °C 813 °C

Actually , the structure of the hypothetical compound BaNLi₃ would be better described as a "semiperovskite", because while the "A" cation , Ba²⁺, is in the supercube center as usual , the "M" and "X" atoms are reversed from their usual positions . The formula of the compound has been written Ba²⁺[NLi₃ (2e-)] to indicate that the barium(0) atom has transferred its two 6s² valence electrons to the Li₃N supercube framework as a whole , and not specifically to any particular lithium atoms . However , the three lithium formula atoms will have the formal charges , Li⁰ – Li¹⁺ – Li⁰ , or Li(0.33+) , a NIOS valence . Barium is a powerful reducer , at $E_{ox}^{0} = 2.912$ V ; it will be stabilized in the solid by donation of its valence electrons to the lattice [the E_{ox}^{0} of lithium(0) is slightly higher , at 3.04 V , but the lithium cations aren't the direct recipients of the electrons ; cf. the tungsten bronzes , page 156].

The skeletal bonding will be ionic in nature , with the metallic bond added over the Li₃N framework . The lithiums have a linear $(2sp_x)$ coordination by the nitride anions , which will leave their $2p_{y,z}$ native orbitals free to accept the barium's electrons . The lithiums' $2p_{y,z}^2$ AOs should be able to overlap with the nitrides' $2p_{y,z}^4$ neighboring AOs to form a pi XO as the metallic bond in the solid . This won't be polarized , as the compound would be a strongly reducing system ; and it may not be a bilayer XO , either . This suggests that the hypothetical BaNLi₃ could well be a bronze metal , and thus a poor candidate for high temperature superconductivity .

Li₃N might be able to function as a "converse MX_3 " host compound , that is M_3X , receiving inserted zerovalent metal atoms to form a series of novel semiperovskites . The very powerful reducers like the alkali , alkaline earth , and lanthanide metals might be inserted with their valence electrons transferred to the Li₃N lattice ; and there would be no electron transfer at all with inserted noble metals such as mercury and bismuth . With base metals a redox resonance of varying magnitude might be observed between the inserted "A" zerovalent atom and the Li₃N lattice , via the valence shell p orbitals on the metal atoms (by leakage from the valence s orbitals , if necessary) and the $2p_{y,z}$ AOs on the lithiums . Alternately , the s AOs on the metal atom might overlap directly with the empty 2s AOs on the lithium cations to form a heterogeneous sort of sigma XO metallic bond . Whatever the electronic structure of the new materials proved to be , they would

certainly be very interesting to prepare and study.

I noticed in the published preparations in the Inorganic Syntheses volumes referred to in ref. 145 that iron containers were used to hold the liquid lithium under the nitrogen atmosphere. Apparently the hot lithium nitride is quite corrosive toward many common materials used in laboratory reaction vessels. This suggests that the Li₃N product from such procedures might be slightly contaminated with iron (also the commercial reagent lithium nitride might be similarly affected). The iron surface would inevitably be coated with a thin film of iron oxide, which would surely dissolve in the hot nitride as it is being formed. Before using these samples of lithium nitride in any experimental procedure, the researcher might find it advisable to carry out an analysis for iron in them. It would also be desirable to devise a new synthesis of lithium nitride which provides either ultrapure product, or at least one in which the contaminants introduced into it from the reaction container are diamagnetic, and not paramagnetic, as the iron impurities would be [such as aluminum (m.p. 660 °C); could a simple, cheap aluminum vessel be used as the reaction container; or more exotically, titanium, zirconium, or tantalum? Alfa Aesar offers various laboratory containers made from such metals. See also the note at the end of ref. 145].

The Alkaline Earth Elements

These highly reactive metals (with the exception of beryllium, which apparently is too tough and refractory) will also dissolve in anhydrous liquid ammonia to provide dilute (blue-black) or more concentrated (bronze) solutions of their electrides. With the exception of the magnesium electride, these electrides can be isolated by careful evaporation of the ammonia to provide the hexammine metal(0) compound. Further warming of the ammoniate will decompose it and restore the original metal.

Assuming that the pure , anhydrous alkaline earth halide salts are soluble to a certain extent in liquid ammonia (I have no data on this) , the mixed-valent composite electrides would be prepared as outlined earlier on page 310 :

I have written the incremental doping as " $1 \rightarrow 0$ "; that is, starting with pure substrate – the metal electride in the reaction flask – and adding increments of the salt dopant, in separate trials, to produce samples of the mixed-valent doped composite for characterization and electrical testing.

Apparently the two lanthanide elements europium and ytterbium can also dissolve in liquid ammonia to produce the corresponding electrides . It is interesting to note in this regard that of all the lanthanide metals , only these two (plus samarium , which wasn't mentioned in Jolly's review , in ref. 142 , page 412) can form stable , accessible divalent cations ; and these latter species are natural reducers . Their electrides thus probably have a divalent cation core , like the alkaline earth metal electrides , and are not trivalent , which is the usual valence state for the low energy lanthanide cations . (Their high energy valences are 2⁺ , reducing , and 4⁺ , oxidizing) . The corresponding pure divalent halide salts would be required as dopants for these latter two electrides . The di-iodides of ytterbium and samarium have been synthesized by a clever procedure devised by the French chemist H. Kagan and his co-workers (ref. 147 , page 413) :

 $Yb^{0} + I - CH_{2}CH_{2} - I \xrightarrow{THF, 25 \circ C} YbI_{2} + ethylene (g) .$ light yellow-green, 100%

Similar procedures might be adapted for the preparation of the pure divalent chlorides and bromides of Eu, Yb, and Sm, using 1,2-dichloro- and 1,2-dibromoethane. The method might also be successful for preparing the alkaline earth halide salts in a very pure, anhydrous condition.

Note that the three divalent lanthanide cations mentioned have 4f valence electrons, which may be in a high spin condition and would therefore make them paramagnetic : Sm^{2+} , $4f^6$; Eu^{2+} , $4f^7$; and Yb^{2+} , $4f^{14}$. [The ytterbium cation's 4f shell is filled, so it should be diamagnetic]. However, these

divalent cations would be shielded by the coordinating ammine ligands, and so their magnetism, which is short range in any case, presumably would be suppressed in the ammonia environment.

Several Interesting Antiperovskites

DiSalvo and co-workers inserted zerovalent atoms from the 3A (nitrogen) and 4A (carbon) families into the lattice of Ca_3N_2 to obtain a series of antiperovskites (ref. 148, page 413) :

$$M^{0} + Ca_{3}N_{2} \xrightarrow{1000 \text{ °C}} M^{3}N^{3}(Ca^{2+})_{3} + \frac{1}{2}N_{2}(g) ;$$

$$M^{0} = P, As, Sb, Bi, Ge, Sn, or Pb.$$

The antiperovskite has an "inside-out" sort of perovskite structure :



Figure 54 : the M3D model of the antiperovskite structure . Example : Ca_3NBi (from DiSalvo et al.) . Yellow sphere in supercube center is the "A" atom , the Bi³⁻ anion ; green spheres at corners are the "M" atoms , the N³⁻ anions ; and the black spheres along the twelve edges are the "X" atoms , the Ca^{2+} cations . This is the A type of antiperovskite unit cell for AMX₃.

As with the classic perovskite structure, the antiperovskite structure should afford the researcher physically with a very compact unit cell with relatively short atomic separations, and chemically with the ability to design mixed-valent compounds by juggling charges on the A, M, and X atoms. For example, DiSalvo's antiperovskites might be doped with the $M^0Li_3N - or Li_3NM^0$ – series of compounds I proposed earlier on page 317 :

(1)
$$\text{Li}_3\text{N} + \text{Bi}^0 \longrightarrow \text{Li}_3\text{NBi}^0$$
; then,
(2) $x \text{Ca}_3\text{NBi}^{3-} + (1-x) \text{Li}_3\text{NBi}^0 \longrightarrow \text{Ca}_{3x}\text{Li}_{3-3x}\text{NBi}^{(3x-)}$

In this case the mixed-valency is in the anions – the voluminous bismuthide anions – rather than in the usual cations. This illustrates the flexibility of Verwey's controlled valence process in perovskites, and why they are so useful as substrates in the design and synthesis of new metallic solids.

The first of the unusual antiperovskites I'll propose is that of the hypothetical **iron** compound , Fe₃OA , where "A" is both the "A" atom in the structure – the large one in the center of the supercube – and an anion , in this case a chalcogenide anion : sulfide , selenide , telluride , and possibly also disulfide , $S_2^{2^2}$. In the above Figure 53 , the chalcogenide anion is the yellow sphere , the oxygen atom is represented by the green corner spheres , and the smaller black spheres stand for the iron(1.33+) atoms . That is , the compound's formula can be written out in full as $(Fe^{2+}-Fe^{0}-Fe^{2+})O^{2-}A^{2-}$, showing the extra pair of electrons over the base of iron(II) cations . By making a judicious selection of the two anions , we can alter the cation charges to create the desired NIOS mixed-valence condition in the compound . The oxide anion is the smaller one , with a crystal ionic radius of 1.26 Å . Sulfide is larger , at 1.70 Å ; selenide is at 1.84 Å ; and telluride is the largest chalcogenide anion , with a crystal ionic radius of 2.07 Å .

The tolerance factors for these three compounds would be : Fe_3OS , 0.86; Fe_3OSe , 0.91; and Fe_3OTe , 0.99 (I have no information about the disulfide anion, $S_2^{2^-}$). The sulfide may be slightly distorted from cubic symmetry.

Synthesis of the compounds should be fairly straightforward : the precursor reagents are all readily available and are inexpensive , and the shake-n-bake technique should suffice for their preparations . The iron part of the compound can be formulated directly from the components , Fe(0) and Fe(II), or the abundant Fe(III) can be used , with reproportionation :



Similarly for Fe₃OSe , Fe₃OTe , and Fe₃OS₂ , substituting the appropriate reagents for those ones above with sulfur atoms (FeS₂ for FeS ; all of the reagents cited are commercially-available , eg. from Alfa Aesar) . The reactions using iron filings and flowers of sulfur are particularly interesting , because they are expected to be somewhat exothermic [caution !] , and the evolved heat might melt the mixture , thus allowing a more intimate mixing of the three elements involved . Hint : try these reactions in the dta apparatus first , using 20 to 50 mg or so of thoroughly ground mixture , to see how the reactions proceed , and thereby determine their optimum experimental conditions .

Assuming that these iron antiperovskites can actually be prepared and characterized in a pure, single phase, and have the anticipated crystal structures, what might we expect of them electronically? The iron atoms will have an octahedral coordination, linear by the oxides, and square by the "A" atom chalcogenides (to avoid a messy looking model, I didn't include the Fe-chalcogenide bonds in it). Iron(II), the base cation, can be affected by Hund's Rule, to the effect that its 3d⁶ valence shell electrons are more energetically stable when they spread themselves out in all five 3d orbitals. Their less stable configuration is when they are squashed down into just three of the 3d (the t_{2g}) orbitals :

stable configuration : high spin (spin free), $\underline{**} \stackrel{*}{=} \frac{*}{**} \stackrel{*}{=} \frac{*}{**} \frac{*}{**} \frac{sp^3d^2}{d^2sp^3}$; less stable configuration : low spin (spin paired), $\underline{**} \stackrel{*}{=} \frac{*}{**} \frac{*}{**} \frac{sp^3d^2}{d^2sp^3}$.

If the iron atoms are in the high spin state, the compounds will still be metallic solids, but will never become superconducting. If they have a low spin electronic configuration, their kernels will be diamagnetic, and the compounds will have a chance of becoming superconducting when they are cooled down sufficiently.

The "extra" electrons in the lattice, formally from the Fe(0) part of the iron triad in the formula $[Fe^{2+}-Fe^{0}-Fe^{2+}]$, will be promoted up into the 5s-p frontier AOs, since the 4 s-p-d orbitals are destabilized by the oxide and chalcogenide ligands (the oxygens are oxide anions; the skeletal bonding in the compounds will therefore be ionic, and not covalent). The iron atoms' 5 s-p AOs can overlap with the oxides' 2 s-p AOs, and with the chalcogenides' 3,4, and 5 s-p AOs to form the sigma-pi XO metallic bond in the compound.

Unlike the oxide anion, the chalcogenide anions are all natural reducers :

I "guesstimated" the standard oxidation potential of the oxide anion to be about -3 V or so, roughly that for oxidation of the fluoride anion to elemental fluorine, at -2.866 V. Both the oxide and fluoride anions are well known to be generally inert in most solid state reactions in which they are found as spectator anions. They can both be anodically oxidized in electrochemical reactions, for example, in the Hall-Héroult process (aluminum electrowinning), and in the industrial production of fluorine from the electrolysis of KHF₂ in HF. We have seen earlier that copper(III) cations, if heated above 500 °C, will oxidize neighboring oxide anions to oxygen molecules. Both fluoride and oxide can indeed be oxidized to their respective elements, but a lot of energy must be used to accomplish these transformations. The chalcogenide anions, on the other hand, are naturally reducing species, completely different in their redox behavior than oxide.

It is interesting to note that in Nature , many if not most of the metal sulfide (or disulfide) minerals are very dark colored , or have a lustrous , metallic appearance , while the oxide minerals are dull and "ordinary" looking ; or so I noticed in a tour of a museum of natural history some time ago . For example , the brassy-looking mineral "fool's gold" (which I commented about on page 290) , is iron(II) disulfide , FeS_2 . Admittedly , this metallic appearance of the mineral sulfide crystals may only be observed in their macroscopic crystals ; when ground to a fine powder , the sulfides will appear black . There unquestionably must be a redox resonance in these metal sulfides :

Fe(II) + **S**₂²⁻
$$\overleftarrow{}$$
 Fe(0) + 2 S⁰.

In some cases, the respective zerovalent elements seem to be favored by the redox resonance, although I doubt that the valence electron transfer actually is quantitative. An example of this is the beautiful mineral galena, which is lead(II) sulfide :

$$Pb(II) + S^{2-} \xrightarrow{[V] = 0.35 V} \underline{Pb(0)} + \underline{S}^{0}$$
Large galena crystals have a bluish-gray color somewhat like lead itself, with a metallic luster ; the powder is black . Galena has the cubic rocksalt crystal structure . X-ray diffraction analysis of PbS seems to show that valence electrons actually have been transferred from the sulfide anions to the lead cations , as predicted by the redox equation :

"The direct integration of charge density, the observed atomic scattering factors, and the population analysis of the valence electrons all indicate that the lead atom is negatively charged, i.e. electrons are transferred from sulfur to lead".

- S.-W. Ng and J.J. Zuckerman, ref. 149, page 413, their p. 313.

In the hypothetical compound Fe_3OS , the sulfide will definitely interact electronically with the iron(II) base cations, with a strong redox resonance between them :

 $Fe^{2+} + S^{2-} = 0.029 V$ $Fe^{(0)} + S^{0}$.

The redox arithmetic indicates a preference for the zerovalent elements in this system, although I think what will actually happen here is that a noticeable, but probably not quantitative, shift in electron density from the sulfide anions to the iron cations will occur.

The reader may be somewhat puzzled by my proposal of these iron antiperovskites as possible superconductor candidates . After all , iron impurities in conventional metallic solids will prevent them from becoming superconducting . Yes , high spin , paramagnetic iron atoms , or cations , and those of most other elements , will generally inhibit the appearance of superconductivity in a solid . But diamagnetic impurities – at low levels , of course – probably wouldn't interfere with the Cooper pair formation . And it is certainly possible to have low spin , diamagnetic iron compounds . One such well known compound is ferrocene [bis(cyclopentadienyl)iron(II)] . The cyclopentadienyl anions (cp) are known to be strong CF ligands , high in the Spectrochemical Series , up there with cyanide and carbon monoxide in bonding strength with transition metal kernels . The cp ligands press down on the iron(II) cations , squashing their high spinning $3d^6$ valence electrons down into the low spin t_{2g} orbitals . As a result , ferrocene is diamagnetic , with a magnetic susceptibility of $\chi_{mol} = -125 \times 10^{-6}$ cgsu at ambient temperature (ref. 150 , page 413) .

A second iron compound interesting in this regard is iron monophosphide, FeP. It exhibits metallic behavior from 4.2 K (liquid helium, 3.3 million ohm⁻¹cm⁻¹) to ambient temperature (12,500 ohm⁻¹cm⁻¹). It almost becomes superconducting near absolute zero, but it is still paramagnetic even at low temperatures (ref. 151, page 414). Iron monophosphide exhibits Pauli paramagnetism over a wide temperature range, typical of many metallurgical metals.

