## Presentation of a research project Searching for Room Temperature Superconductors



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This paper in form of a presentation comprises 186 pages, a content overview, and can be downloaded as pdf via the following link (file size about 11 MB ):
https://novam-
research.com/resources/Research_Project_Room_Temperature_Superconductors.pdf

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Notes:
References to specific pages or parts in this paper appear in red color such as "see page 67" or "see part 1.4". That facilitates their adjustment in case of a modified or updated version of this presentation
The most common units of temperature T are K (Kelvin) and ${ }^{\circ} \mathrm{C}$ (degree Celcius).
They are related by a simple conversion formula, namely
$\mathrm{T}[\mathrm{K}]=\mathrm{T}\left[{ }^{\circ} \mathrm{C}\right.$ ] + 273 K

## Preface

The interesting and fascinating physical phenomenon of superconductivity appears, until now, only at very low temperatures and therefore its technical application is limited to relatively few areas. If it is possible to create materials which are superconducting at room temperature, then this could initiate a revolution in science and technology. This slide set presents some basics, research results, ideas, hypotheses and approaches

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1.1 Introduction
1.2 Applications
1.3 Superconductivity as a quantum physical phenomenon
1.4 Verification of superconductivity by zero resistance and the so-called Meissner effect \& Levitation / suspension of a superconductor in an inhomogeneous magnetic field
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1.6 Do man-made room temperature superconductors already exist?

## 1 Superconductivity

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## Superconductivity is a special physical phenomenon of some materials which appears below a material-specific low temperature $T_{c}$

- The superconducting state shows several special features such as
- Electrical DC resistance disappears, i.e. lossless DC current transport
- Superconductor levitates above magnets or vice versa


Image from
https://flatworldknowledge.lardbucket.org/books/principles-of-general-chemistry-v1.0m/s16-07-superconductors.html

- Superconductivity is very interesting for science, research, and technology
- Cooling down to low temperatures is inconvenient
$\rightarrow$ Desirable is a $T_{c}$ which is as high as possible
- For decades the alloy $\mathrm{Nb}_{3} \mathrm{Ge}$ was that material with the highest $\mathrm{T}_{\mathrm{c}}$, namely $23 \mathrm{~K}\left(-250^{\circ} \mathrm{C}\right)$, and the search for materials with higher $\mathrm{T}_{\mathrm{c}}$ was unsuccessful


## Superconductivity - 1986 surprising breakthrough in Switzerland concerning higher $T_{c}$ and type of materials

- J. G. Bednorz and K. A. Mueller from the IBM Zurich Research Laboratory discovered in oxides $(\mathrm{La}, \mathrm{Ba})_{2} \mathrm{CuO}_{4}$ superconductivity with $\mathrm{T}_{\mathrm{c}}=35 \mathrm{~K}\left(-238^{\circ} \mathrm{C}\right)$, i.e. $12 \mathrm{~K}\left(12^{\circ} \mathrm{C}\right)$ higher than that of $\mathrm{Nb}_{3} \mathrm{Ge}$. For their discovery they received in 1987 the Nobel Prize in physics.

K. A. Mueller and
J. G. Bednorz
- Worldwide avalanche of research activities of unprecedented extent
$\Rightarrow$ Discovery of further oxides with higher $T_{c}$ which are likewise based on copper $(\mathrm{Cu})$, e.g. $\mathrm{YBa}_{2} \mathrm{Cu}_{3} \mathrm{O}_{7-\delta}$ with $\mathrm{T}_{\mathrm{c}}=91 \mathrm{~K}\left(-182^{\circ} \mathrm{C}\right)$ which can be cooled by liquid nitrogen $(77 \mathrm{~K})\left(-196^{\circ} \mathrm{C}\right)$ in a relatively simple and cost-effective way
$\Rightarrow$ March 1987 in the New York Hilton Hotel: Meeting of about 2000 physicists owing to superconductivity, known as "Woodstock in Physics". Wave of enthusiasm due to superconductivity !

Nobel lecture of J. G. Bednorz and K. A. Mueller: https://www.nobelprize.org/uploads/2018/06/bednorz-muller-lecture.pdf

## Crystal structure (crystallographic unit cell) of the high $-\mathrm{T}_{\mathrm{c}}$ superconductor $\mathrm{YBa}_{2} \mathrm{Cu}_{3} \mathrm{O}_{7-\delta}$

- Layered crystal structure
- $\mathrm{T}_{\mathrm{c}}=91 \mathrm{~K}\left(-182^{\circ} \mathrm{C}\right)$ and thus its superconductivity can be maintained in a relatively simple and cost-effective way by using liquid nitrogen which has a temperature of $77 \mathrm{~K}\left(-196^{\circ} \mathrm{C}\right)$
- $T_{c}$ depends on the oxygen deficiency $\delta$. The highest $T_{c}$ is obtained for $\delta \approx 0.07$


## (Superconducting) Materials - Metals or metallic alloys versus oxides

Examples of flexible manifestations of the metal and chemical element niobium ( Nb ) which is also a conventional or classical low- $\mathrm{T}_{\mathrm{c}}$ superconductor with $\mathrm{T}_{\mathrm{c}}=9 \mathrm{~K}\left(-264^{\circ} \mathrm{C}\right)$. If it is needed in the superconducting state, then it will be cooled by liquid helium whose temperature is $\mathrm{T}=4 \mathrm{~K}=-269^{\circ} \mathrm