FeP has the nickel arsenide structure (Wells, ref. 21, page 394, p. 636), with octahedrally coordinated iron atoms and trigonal prismatic phosphorus atoms :



Figure 55: the M3D model of the nickel arsenide crystal structure. The

small blue spheres are octahedral nickel (or iron , for FeP) atoms , and the larger brown spheres represent trigonal prismatic arsenic (or phosphorus) atoms . The model was based on the nice ball-and stick illustration of nickel arsenide in Smart and Moore's textbook (ref. 49 , page 397 , their Figure 1.26 , p. 23) .

We should recognize that iron monophosphide is covalently bonded, with an additional metallic bond. Clearly, the compound isn't Fe³⁺P³⁻; Fe(III) is a natural oxidizer, and would in any case strip electrons off the phosphide anion, which like sulfide, is probably a natural reducer. In one formula unit of FeP there are six covalent Fe-P bonds, requiring a total of twelve valence electrons. The electronic configuration of the valence shells of iron(0) is 3d⁶ 4s², and it will use all eight valence and hypervalence electrons, plus their orbitals, for the required hybrid orbital, which will be the octahedral d⁵s hybrid. The phosphorus atom will contribute its five valence electrons (3s² 3p³) to the covalent bonding of the skeleton. The required trigonal prismatic ligancy for phosphorus might be comprised of two separate, pyramidal hybrid orbitals: 4 (p_{x,y,z}) = p³_a; and 5 (p_{x,y,z}) = p³_b [recalling that phosphorus is a "p-block" element and favors p native orbitals for hybrid orbital formation].

Twelve of the thirteen valence electrons from iron and phosphorus will comprise the six FeP formula unit covalent bonds . The thirteenth electron will be located in a frontier orbital outside the covalent skeleton . The lowest energy empty native orbitals on the iron atoms are the 4s AOs , and that's probably the location of the thirteenth orphan electron . In the nickel arsenide crystal structure the metal and nonmetal atoms are packed into separate alternating layers , with a hexagonal packing pattern . The metal atoms are typically closely packed , with fairly short atomic separations . It's possible the 4s orbitals , with their "extra" valence electrons , can overlap in the iron atom layers to produce the corresponding sigma XO as the metallic bond in the compound [the same configuration as iron(0) atoms , $4s^2$].

Doping of iron monophosphide with a suitable iron compound to introduce holes into the sigma XO might permit it to become superconducting ,

albeit at very low temperatures (FeP could probably be categorized as a bronze metal ; it is a Class 2 metallic solid). According to the bonding picture just presented , we would need as the dopant the nearby 3 s-p atom with one less valence electron than phosphorus . That would be silicon $(3s^2 3p^2)$. The corresponding iron dopant compound would then be iron monosilicide , which like iron monophosphide itself is commercially-available [eg. from Alfa Aesar] :

$$x \text{ FeP} + (1-x) \text{ FeSi} \xrightarrow{x = 1 \rightarrow 0} \text{ FeP}_x \text{Si}_{1-x} .$$

m.p. 1410 °C
$$x = 1 \rightarrow 0$$

Or, Fe⁰ + x P⁰ (red) + (1-x) Si⁰ \xrightarrow{x = 1 \rightarrow 0} \text{ FeP}_x \text{Si}_{1-x} .

Silicon is known to have an octahedral configuration in some compounds, for example, in the hexafluorosilicate anion, SiF_6^{2-} . As for it having a trigonal prismatic configuration in the doped composite, FeP_xSi_{1-x} , that would remain to be seen experimentally. It would be an interesting project.

The third noteworthy iron compound with respect to the iron antiperovskites is iron pyrites , FeS_2 , which occurs naturally as the mineral "fool's gold", because of the shiny, brassy appearance of its fresh, clean surfaces. The reader has probably seen fool's gold before ; iron pyrites is often found in Nature as small (a few millimeters per side) cubes. This suggests an underlying cubic architecture, and indeed iron pyrites and other transition metal pyrites have a cubic rocksalt crystal structure. The sulfur in iron pyrites is in the form of disulfide, $S_2^{2^2}$, a molecular anion. Disulfide is a natural reducer, and as noted above on page 324, there is undoubtedly a redox resonance between the iron(II) cations and disulfide anions.

It has been known for a long time that iron pyrites is diamagnetic , with no significant magnetic susceptibility (ref. 152, page 414). The iron(II) cations are octahedrally coordinated, so they must be in a low spin (t_2g^6) electronic configuration. This latter structure is more germane to the hypothetical iron

antiperovskites than are the two earlier examples of iron monophosphide and ferrocene.

Sulfide anion (and presumably also disulfide) isn't known to be a particularly strong CF ligand . Why does an octahedral coordination by disulfide anions cause the iron(II) cations to become low spin and diamagnetic ? The comparable iron(II) compound with oxygen , FeO , which also has a rocksalt structure , is paramagnetic (actually , antiferromagnetic) . Does the redox resonance between the iron and sulfur atoms have an effect on the material's electronic configuration and magnetic properties ? Most importantly , will square coordination by sulfides of the iron cations in the antiperovskites force them , too , into a low spin , diamagnetic condition ?

The other interesting consideration about the iron(II) oxide system is its antiferromagnetism , as alluded to above : the Néel temperature of FeO is 198 K (-75 °C; page 206); above and below that temperature , the magnetic susceptibility of the iron(II) cations rapidly declines . The iron antiperovskites would be partially iron(II) oxides , with the "extra" valence electrons in the metallic bond above the Fe-O skeleton . We hope that the antiferromagnetic electron ordering régime would extend to those electrons in the metallic bond , helping them to condense into Cooper pairs .

Two independent studies demonstrated that the selenide anion , Se^{2-} , can induce antiferromagnetism in neighboring transition metal cations :

" Se substitution [in CoS_2] introduces strong antiferromagnetic interactions between cobalt atoms".

- Johnson and Wold, ref. 153, page 414, their p. 216.

Adachi, Sato, and Takeda found that while CoS_2 is ferromagnetic, $CoSe_2$ is antiferromagnetic. They concluded that "..... selenides are more metallic than sulfides in the nickel and cobalt dichalcogenides with pyrite structure" (ref. 154, page 414, their p. 637). The iron antiperovskite Fe₃OSe could thus be particularly interesting to prepare and study, combining the various desirable features of metallic behavior, a cubic symmetry antiperovskite

(t = 0.91) with tightly packed atoms , diamagnetic iron kernels , a strong redox resonance between the iron and selenium atoms , and an Fe-O supercube antiferromagnetic base with additional induction from the selenium "A" atoms . We might even optimistically hope to observe high temperature superconductivity in this compound , although how high its T_c could be is entirely open to speculation .

Of course , this begs the question : given that traces of high spin iron impurities in metallic solids can degrade their superconductor behavior , might there not be such high spin iron impurities present in the Fe₃OX compounds that would also prevent them from becoming superconducting ? The implication is that the iron antiperovskites would have to be extremely pure to avoid this possibility . Such highly pure , homogeneous phases might not be accessible via the rather crude shake-n-bake procedures outlined above on page 322 ; but given the proper incentive , I'm confident that chemists could devise new methods to synthesize such highly pure compounds .

A Cobalt Semiperovskite

The hypothetical compound Co_3OX (X = chalcogenide anion) might be a metallic solid, but it wouldn't be able to become superconducting. This is because its valences are wrong : $(Co^{2+}-Co^{0}-Co^{2+})O^{2-}X^{2-}$. The cobalt triad in this case would have the electronic configuration $3d^7-3d^9-3d^7$, or a $3d^7$ base with the two "extra" promoted electrons. These paramagnetic base cations would inhibit the appearance of superconductivity in the solid at any temperature.

There are two possible triads for cobalt superconductor candidate compounds : the high-valent, oxidizing triad, $Co^{2+}-Co^{3+}-Co^{2+}$ ($3d^7-3d^6-3d^7$), assuming diamagnetic $3d^6$ base cations, as with the iron antiperovskites; and the low-valent, reducing triad, $Co^0-Co^{1+}-Co^0$ ($3d^9-3d^8-3d^9$), assuming diamagnetic $3d^8$ base cations. The latter triad, with its low cationic charge, is the more suitable one for inclusion in an anti- or semiperovskite. The charge-balancing arithmetic inclines us toward the latter crystal form , in a compound such as $CsCo_3O$ (t = 0.89 , assuming a crystal ionic radius for low spin Co^{1+} of 0.89 Å). The required low-valent cobalt cations might be prepared from the reproportionation of Co(0) – the finely powdered metal – and the readily available Co(II):

$$\frac{1}{2}$$
 Cs₂CO₃ + 2¹/₂ Co⁰ + ¹/₂ CoO
atmosphere $\frac{1}{2}$ CsCo₃O + ¹/₂ CO₂ (g).

The chemically reducing nature of both the reactants and the product will dictate the use of an inert atmosphere over the heated reaction mixture ; this will preferably be a dynamic atmosphere , to continuously expel by-product carbon dioxide and help drive the reaction to completion .

In the semiperovskite structure proposed for this compound, the inert cesium cation is the "A" cation in the supercube center. Octahedral oxide anions are the "M" atoms at the supercube corners ; and the cobalt cations are the "X" atoms on the supercube sides, in the AMX₃ formula. Since the cesium cations are non-coordinating, the cobalts will have a linear coordination by the oxides . As cobalt is a transition metal element, which in general favor the use of d orbitals in bonding rather than s and p orbitals, the cobalts in CsCo₃O will likely use the d_z^2 s linear hybrid orbital (if treated in VB terms) rather than the pre- and post-transition elements' sp linear hybrid orbital . Or , if treated in ionic CF terms , the cobalts' $3d_z^2$ and 4s orbitals will be destabilized by the oxide anions on each side. In either case, the 3d⁸ valence shell electrons of the base cobalt(I) cations will be in a low spin, diamagnetic condition : <u>**</u> <u>**</u> <u>**</u> <u>**</u> <u>**</u> <u>dz</u>²s . The two "extra" valence electrons, formally from the two Co^0 atoms in the triad, will be promoted into frontier orbitals above the Co-O supercube. The next available vacant native orbitals will be the cobalts' $4p_{y,z}$ AOs (as usual, the $4p_x$ AO will be destabilized by the neighboring oxides). These should be able to overlap continuously in the lattice with the oxides' $2p_{y,z}$ AOs to form the pi XO metallic bond in CsCo₃O.

Cobalt(II) oxide , with its rocksalt structure , has a fairly high Néel temperature of $T_N = 291$ K (18 °C). Although the base cations of the

hypothetical compound $CsCo_3O$ are Co^{1+} and not Co^{2+} , we can hope that this low-valent system will be similarly blessed with a strong antiferromagnetic ordering of the "extra" valence electrons in its metallic bond, that will promote their coupling into Cooper pairs at a respectably high temperature.

Nickel Superconductor Candidate Compounds

The low-valent , mixed-valent nickel triad , $Ni^{2+}-Ni^{0}-Ni^{2+}$, would be suitable for inclusion in an antiperovskite with the formula Ni_3OX , where X = S, Se , or Te . Unfortunately , as the nickel cations are octahedrally coordinated (linear by the "M" oxides , square by the chalcogenide "A" anions) , they will automatically be in a high spin condition . The base Ni(II) cations are $3d^8$ electronically . Octahedral hybrid orbitals are either d^5s , d^2sp^3 (inner) , or sp^3d^2 (outer) . Only the latter hybrid AO [or its CF ionic equivalent] can be used by the $3d^8$ cations , which results in all octahedrallycoordinated nickel(II) compounds being high spin and Curie paramagnetic : $\frac{**}{2} + \frac{**}{2} + \frac{*}{2} + \frac{*}{2} + \frac{sp^3d^2}{2}$.

There are two coordinations of nickel(II) that will permit it to be low spin and diamagnetic . The first is linear , assuming nickel – a typical transition metal element – uses the d_z^2 s hybrid orbital , or its CF ionic equivalent : <u>** ** ** dz^2s</u> . This is more likely than nickel using the pre- and posttransition elements' linear sp_x hybrid AO . The second coordination favorable to low spin , diamagnetic nickel(II) is the square planar one : <u>** ** ** dsp²</u> .

The question is : how can we design extended atomic lattice compounds with nickel(II) in either of these coordinations ? There are numerous coordinate covalent complexes with square planar , diamagnetic nickel(II) ; for example , nickel(II) bis(dimethylglyoximate) , the maroon colored , insoluble complex familiar in the gravimetric analysis of nickel . However , there seems to be no practical method of connecting stacks of these Ni(DMG)₂ molecules with a functional , nodeless XO metallic bond . The corundum crystal structure has four-coordinated anions . A number of M_2O_3 compounds have the corundum structure , most prominently alumina , Al_2O_3 . In this lattice the aluminum cations are octahedrally coordinated , and the oxide anions are four-coordinated . There seems to be some uncertainty about exactly what type of four-coordination is involved . In their excellent textbook , Rao and Gopalakrishnan say that they are "nearly tetrahedral" (ref. 115 , page 408 , their p. 26) . In Sanderson's textbook , they are sketched quite clearly as being square (ref. 32 , page 395 , his Figure 8-10 , p. 119) . There are drawings of the corundum structure in several other textbooks , notably in Wold and Dwight's (ref. 24 , page 394 , Figure 7.16 , p. 112) , but these are in the "polygon" style , which I find quite difficult to understand , unfortunately . See also Note 6 , page 379 . I have tried building an M3D model of corundum , but must confess to being completely defeated by it . The AlO₆ octahedra in the structure share faces , which is rather difficult to construct with a ball-and-stick model :



Figure 56 : an M3D model of two octahedra sharing a common face . The smaller red spheres could be aluminum(III) cations , for example , while the larger aqua spheres would then represent oxide anions .

Building a model of an extended structure of alumina with this feature in it proved too much for my inexpert abilities, so corundum remains for me a conundrum, and its M3D model is still an unscaled Mount Everest for the bold adventurer in crystallographic artistry. Let's assume that the oxides in corundum have an approximately square planar coordination to the metal M^{3+} cations . Suppose we were to take the converse to the corundum structure , namely the anti-corundum structure . In this latter crystal lattice , with a formula of M_3O_2 , the "M" cations now have the four-fold square coordination , and the two oxides must be octahedrally coordinating to them . This formula also implies that the "M" cations will have a rather low valence , and it will be a NIOS mixed-valence as well [(4+) ÷ 3 atoms = 1.33+ per atom].

The three most favored and common coordinations for nickel(II) are square planar, tetrahedral, and octahedral. The first coordination is found with strong CF ligands, eg. $[Ni(CN)_4]^{2^-}$; the second, with weak CF ligands, such as halides, eg. $[Ni(Cl)_4]^{2^-}$. As mentioned, the nickel(II) cations are always low spin, diamagnetic when they are square planar coordinated. When they are tetrahedrally coordinated, they are always high spin, Curie paramagnetic: $\frac{**}{2} \frac{**}{2} \frac{*}{2} \frac{*}{2} \frac{sp^3}{2}$. So if we attempt to prepare a nickel anti-corundum compound, we must hope to avoid a tetrahedral coordination of the nickel cations by the oxides, and pray that it will be square planar:

$$Ni^0$$
 + 2 NiO \rightarrow Ni₃O₂ .
m.p. 1453 °C 1984 °C argon atmosphere

The refractory nature of the nickel metal powder and nickel(II) oxide suggest that this experiment would be conducted best in an arc furnace, with melting of the reactants into a metallic button, as with niobium monoxide (page 125; ref. 58, page 399). Since all the materials involved are readily oxidized, an inert atmosphere in the furnace, such as argon, would be essential to preserve the low valence of the nickel(1.33+) cations.

In the hypothetical compound Ni₃O₂, the nickel triad is Ni²⁺–Ni⁰–Ni²⁺; that is, it has a base of nickel(II) cations, with two "extra" valence electrons promoted into frontier orbitals. The square planar hybrid orbital will use the $3d_{x}^{2}-y^{2}$, 4s, and $4p_{x,y}$ native orbitals; or, in the ionic CF equivalent, these orbitals will be energetically destabilized by the oxide ligands, and will be unavailable for use by the promoted electrons. The next available vacant

native orbital for them will be the $4p_z AO$, and that's probably where they'll be relocated. This nickel orbital can overlap with the neighboring $2p_z AOs$ on the oxide anions to form a partially occupied bilayer pi XO as the metallic bond in the solid (don't forget that there are two promoted electrons per three nickel cations, so there will be vacancies in the nickel layer of the pi XO).

Nickel(II) oxide is known to be strongly antiferromagnetic ; its $T_N = 525$ K, or 252 °C, well above room temperature . If this antiferromagnetism, with its antiparallel spin régime, is imposed on the promoted electrons in the pi XO metallic bond, we could anticipate observing high temperature superconductivity in the compound Ni₃O₂. Certainly, the iron, cobalt, and now nickel compounds discussed should all be black metals, so I think they are good prospects as superconductor candidates. All this is contingent on the coordination of the nickel cations in Ni₃O₂ : if it is square planar, then it will have low spin, diamagnetic base cations, and it will be a possible superconductor; if tetrahedral, then high spin, Curie paramagnetic base cations , and no superconductivity, although the compound should still be a metallic solid to a certain extent.

Shishkebab Compounds

Two research teams have discovered shishkebab solid state compounds , that is , extended atomic lattice (nonmolecular) compounds in which there are long , linear chains of covalently-bound atoms , often with inert spectator cations nested in between the chains . I mentioned one such type of shishkebab compound earlier (page 85) , yttrium cobalt carbide , YCoC , prepared in Germany by Jeitschko and co-workers (ref. 155 , page 414) . In this material the chains are made from alternating cobalt(I) and carbide(IV) atoms , with yttrium(3+) cations nested in between the chains (see Figure 56 at the top of the next page) . YCoC can be considered as a Zintl compound : cobalt(0) , which is $3d^7 4s^2$ electronically (valence shells) , donates an electron to carbon(0) , $2s^2 2p^2$, and becomes cobalt(I) [low spin $3d^8$ when coordinated by the nucleophilic carbides].



Figure 57 : the M3D model of yttrium cobalt carbide , YCoC . The small blue spheres are the cobalt(I) atoms ; the black spheres are the carbides ; and the larger yellow spheres represent yttrium cations . The black lines stand for covalent Co-C bonds . The model was based on Figure 5 , p. 320 , in R. Hoffmann's review , "Carbides" (ref. 156 , page 414) .

The yttrium(0) donates its three valence electrons to the carbon , which has now gained a total of four electrons to become the carbide anion , C^{4-} , having a complete octet of valence shell electrons , $2s^2 2p^6$. It forms the linear sp hybrid orbital to accommodate these eight electrons (see the figure at the top of the next page). The cobalt(I) atom , now $3d^8$ electronically , forms the empty linear d_z^2s hybrid AO above its spin-paired , diamagnetic $3d^8$ shell : <u>**</u> <u>**</u> <u>**</u> <u>**</u> <u>dz^2s</u> . The cobalt(I) cations and carbide(IV) anions polymerize together in long linear chains , alternating in directions from plane to plane , with the inert yttrium spectator cations nested in the cavities between the anionic chains .

We would predict from this bonding picture that YCoC would be an electrical insulator , having no "extra" electrons in any frontier orbitals . The linear chain structure of this shishkebab compound is fascinating , however . It would be challenging to devise a metallic analogue to it , then dope that compound with YCoC to try to make a series of superconductor candidate composites . How about the hypothetical formulation $U^{4+}Co^{0}C^{4-}$? Gerss and Jeitschko actually synthesized the compounds UFeC₂ , UCoC₂ , and UNiC₂ ,



Linear sp hybrid orbital for carbide and nitride anions

(ref. 157, page 414). Possibly the cobalt(0) compound could be made, isostructural with YCoC, with equimolar quantities of the three component elements :

 $\begin{array}{rl} U^{0} + Co^{0} + C^{0} & \xrightarrow{\text{arc furnace }} & U^{4+}Co^{0}C^{4-} \\ \hline m.p. \ 1132 \ ^{\circ}C & 1495 \ ^{\circ}C & 3727 \ ^{\circ}C & argon \ atmosphere \end{array}$

If this strategy is successful, UCoC should be metallic (Class 1), with the "extra" $3d^9$ electron promoted up into the cobalt's $4p_{y,z}$ frontier orbitals (the $4p_x$ AO would be destabilized by the neighboring carbide ligands). These cobalt $4p_{y,z}$ AOs could overlap with the $2p_{y,z}$ AOs on the carbides to form the bilayer pi XO metallic bond in the solid. Doping the metallic UCoC with the insulating YCoC would provide a series of doped composites (Class 3 metallic solids) for electrical testing as superconductor candidates :

$$x = 1 \rightarrow 0$$

 $x = U_x Y_{1-x} Co^{(1-x)+} C$.

The doped composites should be black metals with good prospects for

exhibiting high temperature superconductivity.

Hoffmann, Li, and Wheeler thought that there was "substantial π bonding in these [YCoC] chains" (ref. 39, page 396). The implication of this statement, in the VB/MOT terms in which I have discussed the electronic structure of YCoC, is that even though the Co(I) cations' $4p_{y,z}$ frontier orbitals are empty in the compound, they can still form a pi XO with the carbides' $2p_{y,z}$ AOs, with a subsequent distribution of the carbides' electrons in the XO. That is, the "upper cobalt layer" of the XO would be empty, but the "lower carbon layer" would have a substantial population of valence shell electrons. Then, some of these electrons would presumably leak into the upper layer, making the pi XO a functional metallic bond. In this alternate picture, YCoC could indeed be a metallic solid. Unfortunately I have no information at hand concerning its electrical conductivity properties.

The second research group to discover shishkebab compounds was DiSalvo's team at Cornell University. They have a rather bold and adventuresome approach to the study of solid state chemistry : mix reagents, fire them up in the furnace, and analyze the products to see if new materials have been produced in any reaction (ref. 158, page 414). By now the reader will be well aware of my own research philosophy, which is much more conservative and cautious than Professor DiSalvo's : I tend to be more of an applied, rather than fundamental, scientist. That is, I will learn of interesting new materials, which are usually nothing more than laboratory curiosities, produced by the "pure" scientists like DiSalvo and Jeitschko. These new substances will spark my imagination, and I'll immediately begin thinking of how they might be used in "practical" applications.

For example, DiSalvo and his co-workers discovered (among many remarkable new materials) the interesting new metallic solid, calcium nickel(I) nitride, CaNiN, from the insertion of nickel(0) into the calcium nitride lattice (ref. 159, page 415):

 $\frac{1/3 \text{ Ca}_3 \text{N}_2 + \text{Ni}^0 + 1/6 \text{ N}_2}{\text{m.p. 1195 °C}} \xrightarrow{1000 °C} \text{CaNiN}$.

Calcium nickel(I) nitride is a metallic conductor – a true metal – but doesn't become superconducting , even when cooled to 4.2 K in liquid helium . It has a shishkebab crystal structure somewhat like YCoC :



Figure 58 : the M3D model for calcium nickel(I) nitride , CaNiN . The small blue spheres are nickel(I) cations ; the brown spheres are nitride anions ; and the yellow spheres represent calcium cations . The black lines stand for the Ni-N covalent bonds . This model is based on DiSalvo's Figure 6 , in ref. 158 , page 414 ("Solid-State Chemistry : A Rediscovered Chemical Frontier" , p. 654) .

The bonding and electronic structure of CaNiN will be fairly similar to that of YCoC, discussed above. Calcium(0) and nickel(0) will donate three electrons in total to the nitrogen(0), to become, respectively, Ca^{2+} , Ni(I), and N³⁻. The nitride anions form linear sp hybrid orbitals with their eight valence electrons distributed as shown in the sketch at the top of page 337. The nickel(I) cations are $3d^9$ electronically, and could use either the $3d_z^2s$ hybrid orbital, with promotion of the "ninth" electron up to the $4d_{y,z}$ frontier orbitals, or the ninth electron could be left in the 3d shell. The nickel would use the empty linear sp_x hybrid orbital to bond with the nitrides, but in this case its kernel would be Curie paramagnetic : <u>**</u> <u>**</u> <u>**</u> <u>**</u> <u>*</u> <u>sp</u>. I haven't read DiSalvo's paper (ref. 160), just the abstract in <u>Chemical Abstracts 114</u>, 34736g (1991), which says that CaNiN is "metallic and paramagnetic". But which type of paramagnetism, Curie or Pauli? The former would indicate use of the sp hybrid AO, while the latter would

suggest a spin-paired 3d shell , promotion of the ninth electron to the $4p_{y,z}$ frontier orbitals , and use of the $3d_z^2$ s hybrid orbital for covalent bonding with the nitrides .

Clearly, this is the preferable scenario, as the nickels' $4p_{y,z}$ AOs can overlap with the $2p_{y,z}$ orbitals on the nitrides to form the bilayer pi XO metallic bond in the solid. That would result in CaNiN being a true metal; but since it is a Class 1 metallic solid, it might not necessarily become superconducting. If, on the other hand, the ninth electron remained in the 3d shell, it might be difficult to form a nodeless XO with the 3d native orbitals overlapping with the nitrides' 2p AOs.

Assuming that CaNiN is Pauli paramagnetic – typical of many metallurgical metals – and that the nickel kernel is diamagnetic , with spin-paired 3d shell electrons , we might dope it with the corresponding nickel(II) compound . That could be $\text{Li}^{1+}\text{Ni}^{2+}\text{N}^{3-}$, which would be an electrical insulator , having only "ordinary" ionic components and no "extra" promoted electrons in frontier orbitals :

The by-product lithium chloride could serve as a flux – a molten ionic solvent – for the reaction ; note that lithium nitride is also an extremely aggressive ionic solvent at high temperatures . The LiCl could be removed at the end of the reaction by leaching the ground-up reaction mass in a Soxhlet extractor with a polar organic solvent such as methanol , in which the salt is very soluble (424 g/l at ambient temperature , more in hot solvent) .

Assuming that LiNiN can be prepared, and is also a shishkebab compound, it could be doped incrementally into the metallic CaNiN to produce a series of mixed-valent composites for electrical testing :

$$x \text{ CaNi}^{1+}N + (1-x) \text{ LiNi}^{2+}N \xrightarrow{x=1 \rightarrow 0} \text{Ca}_x \text{Li}_{1-x} \text{Ni}^{(2-x)+}N$$

The nickel(II) cations , in effect , introduce holes into the pi XO , converting the Class 1 CaNiN into the Class 3 mixed-valent composites . In these latter compounds the pi XO electrons can resonate "horizontally" over the atoms in the lattice , rather than "vertically" , so to speak , up through the energy levels in the XO , as happens in a conventional metallurgical metal . If the powerful antiferromagnetism we see in NiO , with its antiparallel electron spin régime , is reproduced in the nickel(II) base of the mixed-valence composites , $Ca_xLi_{1-x}Ni^{(2-x)+}N$, we might reasonably expect these materials to exhibit high temperature superconductivity . The antiferromagnetism should assist the "horizontally resonating" metallic bond electrons to couple together into Cooper pairs at an elevated temperature typical , I would expect , of black metals such as YBCO [See also Note 9 , page 384] .

Nickel(I) might also be the active ingredient in the analogue to YCoC , namely $Y^{3+}Ni^{1+}C^{4-}$, which is isoelectronic to CaNiN . The corresponding dopant for YNiC could then be $Ca^{2+}Ni^{2+}C^{4-}$:

$$x Y^{0} + (1-x) Ca^{0} + Ni^{0} + C^{0} \xrightarrow{\text{arc furnace}} Y_{x}Ca_{1-x}Ni^{(2-x)+}C$$

argon atmosphere

Using a similar technique, it would also be interesting to see if boron could substitute for nitrogen in the hypothetical composites, $Ca_xLi_{1-x}Ni^{(2-x)+}B$. Also, phosphorus could conceivably fill the role of the anion in the shishkebab compounds, although arsenic, antimony, and bismuth might be too heavy for this application (the latter two elements in particular might produce composites that are too "metallic" to become superconducting).

When I first saw the crystal structures of the shishkebab compounds, I immediately thought what excellent pathways for superconductivity those straight long MX chains would be, if the parent material could be modified by doping into a Class 3 metallic solid. The cobalt(II) and nickel(II) bases of the compounds are in the black metal region of the Periodic Table, and they are known to be strongly antiferromagnetic (at least, in CoO and NiO), which is highly encouraging for superconductivity candidate materials. These shishkebab composites deserve a careful, detailed examination.

Low-valent, Mixed-valent Copper Compounds

Moving from right to left across the Periodic Table , we arrive at copper , the neighbor of nickel . In its higher valence states , 2+ and 3+ , copper behaves like a typical transition metal element . However , the 1B family of elements (copper , silver , and gold) and the 2B family (zinc , cadmium , and mercury) are in a border area between the transition metals and the post-transition elements . The low-valent cations of the 1B elements have filled d shells (they are nd¹⁰ electronically) , and their valence electron has been removed from the succeeding (n+1)s orbital . Their chemistry leans more toward a post-transition element behavior , with diamagnetic kernels and often colorless or white compounds .

The low-valent copper triad that might be suitable for inclusion in superconductor candidate compounds is $Cu^0-Cu^{1+}-Cu^0$; that is, it will have a diamagnetic $3d^{10}$ base of Cu(I) cations, with two "extra" valence electrons promoted up into frontier orbitals over the skeleton. If these copper frontier orbitals can successfully overlap with the valence shell orbitals of the neighboring anions, then a metallic bond XO might be formed in the solid.

The perceptive reader will have noticed by now that as we move across the Periodic Table , we alternate between the two crystal forms under consideration : iron , antiperovskite; cobalt , semiperovskite ; nickel , a failed antiperovskite ; and so for copper , we'll predict the use of a semiperovskite again . Continuing on , we'll try an antiperovskite for zinc , and a semiperovskite for aluminum .

Actually, for the low-valent, mixed-valent copper triad we can look first at the anti-rhenium trioxide crystal structure for its inclusion. Copper(I) nitride is known to have this particular crystal structure (see Figure 58 on the following page), so it's not a great stretch of imagination to propose the hypothetical new compound, Cu_3Cl , as a new metallic solid and superconductor candidate material. This structure neatly includes the low-valent, mixed-valent copper triad, although there is no guarantee that this will be the optimum NIOS valence state for observing high temperature

superconductivity (if any) in the compound.

Both atomic components of Cu_3Cl should be comfortable with their coordinations in the anti-ReO₃ structure. The octahedral coordination is a familiar one for chloride, eg. as in NaCl, and the linear coordination is a common one for all the univalent 1B cations, eg. for copper as in the [Cl-Cu-Cl]¹⁻ coordinate covalent complex anion :



Figure 59 : the M3D model of the anti-rhenium trioxide crystal structure . For example , in the known compound copper(I) nitride , Cu_3N , the small blue spheres are the copper(I) cations , and the larger brown spheres represent the nitride anions . In the hypothetical compound Cu_3Cl , the blue spheres are coppers again , while the brown spheres stand for chloride anions .

There are two pictures (at least) of the electronic structure in the proposed Cu_3Cl : the ionic one , and the covalent one . The ionic one is very simple . The chlorine is chloride anion , just as in NaCl , for example . The copper atoms are ionically bonded to the chlorides as copper(I) cations , with their

two "extra" valence electrons promoted up into frontier orbitals . The chloride anions will physically block and repel incoming electrons from the 4s and $4p_x$ native AOs on the copper atoms (as in the VB linear sp_x hybrid orbital), energetically destabilizing them. The extra electrons will thus be located in the coppers' $4p_{y,z}$ AOs, which can overlap continuously in the lattice with the chlorides' $3p_{y,z}$ AOs (filled with valence electrons) to form the bilayer pi XO metallic bond in the lattice.

In the covalent picture , the chloride anion can form the sp³ds hybrid orbital for covalent bonding to the coppers . Chlorine is the neighbor to silicon , phosphorus , and sulfur , all of which can form octahedral hexafluoro molecules : SiF_6^{2-} , PF_6^{1-} , and SF_6 . They might accomplish this by using the octahedral hybrid orbital , sp³ds , which seems most suited for the post-transition elements (recall the discussion about SF_6 on page 157 in which the sp³ds orbital was introduced). The chloride places six of its eight valence electrons in each of the six sigma bonding lobes of the hybrid orbital . The remaining two electrons are promoted up into its 4p frontier orbitals .

The copper atoms use the $3d_z^2$ and 4s AOs to construct their linear d_z^2 's hybrid orbitals for covalent bonding to the chlorides . The $3d_z^2$ orbitals contain two 3d shell valence electrons , which occupy each lobe of the composite orbital . The coppers and chlorides polymerize together in the anti-ReO₃ structure , with its covalent skeleton . The two extra valence electrons of the copper triad are promoted above the skeleton into the $4p_{y,z}$ frontier orbitals (as usual , the $4p_x$ AO is destabilized by the neighboring chlorides) . The coppers' $4p_{y,z}$ orbitals overlap continuously with the chlorides' $4p_{y,z}$ orbitals to form the bilayer pi XO metallic bond in the solid . Interestingly , the copper layer would be electropositive in the sense of delocalizing the net positive charge on the copper triad ; and the chloride layer of the XO would be electronegative , dispersing the anionic charge of the chlorides in the lattice .

Synthesis of Cu₃Cl might be accomplished simply by inserting two copper(0) atoms into the lattice of copper(I) chloride, CuCl :

 $2\ Cu^0\ +\ CuCl \qquad \blacktriangleright \qquad Cu_3Cl \ .$

Use of a very finely divided form of copper powder is suggested, to speed its rate of solution in, or diffusion into, the CuCl. Such fine copper powders are commercially available; for example, "copper powder, dendritic, ca. 3μ , 99.7%" from the Aldrich Chemical Company. The copper(I) chloride reagent is also readily available in high purity. It is thermochromic: when heated, it becomes deep blue at 178 °C, and melts to a dark green liquid at 430 °C. It boils without decomposition at 1490 °C. Pure copper(I) chloride is white, but exposure to air for a while will cause it to turn pale green from copper(II) impurities. All the reactions carried out with the low-valent, mixed-valent compounds mentioned here should be protected by an inert atmosphere of pure, dry nitrogen or argon gas.

DTA would be an excellent technique for monitoring this reaction . Visual inspection of the cooled reaction product – 25 to 50 milligrams or so of mixture in a borosilicate glass or quartz micro test tube – would reveal to the researcher immediately if a reaction has taken place , as I would expect Cu_3Cl to be a black crystalline solid .

The hypothetical compound Cu₃Cl might be the solution to the mystery surrounding the somewhat controversial claims, published in 1978, of the observation of possible high temperature superconductivity in highly compressed (40,000 atm) CuCl . Certainly, pure copper(I) chloride under ambient conditions is an electrical insulator, having no extra electrons in frontier orbitals, nor any metallic bond XO present in its lattice (the diamond-like zinc blende crystal structure). It seems that when CuCl is strongly compressed, its copper(I) cations can disproportionate slightly to copper(0) and copper(II) : $2 Cu^{1+} \rightarrow Cu^{0} + Cu^{2+}$; $E_{T}^{0} = 0.368 V$. This positive cell potential indicates that copper(I) is thermodynamically unstable at STP, and can readily disproportionate to the stabler species, copper(0)and copper(II). The reverse of this reaction is used in a student laboratory preparation of CuCl from copper turnings and copper(II) chloride in hydrochloric acid solution (ref. 160, page 415). Apparently chemical bonding to the chloride anions in the CuCl protects the copper(I) cations, under most normal conditions, from disproportionation.

According to J.A. Wilson, in his review of the CuCl superconductivity

research (ref. 161, page 415), "..... we have a favorable juxtaposition of metallic copper and insulating cupric chloride emerging within the disproportionating host" (p. 435). Copper(I) chloride turns dark under pressure"Optical work under pressure shows some copper to be produced" (p. 428). Could it be that traces of Cu₃Cl, from the very slight reaction of copper(0) with the CuCl host lattice, were formed under these conditions of very high pressure ? Such traces of the metallic Cu₃Cl might have emitted the Meissner exclusion signals detected by the highly sensitive magnetic field detection equipment used by the experimenters. Chu and Rusakov observed repeated magnetic anomalies from the pressurized CuCl at temperatures as high as 200 K, which is an excellent incentive for researchers investigating the pure Cu₃Cl. It would also be nice to solve the mystery of the alleged superconductivity in compressed CuCl.

Another bonus that might be derived from superconducting Cu_3Cl is the possibility of achieving a high critical current, J_c , and a high critical field, B_c , in the material. In Cu_3Cl all its atoms are directly involved in the pi XO metallic bond in which the superconductivity occurs. There are no "junk" spectator atoms in its formulation. The relatively small formula weight of the compound – compared to , say , YBCO – means that more Cooper pairs would be produced per unit of mass than any existing high T_c superconductors : more electron "bang for the buck". The very simple , compact isotropic structure of Cu_3Cl , without planes , or diamonds , or pyramids or other such complex architecture , should result in a higher concentration of Cooper pairs in the structure than in the conventional high T_c cuprate superconductors . In other words , Cu_3Cl should be an efficient structure for generating powerful superconductor currents , if it works .

Will it actually work ? Remember , Cu₃Cl is based on the diamagnetic copper(I) atoms , not the paramagnetic copper(II) . It is copper(II) oxide that exhibits such a powerful antiferromagnetism (that is partially quenched by electron coupling and exchange) . Copper(I) compounds generally are diamagnetic , not antiferromagnetic . Still , Cu₃Cl is unlikely to be a bronze metal , either . Perhaps it will be neither bronze nor black , but let's say a gray metal ? That is , the pre-transition and early transition elements on the left side of the Periodic Chart produce bronze metal

compounds ; the middle and late transition metals produce black metal compounds ; and the post-transition metals provide gray metal compounds . All this is sheer speculation , of course . Only by experimentation can the materials discussed in this report be synthesized and characterized , and thereby these ideas will be verified or refuted .

Other of the simple binary halides of copper(I) and silver(I) could be tried in related experiments : CuBr, CuI [CuF doesn't exist, apparently]; and AgF, AgCl, AgBr, and AgI, with two atoms of silver(0). The hypothetical Ag₃X compounds would have larger cell constants than their copper(I) analogues, and so would be expected to have lower transition temperatures than them.

Other anions could also be tried in place of the halide, but then a chargebalancing cation would have to be inserted into the supercube cavity to compensate for the additional anionic charge. For example, with oxide :

$$\frac{1}{2}$$
 Cs₂CO₃ + 2 Cu⁰ + $\frac{1}{2}$ Cu₂O
- $\frac{1}{2}$ CO₂ (g) CsCu₃O . (t = 0.93)

A flowing inert gas atmosphere of nitrogen or argon is recommended for this reaction, to protect the materials from oxidation, and to assist in driving it to completion by continuously expelling the by-product carbon dioxide gas.

The nitride analogue might be somewhat more involved to synthesize :

$$BaCl_{2} + CuCl \xrightarrow{\text{melt together}} BaCuCl_{3} \xrightarrow{\text{melt with Li}_{3}N},$$

$$BaCuN \xrightarrow{2 Cu^{0}}, BaCu_{3}N \quad (t = 0.79) \quad .$$

The excessively low tolerance factor calculated for $BaCu_3N$ is worrisome, as it implies that the compound might have a crystal structure other than the intended semiperovskite.

Zinc Antiperovskites

The 2B family of elements , zinc , cadmium , and mercury , are considered as transition metal elements , but they and their compounds share the characteristics of the post-transition elements as well . In no instances are their nd^{10} electrons removed , at least in "ordinary" chemical conditions ; only their ns^2 valence electrons are chemically affected . As a result , they behave more like post-transition elements , with low melting points (as the metallurgical metals) , and their compounds have considerable covalent nature .

The divalent cations are the most familiar valence state for the oxidized elements . Their univalent state is less common , and is present only on the diatomic M-M molecules , eg. the mercury(I) cation , $(Hg_2)^{2^+}$. Apparently the monatomic univalent metal cations , eg. Hg^{1^+} , are unknown . Only the mercury(I) cation is stable under ambient conditions . The zinc(I) and cadmium(I) cations have been prepared , but are somewhat unstable .

These elements , and especially zinc , might be fashioned into antiperovskites with the M₃OX formula ("M" is a 2A element ; "X" is a chalcogenide anion , S , Se , or Te) . Their triad for inclusion in this crystal structure is $M^{2+}-M^0-M^{2+}$, with the M^{2+} base of diamagnetic cations and the two extra electrons from M^0 promoted into frontier orbitals . This formulation immediately suggests the components for their syntheses :



Alternately, direct combination of the elements might be tried :

$$2 Zn^0 + ZnO + S^0 \longrightarrow Zn_3OS$$
;
similarly for Se and Te.

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The reaction between zinc dust and flowers of sulfur is known to be highly exothermic, and a mixture of the two elements may violently detonate when ignited (ref. 162, page 415). However, in this case the zinc and sulfur would be diluted with the refractory zinc oxide, which may calm the reaction down somewhat, at least to the point where it is manageable. Nevertheless, I hope that any researcher carrying out this experiment does so in a careful manner, observing all the necessary safety precautions, especially using secure eye protection. Semi-micro quantities of reaction mixes should be used, no more than a gram or so per trial. An efficient combination of the three components will occur if the reaction mass can be heated to the point of incandescence, where there is appreciable sintering of the mixture particles. The Zn₃OX antiperovskites are all chemically reducing materials, so they should be shielded from atmospheric oxygen by a blanket of inert gas such as nitrogen or argon, or if feasible, prepared in a closed container such as a covered crucible, ampoule, or autoclave.

The Zn_3OX compounds would be ionic solids [because of the octahedral oxide anions], with octahedrally-coordinated Zn^{2+} cations (2 x O + 4 x X). The zincs' 4s-p-d orbitals will be energetically destabilized by the surrounding anions, and the next available frontier orbitals will be the 5 s-p AOs. Assuming that the entire system isn't destabilized by promotion of the extra valence electrons from the Zn⁰ component of the zinc triad, that will be their likely location. The zincs' $5p_{v,z}$ orbitals can overlap with the oxides' $2p_{y,z}$ AOs , filled with valence electrons , to form the bilayer pi XO metallic bond in the lattice . The zincs' 5s AO can also overlap with the oxides' $2s^2$ AO, or with the chalcogenide "A" atom's filled $ns^2 AO$, or with its empty $(n+1)s^0 AO$.

There could be significant redox resonance between the zinc cations and chalcogenide anions in the antiperovskite. We know from previous experience (page 323) that the latter species are natural reducers to some extent . The zinc cation is moderately easy to reduce to Zn^0 (-0.7618 V).

$$\underline{Zn^{2+}} + \underline{S^{2-}} \qquad \underbrace{[V] = 0.2858 V}_{Zn^0} + S^0 .$$

$$Zn^{2+} + Se^{2-} \qquad \underbrace{[V] = 0.1622 V}_{Zn^0} + \underline{Se^0} .$$

$$Zn^{2+} + Te^{2-} \qquad \underbrace{[V] = 0.3812 V}_{Zn^0} + \underline{Te^0} .$$

The selenide and telluride anions are actually capable of reducing the zinc cation to zerovalent zinc , although I think what would probably happen in the Zn_3OX compounds is a polarization or flow of the electrons toward the zinc atoms , rather than their clean reduction .

These zinc antiperovskites , if they can be synthesized and characterized as such , would likely be neither bronze nor black metals , but would have to be described more as "gray metals", as with the Cu_3X and Ag_3X series of compounds discussed above . With the bronze metals , I visualize their metallic bond free electrons (above the Fermi level) as having a predominately parallel spin orientation with respect to one another . In the black metals , they will have a predominately antiparallel spin orientation from atom to atom ; or , they might hop-flip as they resonate from atom to atom :

Hop-Flip of Metallic Bond Free Electrons



If the temperature is low enough, the neighboring antiparallel pairs will condense into Cooper pairs, which, located above the Fermi level in the metallic bond, will constitute the superconductor charge carriers.

In the gray metals, I picture their metallic bond free electrons as having a more random orientation of their spins, neither predominately parallel nor antiparallel. They will probably need more cooling than the black metals to become superconducting, all other conditions being favorable for superconductivity in the solid. Rosenberg has commented,

"The list of compounds which become antiferromagnetic , however , is very large , as most paramagnetic substances become antiferromagnetic at a sufficiently low temperature". (ref. 163 , page 415)

So the gray metals, as potential superconductor candidates, would likely have transition temperatures roughly in between those of the bronze metals and the black metals [See also Note 9, page 384].

An Aluminum Anti-Rhenium Trioxide Compound

From the zinc antiperovskite we move over to the 3A family of elements, to aluminum, one of the most abundant elements on Earth. Its common occurrence (in clays, if less so in its industrial ore, bauxite), ready availability, relatively low atomic weight, and cheapness, make aluminum an inviting starting material for conversion into superconductor candidate compounds.

I have already commented on problems associated with trying to make mixed-valent compounds based on aluminum (page 72). Research has clearly shown that Al(I) and Al(II) have a transient stability only at very high temperatures (ref. 35, page 395). However, as I pointed out earlier, the low-valent aluminum compounds studied were oxides and sulfides, in which there was ionic, and not covalent bonding. The anions concerned may have actually been detrimental to the stability of the compounds involved, as they probably occupied the physical volume in the lattice in which the $3s^2$ and $3s^1$ valence electrons of the Al(I) and Al(II), respectively, would normally have been located. By forcing these valence electrons into excessively energetic frontier orbitals, the anions doomed the low-valent

compounds to disproportionation and physical collapse as soon as they were cooled to ambient temperature .

The approach taken here to design and synthesize a stable low-valent, mixed-valent aluminum compound, that in addition should be a metallic solid, and may be superconducting (albeit a gray metal), is to incorporate the low valent aluminum triad, $Al^0 - Al^{1+} - Al^0$, into an anti-rhenium trioxide crystal structure, M_3X . We will use chloride as the "X" anion, and could thereby have covalent, rather than ionic bonding (as with oxides and sulfides) of the crystal skeleton.

The proposed compound , Al_3Cl , tris[aluminum(0.33+)] chloride , might be prepared by reproportionation of aluminum(0) metal powder and anhydrous aluminum(III) chloride :

 $8/3 \text{ Al}^0 + 1/3 \text{ AlCl}_3 \xrightarrow{\text{inert atmosphere}} Al_3Cl$. m.p. 660 °C 178 °C (subl.)

Aluminum chloride is a covalent material , low melting and soluble in many organic solvents . It is a Lewis acid (page 256) and is probably the best known of the Friedel-Crafts catalysts used in organic synthesis . Anhydrous aluminum chloride is very hygroscopic , and that and the reducing nature of the Al^0 - Al_3Cl system will oblige the researcher to conduct the preparation in a sealed crucible , test tube , ampoule , or autoclave under an inert atmosphere of pure , dry argon or nitrogen .

In a covalent bonding environment, aluminum(0) – which is $3s^2 3p^1$ electronically – should be able to assume the classic VB coordinations of linear (sp), trigonal planar (sp²), and tetrahedral (sp³). The aluminum(III) in AlCl₃ has a tetrahedral coordination by the chlorides. Thus, the anti-rhenium trioxide crystal structure proposed for the hypothetical compound Al₃Cl is not unrealistic, given the 3:1 Al:Cl stoichiometry.

Assuming that the compound can be made , and has this structure , the base cations of the aluminum triad in it , $Al^0-Al^{1+}-Al^0$, are $Al^{1+}(3s^2)$, with the

two extra electrons per aluminum triad located in any available empty frontier orbitals . The 3s and $3p_x$ native orbitals can form the linear sp_x hybrid orbital , with the $3s^2$ electrons in the two sigma bonding lobes ; then the two extra valence electrons will be located in the $3p_{y,z}$ AOs , which they were in anyway , in the aluminum metal ; no promotion energy will be required in this case .

The chloride anion can form an octahedral sp^3 ds hybrid orbital, as was discussed for Cu₃Cl on page 344, placing six of its eight valence electrons in the six sigma lobes of the composite orbital. It then promotes the remaining two electrons to the next available empty native orbitals, which would be the $4p_{y,z}$ AOs (the $4p_x$ AOs are non-bonding "duds").

The chlorides and the aluminums polymerize together to form the covalent anti-ReO₃ skeleton of the compound . The chlorides' $4p_{y,z}$ and the aluminums' $3p_{y,z}$ orbitals also polymerize over the skeleton to form the bilayer pi XO metallic bond in the solid . This is something of an "upside down" XO, since the higher energy chloride layer will be on top of the aluminum layer , the reverse of what usually happens in the metal-anion pi XOs . As in Cu₃Cl, the aluminum layer will disperse the cationic charge in the lattice , while the chloride layer will distribute the anionic charge throughout the structure : a rather odd sort of metallic bond !

In this bonding scenario , the aluminum valence electrons aren't forced into high energy , destabilizing frontier orbitals by lattice anions . There is no promotion at all of the aluminum valence electrons ; on the contrary , they remain in their normal orbitals , which are then used to create new , stabilizing covalent and metallic bonds . I think that Al₃Cl , even though it is a counter-intuitive "impossible" compound , actually has a good chance of being stable and isolable under ambient conditions . It also has the proper electronic structure as a Class 3 metallic solid to possibly be superconducting at low temperatures . However , as a post-transition element gray metal , it probably wouldn't have a very high superconducting T_c . The Bell Labs' bismuth superconductor , $Ba_{0.6}K_{0.4}BiO_3$ (page 243) , had a transition temperature of about 30 K ; since it can be considered as a gray

metal , this is likely a representative T_c for that class of superconductors .

The three elements , magnesium , aluminum , and zinc , are abundant and cheap . While being excellent electrical conductors in their own right , they might be even more valuable if they could provide us with a virtually unlimited supply of high temperature superconductors and other such metallic solids . I hope that my suggestions in this area will stimulate further thought and research efforts to design and synthesize such remarkable new materials .

Several Tin-based Metallic Solids

The last element we'll visit in this guided tour of the Periodic Chart is tin ; actually , it will be a revisit , since we looked earlier at the crystal and electronic structures of white tin metal (page 164) , tin(III) phosphide (page 160) , and cesium tin(II) tribromide (page 285) . Since tin is a post-transition metal element , we would expect its metallic solids to be gray metals . This should be reflected in medium range transition temperatures (I'm guessing 25-50 K) for any tin-based superconductors .

There are two potential superconductor triads for tin : the low-valent triad , $Sn^{2+}-Sn^0-Sn^{2+}$, and the high-valent one , $Sn^{4+}-Sn^{2+}-Sn^{4+}$. The former triad would commend itself to the antiperovskite crystal structure . However , at this point the tin atoms are getting rather large and unwieldy for the antiperovskite . The latter triad seems to be the more practical one for fitting into familiar crystal structures .

Of course , our favorite structure has always been that of the perovskite , with its compact atomic packing and flexibility in juggling the "A" and "M" atom valences so as to obtain the desired NIOS valence state for the "M" component . In the case of tin , the compound CaSnO₃ is known to be a perovskite with cubic symmetry (a = 3.92 Å). Rather than trying to prepare a perovskite with the very large Sn(II) component (r = 1.22 Å), it might be more practical to aim for a tin(III) perovskite, such as LaSnO₃. This should be a metallic solid in its own right (Class 1), as we know that the base tin atoms will actually be tin(IV), with the extra 5s¹ electron promoted up into a frontier orbital (probably the 6p_{y,z} AOs).

The following preparations, culminating with the doping trials to prepare a series of mixed-valent composites for electrical testing, are suggested :

 $CaCO_3 + SnO_2 \xrightarrow{flowing air} CaSnO_3 + CO_2(g);$ shake-n-bake

$$\frac{1}{2} \operatorname{La}_{2}O_{3} + \frac{1}{2} \operatorname{SnO} + \frac{1}{2} \operatorname{SnO}_{2} \xrightarrow{\text{inert atmosphere}} \operatorname{La}_{3}O_{3} ; \text{ or ,}$$

$$\frac{1}{2} \operatorname{La}_{2}O_{3} + \frac{1}{4} \operatorname{Sn}^{0} + \frac{3}{4} \operatorname{SnO}_{2} \xrightarrow{\text{inert atmosphere}} \operatorname{La}_{3}O_{3} ; \text{ then ,}$$

$$x \operatorname{La}_{3}O_{3}^{+}O_{3} + (1-x)\operatorname{Ca}_{3}O_{3}^{++}O_{3} \xrightarrow{x=1 \to 0} \operatorname{La}_{x}Ca_{1-x}\operatorname{Sn}^{(4-x)+}O_{3} .$$

Doping the Class 1 metallic solid $LaSnO_3$ with the insulating $CaSnO_3$ would convert it into the Class 3 composite with mixed-valent tin . The composite should have a good chance of superconducting , but being a gray metal , it would probably have only a medium , and not high , transition temperature .

I mentioned the titanium(III,IV) spinel, $LiTi_2O_4$, with $T_c = 13.7$ K, above on page 183 (D.C. Johnson, ref. 84, page 403). It would be interesting to compare the tin analogue to this compound :

 $\begin{array}{r} & -\frac{1}{2} \operatorname{CO}_2(g) \\ & & \\ \hline & & \\ & &$

Will tin (gray) trump titanium (bronze)? Try it and see !

The "all-tin(III) spinel" $MgSn_2O_4$ would also be a metallic solid (Class 1), and could be converted into a Class 3 mixed-valent compound by doping with a suitable tin(IV) dopant :

It would also be possible to obtain mixed-valence composite spinels from doping $MgSn_2O_4$ with $LiSn_2O_4$ (see above), which contains tin(IV):

$$x = 1 \to 0$$

x MgSn₂O₄ + (1-x) LiSn₂O₄ \longrightarrow Mg_xLi_{1-x}[Sn^{(3.5-0.5x)+}]₂O₄.

These could be compared to the corresponding titanium compounds , $MgTi_2O_4$, $Mg_xTi_2O_4$, and $Mg_xLi_{1-x}Ti_2O_4$, with similar preparations .

Tin(IV) oxide , SnO_2 , has the rutile structure (Figure 24 , page 132) . Suppose it was possible to partially reduce the tin(IV) in SnO_2 to tin(III) with lithium metal :

$$x Li^0 + Sn^{4+}O_2 \xrightarrow{x = 0 \rightarrow 1} Li_x Sn^{(4-x)+}O_2 .$$

The inert lithium spectator cations would be nested in cavities in the rutile crystal structure .

This is only a "thought experiment", as the direct reaction of lithium metal, a powerful reducer, and tin(IV) oxide, a mild oxidizer, might be rather exothermic, and possibly violent. The partially reduced SnO_2 , containing tin(III), should be a metallic solid, and possibly superconducting in the gray metal range. A gentler and safer method of preparing the partially reduced

rutile would be the reproportionation of Sn(II) and Sn(IV), or of Sn(0) and Sn(IV):

$$\begin{array}{r} \frac{1}{2} \operatorname{Li}_{2} \operatorname{CO}_{3} + \frac{1}{2} \operatorname{SnO} + \frac{1}{2} \operatorname{SnO}_{2} & \xrightarrow{-\frac{1}{2} \operatorname{CO}_{2}(g)} \\ \frac{1}{2} \operatorname{Li}_{2} \operatorname{CO}_{3} + \frac{1}{4} \operatorname{Sn}^{0} + \frac{3}{4} \operatorname{SnO}_{2} & \xrightarrow{-\frac{1}{2} \operatorname{CO}_{2}(g)} \\ x \operatorname{Li}_{3} \operatorname{Sn}^{3+}O_{2} + (1-x) \operatorname{Sn}^{4+}O_{2} & \xrightarrow{x = 1 \to 0} \\ \end{array}$$
 LiSnO₂; then,

I am assuming that insertion of the lithium cations into the structure won't significantly distort or alter the rutile lattice . Since tin(IV) is only covalently bonded to ligands, and cannot be ionic, the structure of the mixed-valent composite is unlikely to rearrange to the rocksalt structure (which some AXO_2 formula compounds have). I have sometimes represented tin(IV) in the text as the ionic Sn^{4+} , but that is just an arithmetic convenience ; it is correctly written as the covalent Sn(IV).

Note that , at the doping level of x = 0.5, we have the compound $Li_{0.5}SnO_2$, which is also $LiSn_2O_4$, the spinel discussed on page 355. In practice , the lithium doping levels might be fairly low , possibly not higher than $x \sim 0.1$ or so . As with the previously mentioned tin compounds , it might be instructive to compare this series of doped tin rutiles with the corresponding titanium analogues , Li_xTiO_2 , assuming of course they can be synthesized .

The "inert pair effect" (page 69) plays an influential role in the chemistry of divalent tin compounds . We saw in the examples of the cubic tin(III) phosphide and cesium tin(II) tribromide how the formation of the three-dimensional covalent tin-anion skeleton could sometimes force the $5s^2$ inert pair to participate in the bonding . When this is accomplished , we usually observe a pronounced enhancement in the electronic activity in the solid . We can use this dispersal of the inert pair in certain cases to produce the metallic tin(III) valence state , which can in turn be utilized in the high-valent tin triad for superconductivity , $Sn^{4+}-Sn^{2+}-Sn^{4+}$, written alternately as $Sn^{3+}-Sn^{4+}-Sn^{3+}$. A detailed study of the solid state chemistry of the metallic tin(III) valence state would thus be very valuable .

Metallic Solids and Superconductivity

In conclusion, I'll highlight the main points of interest concerning metallic solids, and the relationship of superconductivity to them.

First, a metallic solid is characterized by the presence in it of "free electrons", which are itinerant in the lattice and will physically move in it under an applied potential difference. These free electrons are "extra" to those valence electrons that bond the atoms in the solid together in covalent bonds. I have referred to the collective crystal-wide orbital the free electrons are located in , or comprise , as the crystal orbital , XO . This orbital is similar to a bonding molecular orbital , and can be considered as the metallic bond in the solid . Therefore , a metallic solid is any solid with a metallic bond containing free electrons . The metallic bond is at a higher energy level than the underlying skeletal covalent bonds , and is physically further outward from the atomic kernels than them as well .

There are several classifications of metallic solids , depending on how you are studying them . In orbital terms , we can distinguish the two main types : true metals , in which there are no nodal points or surfaces in the XO along at least one crystal axis ; and pseudometals , in which the XO is periodically intersected by nodal points or surfaces at or around the kernels . Nodes are regions of interatomic space in the lattice in which there is no appreciable free electron probability density . They represent a physical barrier to the passage of the free electrons under an applied potential difference . The free electrons can tunnel through the nodes , but require energy to do so , which must be obtained from the environment of the solid . The more energy is provided to pseudometals , the more of their XO's free electrons can tunnel through the nodes in the XO . Hence , their electrical conductivity rises with increasing temperature : this is the "direct" relationship of electrical conductivity to the solid's temperature .

The true metals have nodeless XOs, so in theory their conductivity should be unaffected by their temperature. In practice, because of the presence in their crystals of lattice imperfections, defects, and chemical impurities, and also of the vibrating kernels – phonons – whose amplitude increases with temperature, the free electrons are slowed down and scattered more and more with increasing temperature. The conductivity of true metals falls as they are heated : this is the "inverse relationship" of electrical conductivity and temperature of the solid.

Measurement of the electrical conductivity of a given solid over a reasonably extended temperature range should provide information as to which relationship holds true for the material studied : direct or inverse . This information will give us an idea as to the electronic structure of the solid , and as to which orbitals may be forming its metallic bond XO .

Metallic solids may also be classified according to their chemical makeup. The Robin-Day classification of mixed-valent compounds is a valuable chemical concept, as it provides a clear and comprehensive sorting of a wide variety of mixed-valent compounds into four well-defined groups. Two of the Robin-Day groups, Classes II and IIIB, are of interest with respect to metallic solids, since they encompass some materials that are electrically conducting, and may even be superconducting (materials from Classes I and IIIA are generally insulators or poor semiconductors).

The Robin-Day concept can be broadened for general usage with a wide range of metallic solids . In Class II compounds , the mixed-valent cations are separated by anions ; in the Class IIIB compounds , there is direct metal cation-to-cation electronic interaction . In the metallic solids classification , Class II would mean , more generally , that the metallic bond includes both the anions and cations (or metal and non-metal atoms) ; in the Class IIIB metallic solids , the metallic bond includes the metal atoms or cations , but excludes the nonmetal atoms or anions .

The chemical classification of metallic solids goes beyond the Robin-Day concept, in that it includes both mixed-valent [heterovalent] and homovalent cation systems (and in a few rare cases, might even include mixed-valent anions). So we can have homovalent Class II or Class IIIB metallic solids; and we can have mixed-valent Class II or Class IIIB metallic solids.

From these considerations I have proposed a fairly comprehensive classification of metallic solids, starting first with the two orbital types of XOs, nodeless \rightarrow true metals, and nodal \rightarrow pseudometals. Then these two general types are each subdivided into the four subtypes mentioned above, based on their chemical makeup, and borrowing from the Robin-Day (RD) concept:

- □ Class 1 : true metal , homovalent , RD II ; eg. ReO₃
- \Box Class 2 : true metal , homovalent, RD IIIB ; eg. MgB₂
- □ Class 3 : true metal, mixed-valent, RD II ; eg. YBCO
- □ Class 4 : true metal , mixed-valent , RD IIIB ; eg. Ag₂F
- Class 5 : pseudometal , homovalent , RD II ; eg. NiO
- Class 6 : pseudometal , homovalent, RD IIIB ; eg. Si
- Class 7 : pseudometal, mixed-valent, RD II ; eg. magnetite
- Class 8 : pseudometal, mixed-valent, RD IIIB; eg. KCP

Metallic solids can be further classified – albeit with less precision , and more speculatively – into the three hazily defined groups of bronze , black , and gray metals . The first group , named after the tungsten bronzes , physically look metallic , with a lustrous appearance and metallic color (bronze , coppery , silvery , golden , etc.) . Classes 4 and 8 metallic solids , the "synthetic metals" and "molecular metals" , would immediately be assigned to the bronzes . I have placed the tungsten bronzes in Class 3 ; silicon , in Class 6 , has a bluish-gray , metallic appearance , like lead (I'm looking at a chunk of it sitting on my desk at this moment) ; and magnetite , in Class 7 , when in a bulk crystal form , has a dark-gray , lustrous appearance , like graphite (Class 2) . Clearly , the bronze metals are pervasive materials .

The black metals were named after the jet-black transition metal oxide , copper(II) oxide , the parent material for many high transition temperature superconductors such as YBCO (which are also black) . The black metals are typically refractory "ceramic" materials with poor ambient electrical conductivities , but which comprise – so far – the highest T_c group of superconductors . Their electronic structures must be quite different than those of the various bronze metals .
The gray metals are basically the "leftovers", those metallic solids that can be described neither as black nor bronze. Most if not all of the metallic compounds derived from the post-transition metal elements, or generally from those elements on the right-hand side of the Periodic Table, are expected to be of the gray variety.

The defining conditions of the bronze , black , and gray metals are the predominate spin orientation of the free electrons above the Fermi level in their metallic bond XO , and how the free electrons move about in the lattice under the influence of ambient energy input . This is pure speculation on my part , and just a simple picture I have made to try to understand the behavior of these extraordinary substances . The reader should feel free to supplant this with his or her own interpretation or understanding of them .

In the bronzes , the free electrons have a predominately parallel spin orientation with respect to each other . They absorb energy readily from the environment , moving vertically in the vast multitude of energy levels comprising the metallic bond XO . They can radiate that energy away just as readily , falling back down in the energy levels (the basis of metallic luster and high reflectivity , including mirror reflection) . They can also move horizontally , from atom to atom , but only downfield in an applied potential difference ; then the entire population of free electrons in the XO shifts "en masse" in the direction of the lower p.d. , toward the "ground" . This is the electron drift in metals and the actual electrical current in conductivity .

In the black metals, the free electrons have a predominately antiparallel spin orientation with respect to each other. They also absorb environmental energy, but retain it, dispersing it into the kernels as phonon energy (kernel vibrations : heat), or causing the free electrons to hop about horizontally from atom to atom, especially in Class II and IIIB mixed-valent systems. Since they reflect very little of the light incident to their surfaces, they appear black.

The free electrons in the gray metals may have a random spin orientation, neither predominately parallel nor antiparallel. When gray metals are cooled down toward absolute zero, their free electrons will gradually assume the

antiparallel spin orientation . Never having seen a gray metal , I can only assume that they would have a dark or possibly even black appearance , especially if they are based on a mixed-valent system ; Class II mixed-valent compounds are known to have intense colors , and are often dark blue or black .

The classification of metallic solids as bronze , black , or gray , despite its imprecision , is helpful in the area of predicting the material's behavior as a superconductor candidate compound . The parallel spin orientation of the free electrons in the bronzes is antithetical to the condensation of Cooper pairs , with their antiparallel spin electron pairs . Tremendous cooling is required to permit the BCS type of Cooper pair formation from bronze free electrons , and some metallurgical metals (eg. copper , silver , and gold) never become superconducting , even very close to absolute zero .

The antiparallel spin orientation of the black metals' free electrons , in contrast , is much more conducive to their condensation into Cooper pairs , and indeed we find all the high temperature superconductors in this broad group of metallic solids . The behavior of the gray metals in this respect will fall in between that of the bronzes and the black metals . The transition temperatures of the bronze metals will lie roughly in the range of $0-25~{\rm K}$; that of the gray metals , $25-50~{\rm K}$; and the black metals should have T_c values of 50 K and upwards . There will be overlapping and exceptions , of course (for example , Bednorz and Müller's Ba/Sr-La-Cu-O superconducting cuprates , with $T_c \sim 30-40~{\rm K}$) .

I proposed a new , rather simple – admittedly somewhat simplistic – picture of the formation of Cooper pairs in the high temperature superconductors . It is easy to calculate that the attractive magnetic force between antiparallel electrons is nearly 1200 times as strong as their repulsive electric force . In absolute terms , which I haven't calculated , these forces must be vanishingly small in the bronze metals , in which the Fermi distribution places only a very small population (perhaps 1% in a typical metallurgical metal) of XO electrons above the Fermi level . Even if antiparallel pairs of free electrons do form at extremely low temperatures , they are likely to have , on average , very wide separation distances , making the force values

essentially nil . However , the BCS mechanism of Cooper pair formation in these deep cryogenic superconductors will nudge the free electrons together at the appropriate low temperature .

The black metals , on the other hand , are chemically characterized by the participation of the anions , together with the electronically active cations , in the metallic bond XO . I have suggested the idea of the bilayer metallic bond , with the anion contribution generally forming the lower energy layer of the XO . The Fermi level will occur at , or near the boundary of the two layers . All , or most of the cations' free electrons will thus be above the Fermi layer , so the black metals will have a very rich population of free electrons compared to the bronze metals . Better yet , the antiparallel spin orientation of the free electrons in them will result in many neighboring free electrons being antiparallel to each other . Their separation distance is much shorter (possibly 100 times less) than in the bronzes) a new power to be reckoned with . Condensation of the free electrons into Cooper pairs is much easier now than in the bronzes , and can take place at significantly higher temperatures in black metals than in bronze metals .

As for the gray metals, they probably have a small population of antiparallel spin free electrons even at, say, liquid nitrogen temperature, so they will require less cooling than the bronzes for the onset of the Cooper pair formation below the transition temperature of the gray metal.

Clearly, the black metals will be of greatest interest as far as designing and synthesizing new high temperature superconductor candidates is concerned. In chemical terms, we should look for antiferromagnetic compounds, with as high Néel temperatures, T_N , as possible. True to form, the strongest antiferromagnetic compounds are all derived from transition metal elements roughly in the middle of the Periodic Table : FeO, CoO, NiO, and CuO. The antiferromagnetic materials' valence electrons have an antiparallel spin régime of one sort or other. If we can convert these antiferromagnetic non-metallic precursor compounds into metallic solids, and if the antiparallel spin orientation régime is preserved in the metallic bond's free electrons, we will have prepared a new black metal as a superconductor candidate.

As is well known , superconductors are strongly diamagnetic substances . It is occasionally possible to have a high spin , paramagnetic component in a superconducting compound , providing that atom's orbitals aren't overlapping with the metallic bond XO . For example , in the YBCO analogues , $MBa_2Cu_3O_7$, paramagnetic M^{3+} rare earth cations can successfully substitute for the diamagnetic Y^{3+} : Nd^{3+} ($4f^3$) , $T_c = 78$ K ; Sm^{3+} ($4f^5$) , 87 K ; Gd^{3+} ($4f^7$) , 91 K ; Dy^{3+} ($4f^9$) , 92 K ; Er^{3+} ($4f^{11}$) , 91 K ; and Yb³⁺ ($4f^{13}$) , 89 K (ref. 12 , page 391 , Table VII-2 , p. 125) . The 4f orbitals in the rare earth elements are thought to be small and to lie close to the kernels ; their valence electrons probably interact very little , if at all , with the surrounding 5d , 6s , and 6p orbitals which are active in the lanthanide cations .

Metallic solids of the extended atomic lattice (nonmolecular solid) variety can be thought of as a combination of a rigid , low energy covalently (or ionically) bonded skeletal framework , surrounded by a higher energy "sheath" of the metallic bond . Most of the valence electrons surround the atomic kernels , but one or occasionally two valence electrons may not be accommodated in the skeleton , and will be promoted to outer , higher energy frontier orbitals . If these outer orbitals can overlap with each other continuously throughout the lattice , a metallic bond XO will be formed . Alternately , we can take an established crystal skeleton of appropriate structure , and chemically force a few extra electrons into those frontier orbitals ; the metallic bond is created by reduction . Or , we can take a solid in which the outer orbitals are completely filled with valence electrons , and by an oxidation procedure remove some of those electrons . The "holes" left in the otherwise filled outer orbitals will permit them to function as the XO .

If a metallic solid is intended as a superconductor candidate compound, we should try to ensure that its base atomic kernels are low spin (spin-paired) and diamagnetic in nature. Then, all conditions being favorable, the XO free electrons will condense to Cooper pairs at a lowered temperature. Note that the XO electrons below the Fermi level are already spin-paired. At the material's T_c , all of its electrons will be spin-paired : in the kernels, and below and above the XO's Fermi level. Unfortunately, the most promising precursors for modifying into metallic solids, and into superconductor

candidate compounds – the strongly antiferromagnetic transition metal oxides – have base cations that generally demonstrate a strong preference for high spin , paramagnetic electronic configurations . Finding crystal structures in which these iron , cobalt , nickel , and copper oxides can have diamagnetic base cations , and can be modified into black metals , is an interesting and potentially valuable chemical challenge . I have suggested a few promising systems in this area in earlier pages .

All superconductors are metallic solids (actually, true metals), but not all metallic solids are superconductors. We see this happen, in particular, with the homovalent metallic solids of Class 1, such as rhenium trioxide. It is a splendid metal, with a superb electrical conductivity, but fails to become superconducting. Similarly for, say, the compound CaNiN. This latter material is especially interesting. because its base cations are nickel(II), and they may be diamagnetic (I'm not sure of this, but I think so). Nickel(II) oxide is very strongly antiferromagnetic; of course, that may not hold true when the nickel(II) base cations have nitride, rather than oxide, ligands. In any case, CaNiN, with its nice long, straight Ni-N chains, looks custommade for conversion into a high temperature superconductor.

Is it possible that the extra electrons in CaNiN have a parallel orientation, making it behave like a bronze metal, despite nickel being in the black metal region of the Periodic Table?



The hop-flip process may be less favorable energetically – or even fail completely – if the hopping extra electron in the XO encounters another free electron on the kernel it is transferring to . On the other hand , the beauty of Robin-Day Class II mixed-valent compounds is that there is no electronic

barrier to the hopping of the free electrons in them ; that is , [V] = 0 V :



The hopping electrons in this Robin-Day Class II mixed-valent system transfer smoothly to the empty nickel(II) cations, not encountering any other repulsive free electrons there when they arrive on the kernels. If the compound is cold enough, the neighboring antiparallel pairs will have a chance to condense into Cooper pairs, and then superconductivity !

This is why I have recommended in so many cases that mixed-valent composites of parent metallic compounds be investigated as potential superconductor candidates ; for example , with CaNiN , the corresponding mixed-valent composite might be $Ca_xLi_{1-x}Ni^{(2-x)+}N$, where $x = 1 \rightarrow 0$. The chemist could prepare as many Ca-Li composite samples to study as was deemed feasible by the research protocol (personnel , budget , time constraints , etc.).

To help determine which valence states might be suitable for selection in designing mixed-valent composites for the various elements , I have devised the concept of the "triad". This is a group of three mixed-valent cations which would produce a single Cooper pair overhead in the metallic bond . Their kernels would be diamagnetic . For example , the CaNiN triad is shown at the top of this page , on the left side : $Ni^{1+}-Ni^{2+}-Ni^{1+}$. This can also be expressed as $Ni^{2+}-Ni^{2+}-Ni^{2+}$ (e_2^{2-}), with the three diamagnetic nickel(II) kernels , and a Cooper pair above them in the metallic bond . The triad is just a simple picture I use to help visualize the chemistry of the various mixed-valent systems . Most of the time , as you have seen , I have recommended the doping process , in which the parent metallic compound (CaNiN , Ni¹⁺) is incrementally doped with increasingly greater mole fractions of the insulating dopant (LiNiN , Ni²⁺) , to produce samples of the

mixed-valent composite for electrical (and other) testing .

Occasionally , the cation triad can be fitted into the unit formula of a crystal structure ; for example , in the hypothetical compound Ni_3O_2 , which is $(Ni^{1+}-Ni^{2+}-Ni^{1+})O_2$. This is merely a convenience , but it may not represent the optimized NIOS valence for the highest possible transition temperature for that compound . It might be difficult to incrementally dope that structure and still maintain its integrity . That's another challenge for solid state chemists investigating these mixed-valent systems : doping or "pure" triad ?

Incidentally, there is also a higher valent triad for nickel : $Ni^{3+}-Ni^{4+}-Ni^{3+}$, which will be $3d^7-3d^6-3d^7$ electronically. Nickel(III) is a moderately strong oxidizer (1.17 V, to Ni^{2+}), and Ni(IV) is an even stronger oxidizer. I have chosen to focus on what are (for me) the more interesting low-valent, mixed-valent (reducing) triads and compounds of various elements. Not that the high-valent triads are any less rewarding in superconductivity research; YBCO, for example, containing the complete high-valent copper triad per unit formula, $Cu^{2+}-Cu^{3+}-Cu^{2+}$, inspired in me the idea of the cation triads over a decade ago.

In any case , we should achieve the best results in designing and synthesizing new superconductor candidate compounds with Robin-Day Class II mixed-valent compounds (Class 3 metallic solids) . By permitting a barrier-free horizontal movement of the XO free electrons , instead of the vertical free electron movement of the bronze metals , we will have accomplished one objective of the design . The second objective is to have a black metal , but only Nature can provide us with antiferromagnetic precursor compounds to modify . If we have both a Class 3 metallic solid , and it is in an antiferromagnetic precursor , then we will have a black metal and an excellent high temperature superconductor candidate . If we have only the Class 3 metallic compound but no antiferromagnetism in the precursor , then we may have either a bronze or a gray metal . The former , while a fascinating material in its own right , will prove to be a disappointing superconductor candidate . The gray metal under optimum conditions would yield only a medium temperature range superconductor , if that . A conference, "The Search for Room-Temperature Superconductivity", held at Bodega Bay, California, on October 19-21, 1992, was attended by many prominent superconductor researchers. Their discussions were highlighted in an article, "Paths to Higher-Temperature Superconductors", by T.H. Geballe (ref. 164, page 415). In a sidebar, "Helpful Hints for Finding New Superconductors", Geballe summarized the desirable features of high temperature superconductors. Owens and Poole have provided a similar sort of list (ref. 165, page 415). I'll comment on their recommendations, some of which I agree with, and some I don't, as follows. First, we'll consider Geballe's suggestions :

"Materials should be multicomponent structures with more than two sites per unit cell, where one or more sites not involved in the conduction band can be used to introduce itinerant charge carriers".

¶ This reminds me of the Zintl concept applied to , say , a perovskite , where the metallic bond lies over the supercube framework , but does not include the inert "A" cation . The "A" cation has donated its valence electrons to help form the surrounding MX₃ supercube cage , with its accompanying metallic bond . The chemical approach to high temperature superconductors at that time (and I suppose to the present) , is to have one layer act as the charge carrier – the copper oxide layer , with its diamonds and pyramids – and the layers sandwiching it to contain the spectator cations , which have donated charge to the Cu-O layer ; these are the "charge reservoir" layers , containing the Ba²⁺ , Y³⁺ , Tl(III) , Bi(V) , Hg(II) , and so on . As we have seen , the inert cations such as Ba²⁺ and Y³⁺ are acting in a Zintl manner , while the covalently bonded metal atoms [Tl(III) , Bi(V) , and Hg(II)] are moderate to strong oxidizers , and probably function by polarizing the metallic bond XO .

I have also suggested very simple , isotropic crystal structures , such as for Cu_3Cl , Al_3Cl , and Ni_3O_2 , which aren't layered at all , and have neither Zintl spectator cations nor polarizing oxidizer atoms . The layering feature is not really an essential feature of high temperature superconductors , although it is appropriate for certain systems , of course , such as the copper(II) oxide derivatives , whose stereochemistry is strongly influenced by the Jahn-Teller effect , which tends to give them a "layered" aspect .

"Compositions should be near the metal-insulator Mott transition".

¶ I disagree . Superconductors are true metals , from absolute zero up to their decomposition (or melting) points . They don't have a metal-insulator transition . They do have a superconductor-conductor transition , at T_c . However , even above T_c , they remain true metals and electrical conductors (not very good ones , compared to the metallurgical metals , but still).

"On the insulating side of the Mott transition , the localized states should have spin $-\frac{1}{2}$ ground states and antiferromagnetic ordering of the parent compound".

¶ Yes ! The precursor compound , such as La_2CuO_4 , should be antiferromagnetic , the stronger the better , and should have , in its electronically active metal atoms (Cu) singlet valence electrons (3d⁹) in its frontier orbitals (4p_z) .(I'm liberally translating Geballe's physics into chemistry , using La_2CuO_4 as an example) .

"The conduction band should be formed from antibonding tight-binding states that have a high degree of cation-anion hybridization near the Fermi level . There should be no extended metal-metal bonds".

¶ Yes and no . As the perceptive reader will have noticed , I have made no reference anywhere in this work to antibonding bonds in the metallic solids I have discussed . Why ? Because they are **completely unnecessary** ! Why resort to employing antibonds , which weaken and may even destroy a compound [recall the detonation of poly(sulfur nitride) , $(SN)_x$], when perfectly good bonding bonds are available to account for the metallic bond XO ? Antibonding molecular orbitals (ABMOs) are a very useful concept , and a valid construct of MOT . For example , they are key to explaining bonding in the oxygen and nitric oxide molecules . In metal cation – nonmetal anion extended atomic lattices , though , there are a profusion of valence shell and frontier orbitals that can be used in constructing a bonding crystal orbital – BXO , if you will – for the conduction band in the solid .

 \P I agree with the point about the "cation-anion hybridization near the Fermi level". In chemistry terms, this is the bilayer metallic bond, usually with

the low energy anions' filled valence shell orbitals as the lower layer , and the higher energy cations' frontier orbitals as the upper layer . The Fermi level may occur at the boundary between the two layers . That feature seems to be absent in the bronze metals , which have monolayer XOs , and whose component electrons are "crunched" (distributed) in the Fermi-Dirac distribution . Thus , the black , and possibly gray , metals seemed to have escaped the Fermi-Dirac crunch rather nicely , thanks to their bilayer XO .

¶ I agree with the comment about the absence of extended metal-metal bonds . These are a feature of the Classes 4 and 8 synthetic and molecular metals , the delightful and pretty crystals that , as bronze metals , are a complete failure as high temperature superconductors.

"Structural features that are desirable include two-dimensional extended sheets or clusters with controllable linkage, or both".

¶ As discussed in the section about the cuprates , the two-dimensional Cu-O sheets , such as are found in Nd₂CuO₄ and its derivatives , are probably going to be the source of the highest T_c candidate compounds . However , the sheet geometry implies a square planar coordination of the anions , or ligands , about the metal cations , and this is not the most common coordination for them (except for 3d⁸ and 3d⁹ transition metal cations) ; the octahedral six-fold coordination is probably the commonest cation-anion coordination found across the Periodic Chart . In my approach to designing new metallic solids and superconductor candidate compounds , we can start off with any given crystal structure , then try to find the right chemistry , mixed-valent or otherwise , to create the metallic bond in that lattice . For example , we might obtain excellent results with the black metal antiperovskites , which have isotropic structures , and aren't layered at all .

¶ The mixed-valent cluster-type compounds are the Robin-Day Class IIIA compounds , which as we saw earlier were either insulators or poor semiconductors . The Chevrel phases , which have cluster-like crystal structures , are all very low temperature superconductors (if at all) , to the best of my knowledge . I wouldn't recommend cluster-structured compounds as any sort of superconductor candidate material .

Owens and Poole's recommendations for designing new high temperature superconductors include the following points :

"Materials should be layered , with one or more planes capable of electron or hole conduction ; these are the CuO planes in copper oxide superconductors ."

¶ Yes, the copper(II) oxide-based compounds should be, and are layered, thanks to the Jahn-Teller effect. Other compounds of interest may have layered crystal structures as well, such as those based on the transition metal dichalcogenides (TiS₂, MoS₂, TaS₂, etc.). My point, though, is that the crystallography is of secondary interest. The chemistry (of the metallic bond) will be of primary concern. We always start with the assumption that a compound with any given crystal structure – including layered structures – can be converted into a metallic solid that might, under favorable circumstances, become superconducting at a lowered temperature.

"Localized states in the conduction plane should have a spin of one-half; copper in copper oxide superconductors has a net spin of one-half."

¶ Yes, at least for the copper(II) oxide systems. The substrate precursor (eg. La_2CuO_4) should , and does , have its singlet "ninth" (3d⁹) valence electron pinned in the $4p_z$ frontier orbital, which becomes part of the "conduction plane" when it overlaps with the oxygens' filled $2p_z$ valence shell orbitals to form the bilayer pi XO in the lattice. Doping the insulating La_2CuO_4 with a copper(III) dopant then coverts it into the mixed-valent Class 3 metallic solid, black metal, and superconductor. Other chemical techniques may apply in other chemical systems. For example, the metallic substrate, eg. CaNiN, can be doped with an insulating dopant (eg. LiNiN). Or, it might be possible to include the full triad of cations, appropriate to generating Cooper pairs, directly in the unit formula (eg. the hypothetical Ni_3O_2). I hope this report will cause solid state chemists to look beyond the layered copper(II) oxide compounds as sources of marvelous new metallic solids and superconductors, and to study new materials based on elements from across the Periodic Chart. The cuprates have been very exciting and educational, but we should expand our search beyond them !

"In between the layers of conducting planes, there should be layers of other ions that act as charge reservoirs to dope conducting planes".

¶ Yes, in a limited sense. In the broader sense, we should now understand that the "charge reservoir" layers are actually the receptacles for either the inert spectator cations (eg. Y^{3+} , Ba^{2+}) left over from the Zintl structure formation process, or the covalently-bonded metal atoms, such as Tl(III), Bi(V), Hg(II), and so on, that by virtue of their medium to strong oxidizing power, are capable of polarizing the pi XO metallic bond and thereby greatly promoting its conductivity and superconductivity capacity [as the intercalated SbF₅ does to graphite].

"The concentration of charge carriers in conducting planes should be such that the system is close to a metal insulator transition . In copper oxide superconductors, there is generally a hole concentration where the material is not superconducting but can undergo a metal insulator transition ".

¶ This may be true for the copper(II) oxide superconductors, but it isn't true for all metallic systems. Suppose we dope La₂CuO₄ with the copper(III) dopant LaSrCuO₄. Both the precursor and the dopant are insulators, or at best very poor semiconductors over a wide temperature range. The doped, mixed-valent composite, $La_{1+x}Sr_{1-x}Cu^{(3-x)+}O_4$ (x = 1 \rightarrow 0), will be an electrical conductor and superconductor (T_c ~ 40K) at a point where there are sufficient Cu(II) – Cu(III) interactions to permit valence electron mobility. Over the complete doping progression, from pure La₂CuO₄ to pure LaSrCuO₄, there will be two metal insulator transitions, as the phases change from the "filled" – but insulating – copper(II) precursor, to the "empty", and also insulating copper(III) dopant.

Would this scenario be true for all doped systems ? For example , CaNiN is an excellent conductor over a wide temperature range . Its proposed dopant , LiNiN , is probably an insulator . How close to LiNiN (x = 0) in the suggested mixed-valent , doped composite $Ca_xLi_{1-x}Ni^{(2-x)+}N$, $x = 1 \rightarrow 0$, do we have to go to see if Owen and Poole's recommendation is valid ? By the way , the Ni¹⁺–Ni²⁺–Ni¹⁺ low-valent , mixed-valent triad for superconductivity would occur at x = 0.67 . Might the optimum T_c for the

composite occur roughly at this doping level, rather at higher LiNIN concentrations, as Owen and Poole suggest? And of course, there would be the non-doped "full triad" type of superconductor candidate compounds in which the stoichiometry is fixed. Even YBCO itself has the full high-valent copper triad, with a fixed formula. I regard the above recommendation by Owen and Poole as being imprecise or restrictive, rather than incorrect.

"In undoped material , for example La_2CuO_4 without Sr , [the] material should display antiferromagnetic ordering".

 \P Yes, the stronger the better, at least for the black metals. Unfortunately we cannot expect this for any gray metal materials we wish to investigate.

"In analogy with organic superconductors, superconducting candidates could be one-dimensional materials displaying superconductor fluctuations and metal-insulator transitions. Either subjecting possible superconductors to pressure or doping them with appropriate additives to increase dimensionality, could help".

¶ I suppose this is true, although the highest temperature superconductors have so far been the layered ("two dimensional") cuprates ; and I have discussed a number of isotropic, "three-dimensional" superconductor candidate systems in this study. I haven't discussed pressure effects with metallic solids, because it is an unfamiliar physics topic for me, and because I think that any realistic, "practical" application of superconductors will have to be made at ambient, and not at an elevated, pressure.

To be fair , the recommendations by Geballe and by Owens and Poole were doubtless written with the high T_c cuprate superconductors in mind , while my comments were made taking the broader view of the entire Periodic Chart , and with a much wider choice of crystal structures available than just the layered cuprates . They expressed themselves mostly in physics or semiconductor terms , while I try to stay away from those areas and describe metallic solids and superconductors in a chemistry context . In particular , I have found the orbital model of metallic solids and the metallic bond , using VB and MOT descriptions , indispensable in visualizing these phenomena .

I am mystified why materials scientists persist in trying to describe metallic solids and superconductors in semiconductor language. It's like trying to force a square peg into a round hole [you can do it if the peg is small enough , but even then it's not a snug fit]. I hope that the orbital pictures I have presented of various selected metallic solids , including superconductors , will convince the reader that this is a simpler , clearer , and more practical approach to understanding their remarkable nature . It's also possible to describe the semiconductors (the pseudometals , Classes 5 to 8) in orbital terms .

I also hope that the reader will agree with me that chemists should play a more important role in the development of novel metallic solids and superconductors, not only as laboratory "cooks", but also as their planners, designers, and developers. If at least a few of the ideas presented in this report prove fruitful, I believe a new impetus and momentum will be given to the study of solid state chemistry in general, and especially to that of metallic solids and superconductors. Suffice it to say that I believe the brightest days for rewarding research and exciting new discoveries in these fields are yet to come.

Notes

1. In his excellent textbook <u>Seven Solid States</u> (ref. 14, page 392, his p. 76), Moore has shown how to calculate the ratio of the thermally excited sigma bond electrons in silicon to the number of valence electrons in the bond, using the factor,

 $exp(-\epsilon/2kT)$,

where ε is the band gap for silicon, k is Boltzmann's constant, and T is the absolute temperature of the silicon. At 1000 K, the ratio would be 1.78 x 10^{-3} . The electrical conductivity, σ_T , of a semiconductor at temperature T kelvins, is given by the equation, $\sigma_T = \sigma_0 \exp(-\varepsilon / 2kT)$ [Moore, p. 78]. The term σ_0 is the semiconductor's electrical conductivity at absolute zero.

Moore states , "We can therefore predict that [at 1000 K] an appreciable fraction of electrons (about one in every six hundred) acquire enough thermal energy to jump the band gap . Once in the conduction band they can be accelerated by electric fields and contribute to the conductivity" (pp. 76-77) . So yes , the tunneling of electrons through nodes in covalent bonds does indeed require energy , which is usually obtained from the environment of the solid (that is , heat and light energy) .

2. The picture of positive holes in semiconductors is a key concept in materials science, one I have no intention of usurping with the orbital model of the metallic bond, even though I haven't referred to positive holes in this report. Hall effect experiments on semiconductors prove definitely that the electrical charge in p-doped semiconductors is indeed carried by positive entities (Moore, op. cit., pp. 78-82), and by electrons in n-doped semiconductors.

Recall that thermal promotion of valence electrons from the Si-Si covalent bonds will relocate a small population of 3 s-p valence electrons up to the 4s AOs, which can form a sigma XO in the silicon lattice. Granted, this will be a very thin, tenuous, and feeble metallic bond. The underlying Si-Si covalent bonds, now with holes here and there in them, can also act as a pseudometal's nodal metallic bond. However, the lower energy covalent bonds will have a net positive charge, while the higher energy 4s sigma XO will have a net negative charge. I was wondering could it be that the Hall effect experiments are actually indicating the positive nature of the lower energy nodal XO in which the vast majority of the conduction electrons in silicon are located ?

This interesting idea resonates with the concept of the bilayer metallic bond, which will be developed later in the text . In compounds with recognizable anion and cation contributors to the metallic bond, the lower layer of the XO (usually pi in nature) is contributed by the filled s-p valence shell orbitals from the anions, and is negative in charge. The upper layer of the XO is contributed by the metal cations, and is positive in charge. Since the upper layer is mostly or entirely above the Fermi level – according to

this picture of the bilayer metallic bond – it will be the one contributing to the electrical properties of the compound, including conductivity. The compound should therefore have an experimentally measured positive Hall potential and a positive Hall coefficient, + R (ref. 166, page 415).

In the hypothetical low-valent , mixed-valent anti-ReO₃ compound Al₃Cl (page 351) , with its "upside down" pi XO metallic bond , the electrically active upper layer may be derived from the formula's chloride anion , so in this case measurement of the Hall potential and Hall coefficient "R" for Al₃Cl may result in negative values . If this proved to be the case , we would be tempted to attribute the sign or polarity of the Hall effect values (potential and coefficient) to the net positive or negative charge on the pi XO upper layer (above the Fermi layer) of the compound's metallic bond .

3. I wonder if anyone has plotted the Brillouin surface for a pseudometal (semiconductor) such as silicon, germanium, or gray tin. It would be interesting to see if the surfaces of the individual atoms were connected together somehow, and if so, how. If they aren't connected, would the spaces between the surfaces represent the nodes in their XOs, as described in MOT?

4. In his review article for the generalist , "Carbides" (ref. 156 , page 414) , Hoffmann points out in Figure 2 , p. 319 , that the compound niobium carbide , NbC , has what amounts to a rocksalt structure : both the niobium and carbon atoms have octahedral coordinations with each other in an AB formula . Niobium could conceivably have such an octahedral coordination , even though it has only five usable valence electrons (4d⁴ 5s¹) . But carbon is never known to have an octahedral coordination in any of its compounds . It doesn't have enough valence electrons (2s² 2p²) , nor does it have enough valence or hypervalence shell orbitals to create an octahedral hybrid orbital suitable for covalent bonding with the niobium . A discrete , spherical carbide anion , C⁴⁻ , also seems unlikely .

The answer, as with niobium monoxide, may lie in considering the Nb₆ metal cage octahedrons that occur in the body centered cubic (bcc) crystal structure of the parent niobium metal (Figure 23, page 127). Suppose we

were to place a carbon atom in the center of each of these octahedrons :



Figure 60 : the M3D model of niobium carbide , NbC . The large aqua spheres are niobium atoms , while the small black sphere represents a carbon atom . The heavy black lines stand for Nb-Nb and Nb-C covalent bonds .

If a carbon atom is placed in each of the octahedron centers, we will have a 1:1 stoichiometry in the compound, that is, NbC. The carbons will also have an octahedral coordination by the neighboring niobiums.

How can the native unhybridized carbon orbitals interact and bond with the niobium orbitals ? In the discussion of the electronic structure of niobium monoxide (sketch, page 129), I suggested that the niobium octahedrons were strongly bound by the 4d⁴ valence electrons in the d⁴ square pyramid hybrid orbital. That will still leave the 5s¹ valence electron available for a sigma XO metallic bond in niobium metal. In niobium carbide, it might be possible to continuously overlap the filled, low energy 2s² native orbitals on the carbons with the half filled, higher energy 5s¹ native orbitals on the niobiums, to produce a bilayer sigma XO metallic bond in the compound. There might also be some overlap of the carbons' $2p_{x,y,z}^2$ orbitals with the corresponding $5p_{x,y,z}^0$ orbitals on the niobiums to form a bilayer pi XO (5s¹ orbital electron density could also leak into the 5p AOs), but this would be

a very thin , weak sort of metallic bond . The stronger sigma XO would be the main metallic bond in niobium carbide .

Niobium carbide is indeed a metallic solid . I don't know what its ambient electrical conductivity is , but its superconducting T_c is 10.3 K , so NbC must be a true metal and a Class 1 metallic solid . Niobium nitride , NbN , with a transition temperature of 15.6 K (or 17 K , depending on the reference consulted) , is a similar Class 1 compound . Generalizing , if these AX rocksalt compounds (with "A" a transition metal element , and "X" a nonmetal element) are metallic solids and deep cryogenic superconductors , they will have zerovalent "X" atoms inserted into the centers of A_6 metal cage octahedrons , and will likely also have electronic structures much the same as described for NbC .

5. It might be possible to insert zerovalent nonmetallic atoms into MX_3 host lattices, to prepare interesting new perovskite-like compounds :

				-	
<u>Atom</u>	<u>Atomic Wt.</u>	<u>Covalent Radius</u>	<u>Melting Pt.</u>	<u>Boiling Pt.</u>	Valence Shell
Phosphorus	30.974 g/mol	1.06 A	44 C (wh	ite) 280 C	3s² 3p ³
Arsenic	74.922	1.20	613 (sublimes)		4s ² 4p ³
Sulfur	32.066	1.02	119	445	3s ² 3p ⁴
Selenium	78.96	1.16	217	685	4s ² 4p ⁴
Tellurium	127.60	1.36	450	990	5s² 5p ⁴
Bromine	79.904	1.14	- 7	59	4s ² 4p ⁵
lodine	126.904	1.33	114	185	5s ² 5p ⁵

Possible Nonmetal Atoms for Insertion Into MX₃ Host Lattices

For example : $\frac{1}{2}$ I₂ + AlCl₃ $\xrightarrow{\text{melt together}}$ I⁰AlCl₃ (t = 0.90) . m.p. 114 °C 178 °C (subl.)

Alternately, the product I⁰AlCl₃ might be crystallized from a solution of the

two reagents in an aprotic organic solvent such as carbon disulfide .

That brings to mind an experiment I carried out in 1975, in which iodine was combined with the cyclic polyether, 18-crown-6, to produce acicular orange crystals. The product was identified as I^0 –18-crown-6 by NMR and MS analyses : a zerovalent iodine atom "capped" by the cyclic polyether "crown" (this work was never published).

6. I made a molecular model of the pair of face-sharing AlO₆ octahedra in the corundum crystal structure, as illustrated in Figure 56, page 333. For this purpose I had at hand my old "Framework Molecular Model" kit (Prentice-Hall Inc., Englewood Cliffs, NJ, 1965) from university days. This kit contains metal "jacks" of the tetrahedral, trigonal bipyramid, and octahedral variety (I used only the latter type of jack). The bonds were made with narrow, flexible polyethylene tubes, fitting on the ends of the jacks.

There was considerable strain in the model , with a resultant bowing of the inner bonded tubes . I measured the Al–O–Al bond angles with an old plastic protractor from High School geometry ; these will become the O–Ni–O bond angles in the Ni₃O₂ anticorundum structure . Obviously , because of the appreciable bowing of the plastic tube "bonds" , the measurement is somewhat crude , but the bond strain actually reduced the O–Ni–O bond angle from the unstrained 90° to about 86° . Certainly , the tetrahedral angle (ideal) of 109° 28′ would not have been favored in this face-sharing octahedra structure ; just the opposite : there would have been far too much strain in the model to permit tetrahedral O–Ni–O bond angles . I conclude that the nickel atoms in the hypothetical anticorundum compound Ni₃O₂ would probably be square coordinated by the oxides , although I'm still keeping my fingers crossed about this .

7. I have repeatedly stressed the necessity of having diamagnetic base cations in the triads , and generally in those metallic solids designated as superconductor candidates . A few chemical "tricks" can achieve this . For example , we can try using strong CF ligands , those high in the Spectrochemical Series , such as cyanide , cyclopentadienide , carbon

monoxide, and so on, to coordinate the cations. However, the coordinate covalent compounds fashioned from such metal-ligand combinations are often unsuitable for one reason or another, either as metallic solids or as potential superconductors.

We can also use non-transition metal cations , those with inert gas kernels and that are naturally diamagnetic , to serve as the base cations ; those , for example , in the alkali metal-ammonia electrides . We have also noted that in certain examples of transition metal nonmolecular [extended atomic lattice] compounds , the nonmetal atoms have "squashed" the high spin cations into a low spin configuration ; for example the iron cations in iron pyrites , FeS_2 , are diamagnetic , as are those in the metallic iron monophosphide , FeP . We also know that if certain transition metal cations can be coordinated in a certain way , they will be low spin diamagnetic , and not high spin Curie paramagnetic (or other) . For example , square planar nickel(II) is always low spin , while octahedral nickel(II) always has a high spin configuration . Finally , certain coordinating atoms seem to have an almost "magical" (not fully understood !) effect on paramagnetic transition metal compounds , reshaping their electronic structures . The selenide anion , Se^{2-} , is quite notable in this respect , inducing antiferromagnetism in certain compounds .

In my study of the chemistry of superconductors I have noted an interesting physical effect that might also be employed by the chemist to force high spin transition metal cations into a low spin state . I have named this phenomenon the **Hagenmuller effect** after a prominent solid state chemist who observed its remarkable effects in his experimental work .

In 1974, a team of French researchers at the Université de Bordeaux, led by Professor Paul Hagenmuller, reported on the electrical and magnetic effects in a series of cobalt(III) ternary compounds (ref. 167, page 416). These perovskites, of a distorted symmetry, had the general formula $LnCoO_3$, where "Ln" was a trivalent rare earth cation, such as Y^{3+} , La^{3+} , Lu^{3+} , and Gd^{3+} ; they were the "A" cations in the structure. Striking effects in the electrical and magnetic properties of the compounds were noted, in varying the "A" cations. Hagenmuller and his co-workers suggested that a transition in the electronic configuration of the cobalt(III) "M" cation was causing the

corresponding transitions in the electrical and magnetic properties experimentally observed , from the high spin to low spin state .

"A" Cation	Cation Radius	TransitionTemp.	<u>"a" Length</u>
La ³⁺	1.30 Å	below 100 K	5.379 Å
Gd^{3+}	1.19	270	5.228
Y^{3+}	1.16	~ 440	5.137
Lu ³⁺	1.12	~ 540	5.065

The following four transition temperatures were determined for ACoO₃ :

The cation radii are per Shannon-Prewitt, for eight-coordination; data for the transition temperatures were from ref. 169, Tableau III, p. 207. Lattice constants data were from Tableau I, p. 203, and Tableau II, p. 204.

A graph of the magnetic susceptibilities of $YCoO_3$ and $LuCoO_3$ from about 77 K (liquid nitrogen) to almost 900 K is presented in Figure 6, p. 206 of ref. 169. It certainly looks to me like these two compounds are antiferromagnetic, with Néel temperatures corresponding to the transition temperatures noted above for Y^{3+} (440 K) and Lu^{3+} (540 K). It seems that above these temperatures, the cobalt(III) cations in the compounds are in a high spin $[t_{2g}^4 e_g^2, ** ** * dsp^2 - sp_z]$ configuration, while below T_N they gradually begin to change into a low spin state $[t_{2g}^6 e_g^0, ** ** ** d^2sp^3]$ as the compounds are cooled down. Their magnetic susceptibilities thus gradually decline with deeper cooling. Above T_N the susceptibilities also decline because of the randomizing effect on the magnetic spin moments by the increasing phonon amplitudes with heating.

The Hagenmuller effect arises here because of the influence of the "A" cation size on the transition temperature . As you can see in the tabulation above , there is a rough inverse correlation between the crystal ionic radius and the observed transition temperature , which magnetically is expressed as the Néel temperature of the antiferromagnetism in the cobalt compounds . The smaller the cation size , the higher T_N is . We also note that there is a direct correlation between the "A" cation size and the unit cell length , "a".

Naturally , this observation immediately caught my attention as a physical "trick" to induce spin pairing and diamagnetism in the base cations of transition metal compounds . By using smaller and smaller "A" cations in perovskites , we can cause the MX_3 framework to shrink around them to a greater and greater extent , eventually forcing the "M" transition metal cation into a low spin configuration . The CoO₃ framework shrinkage with smaller "A" cation radii is shown in the tabulation on the preceding page . A point is reached where the low spin configuration of the 3d⁶ valence shell electrons in cobalt (III) , which is physically smaller and denser than the high spin state , becomes more energetically favorable as the cobalt "M" cations are compressed by the surrounding oxides .

The practical value of the Hagenmuller effect may be considerable in superconductor design and synthesis . The high temperature superconductors have undoubtedly benefited from the physical effect of using small rare earth spectator cations , such as Y^{3+} , in formulations ; for example ,

$$\begin{split} YBa_2Cu_3O_7 \hdots r = 1.16 \mbox{ \AA }; \ a = 3.86 \mbox{ \AA }; \ T_c = 93.3 \mbox{ K }; \\ LaBa_2Cu_3O_7 \hdots r = 1.30 \mbox{ \AA }; \ a = 3.94 \mbox{ \AA }; \ T_c = 59.2 \mbox{ K }. \end{split}$$

On the following page I have presented a rough graph of the crystal ionic radii of the rare earth cations "M" in the YBCO family of high temperature superconducting cuprates , $MBa_2Cu_3O_7$, versus the transition temperatures of the corresponding compounds . The data were taken from Table VII-2 , p. 125 , of ref. 12 (Poole , Datta , and Farach's textbook) , page 391 . There is an approximately linear correlation between the cations' radii and their compounds' T_c values . Admittedly , I am guilty of "data selectivity" here , choosing – for graphical clarity , of course ! – the better behaving points , while ignoring the repetitive ones , or the "misbehaving" data set , that of the lutetium cation (r = 1.12 Å , T_c = 72.6 K).

The Hagenmuller effect may be a general sort of phenomenon found across the breadth of solid state chemistry. It may strongly influence magnetic effects such as antiferromagnetism, as we have seen. In a practical sense, the Hagenmuller effect could be fruitfully employed by researchers in controlling magnetic and electrical effects in crystalline solids, as in the $LnCoO_3$ and $MBa_2Cu_3O_7$ series of compounds . We should certainly keep it in mind as we pursue our studies of the chemistry of metallic solids and superconductors .



This graph concerns the $MBa_2Cu_3O_7$ series of high temperature superconducting compounds , with "M" being a trivalent rare earth spectator cation . The following sets of data points were selected for the graph ; the transition temperatures were from Poole , Datta , and Farach's book (ref. 12 , op. cit.) :

$$Y^{3+}$$
, 1.16 Å, 93 K;
 Dy^{3+} , 1.17 Å, 92 K;
 Gd^{3+} , 1.19 Å, 91 K;
 Sm^{3+} , 1.22 Å, 87 K;
 Nd^{3+} , 1.25 Å, 78 K; and 1.23 Å, 59 K.

8. I found the following redox half-reaction for $Re(VI) \rightarrow Re(IV)$ in Bard's electrochemistry encyclopedia (ref. 168, page 416):

 $\text{ReO}_3 + 2 \text{H}^+ + 2\text{e}^- \longrightarrow \text{ReO}_2 + \text{H}_2\text{O} ; \text{E}_{\text{red}}^0 = 0.400 \text{ V}$.

This standard reduction potential was reported in the tabulation of possible MX_3 host structures for zerovalent atom insertion, on page 279. Rhenium(VI) is thus a relatively mild oxidizer, suggesting only a weak polarization of the bilayer Re-O pi XO metallic bond in the extraordinary electrical conductor, ReO₃.

9. It might be possible to design a series of zinc shishkebab metallic solids . Chern and DiSalvo at Cornell University prepared the novel shishkebab structures CaNiN, discussed earlier (page 338), and Ca₂ZnN₂. The latter compound proved to be insulating and diamagnetic (ref. 169, page 416), which isn't surprising, since the valences are all normal in the material, and there are no "extra" valence electrons promoted into frontier orbitals where they might form a metallic bond. It was synthesized as follows :

$$2/3 \text{ Ca}_3\text{N}_2 + 2\text{n}^0 + 1/3 \text{ N}_2(\text{g}) \xrightarrow{\text{nitrogen atmosphere}} \text{Ca}_2\text{ZnN}_2$$

This compound could probably be made more simply by a solid state metathesis reaction between the "ordinary" reagents $2 \text{ CaCl}_2 + 2n\text{Cl}_2 + 2 \text{ Li}_3\text{N} \longrightarrow \text{Ca}_2\text{ZnN}_2 + 6 \text{ LiCl [extract with methanol]}.$

The zinc atoms form long straight Zn–N chains with the nitride anions, so Ca_2ZnN_2 can be considered as a shishkebab compound. Its **metallic** analogue might be prepared by inserting another zinc atom into its lattice :

$$\frac{1}{2} \operatorname{Ca}_2 \operatorname{ZnN}_2 + \frac{1}{2} \operatorname{Zn}^0 \xrightarrow{\text{shake-n-bake}} \operatorname{CaZnN}_{\text{argon atmosphere}}$$

The zinc in this latter compound has a formal valence of 1+, which

corresponds to an electronic configuration of $4s^1$. However, with a linear sp_x coordination, the extra valence electron (above the Zn^{2+} base kernel with the $3d^{10}$ electron shell) should be located in the $4p_{y,z}$ frontier orbitals, which can overlap with the corresponding $2p_{y,z}$ valence shell orbitals on the linear nitride linking anions (sketch, top of page 337). The bilayer pi XO metallic bond will form over the Zn-N chains from this 2p-4p overlap.

The zinc(II) analogue compound, which should be insulating and diamagnetic, is LiZnN, similar to the LiNiN discussed earlier (page 340), and prepared in an analogous manner :

solid state

$$Li_3N + ZnCl_2 \longrightarrow LiZnN + 2 LiCl$$

m.p. 813 °C 283 °C metathesis 605 °C

The series of mixed-valent zinc composites would be prepared by doping the metallic CaZnN with increasingly larger mole fractions of the insulating dopant LiZnN :

These doped composites with mixed-valent, low-valent zinc should be Class 3 metallic solids, and would be possible superconductors. However, as gray metals, their transition temperatures would probably fall in the 25-50 K range, and they couldn't really be classified as high temperature superconductors.

It would be most interesting to compare them with the corresponding nickel composites (page 340). Nickel is in the "black metal" region of the Periodic Table , and we might be able to prepare novel high temperature superconductor compounds with electronically active nickel atoms . This is true , I think , when oxide anions are used in the compounds . But what about nitride anion compounds , such as the composites $Ca_xLi_{1-x}Ni^{(2-x)+}N$? Would they also be black metals with relatively high superconductor transition temperatures ? Experiment and see !

10. The lattice compound barium titanate , $BaTiO_3$, is a well-known commercial material with numerous industrial applications derived from its pronounced ferroelectric and piezoelectric properties (ref. 170, page 416). We would expect that $BaTiO_3$, with its AMX₃ formula and large "A" central cation , would be a perovskite , and this is indeed the case . Its tolerance factor "t" in the Goldschmidt equation is calculated to be 0.99 , so we would predict its unit cell to have a cubic symmetry .

This is partly true . It actually has four different symmetries over a wide temperature range . Only above 130 °C (its Curie temperature) does it have a cubic symmetry . Below that temperature to 5 °C , the crystal structure is tetragonal ; from 5 °C to -90 °C it is orthorhombic ; and finally , below -90 °C it has a rhombohedral symmetry :



Why does the crystal structure of BaTiO₃ distort from the ideal cubic symmetry as it is cooled down from 130 °C ? First , we recognize that BaTiO₃ is a Zintl structure , in the general sense of that term . The TiO₃ supercube framework around the inert Ba²⁺ spectator cation is covalently bonded , as no discrete Ti⁴⁺ cation can exist . As an early transition metal element , titanium would be expected to use its 3d valence shell orbitals to the maximum extent in its covalent bonding to oxygen . The d⁵s hybrid atomic orbital is thus the likely candidate for use by the titanium(0) atoms ,

having the $3d^2 4s^2$ electronic configuration , in forming an octahedral bonding architecture for the TiO₃ supercube skeleton .

In the cubic symmetry perovskite , there are six Ti-O covalent bonds per unit formula , requiring twelve valence electrons for completion . The titanium(0) atom places its four valence electrons , plus the two 6s² valence electrons from the barium(0) atom , in each of the six sigma bonding lobes of the d⁵s hybrid orbital . Each of the three oxygen ligands has two singlet electrons in their linear sp_x hybrid orbitals : $\sigma_a^{-1} \sigma_b^{-1} 2p_y^{-2} 2p_z^{-2}$. The oxygen links polymerize with the titanium atoms to form the TiO₃ skeletal structure , with the barium cations nesting in the supercube centers .

Below 130 °C bond strain in the framework becomes excessive , with the heterolysis of an axial set of Ti-O bonds , one per unit formula , to form a layer of axial oxides : $Ti-O-Ti \rightarrow Ti-O^- + Ti$. We thought this might be happening in the tetragonal form of tin(III) phosphide (page 163) , and possibly in the distorted variants of CsSnBr₃ (page 287) . The five-coordinated titanium atom in the distorted structure can use the d⁴s hybrid orbital (page 64) to form the tetragonal pyramid geometry in the resulting layered architecture . It will require eleven valence electrons [4 Ti + 5 O + 2 Ba] : ten for the five Ti-O covalent bonds per unit formula , plus the eleventh electron to make the axial oxygen atom an oxide anion .

There are , in effect , three inert pairs of electrons on the oxide anions that tend to be stereochemically voluminous , and they repel the atoms immediately above it . At the same time , the oxygens try to remain clustered around the barium cation as closely as possible . This causes a buckling or kinking of the TiO_3 skeletal framework around the barium cations , resulting in a distortion of the cubic unit cell into the elongated tetragonal form (see Figure 61 on the next page).

It is generally thought that the distortion from cubic symmetry in the ambient tetragonal form of barium titanate is what induces the electric dipoles in the Ti-O bonds, and causes the material to be ferroelectric, and piezoelectric under pressure. In this chemical picture, though, we see that in the cubic form the anionic charge is evenly distributed over the TiO_3



Figure 61 : the M3D model of the tetragonal form of barium titanate , BaTiO₃ (stable from 5–130 °C) . The small red spheres are titanium(IV) atoms ; the green spheres represent oxygen atom covalent links ; and the large violet spheres stand for barium spectator cations . The solid black lines are Ti-O covalent bonds . This model was based on Figure 3.5 , p. 112 , in Ball's nice book about solid state science , <u>Made to Measure</u> (ref. 171 , page 417) .

framework . In the tetragonal form , the anionic charge becomes concentrated in the layer of axial oxides in which the barium cations are nested . The shift of anionic charge distribution , and its proximity to the positive barium centers in the tetragonal form , may account for the electric dipoles in the material , and its piezoelectric behavior under pressure .

As to why this tetragonal distortion occurs in $BaTiO_3$, we have only to look at $SrTiO_3$ (t = 0.94), which is a cubic symmetry perovskite at ambient temperature. Perhaps the barium cation is just a little too large to fit comfortably in the TiO₃ supercube. At higher temperatures, the TiO₃ "cage" around the barium cation expands , and the Ti-O bond strain decreases , but as the compound is cooled , the cage contracts to the point where the axial Ti-O bonds break and the layering appears . It is thus quite interesting to look at the crystallography and distortion of barium titanate from a chemical bonding point of view .

11. If a single carbon monoxide ligand could be displaced from the $Ni(CO)_4$ substrate by the growing metallic bond, it might then be possible to form a synthetic metal stack compound from the sp² trigonal planar Ni(CO)₃ units :



Here , the aqua spheres are Ni(0) atoms , $3d^{10}$; the black and red spheres are carbon and oxygen atoms respectively , triply bonded to form the CO ligands . The solid black lines are covalent bonds ; the dashed lines are the Ni-Ni $3d_z^2$ sigma XO metallic bond in the stacks . The nickel atoms are partially oxidized in the electrocrystallization to Ni^{x+}(A¹⁻)_x, where "A" is an anion such as BF₄⁻ or PF₆⁻, and x is a mole fraction found experimentally from $0 \rightarrow 1$. The anions and any solvent molecules of crystallization are omitted from the M3D model for the sake of clarity . Another possible Ni(0) substrate might be the cyano complex Li⁺[Ni(CO)₂CN]⁻, by analogy with the proposed anionic iron compound , Li⁺[Fe(CO)₃CN]⁻ (page 104) .

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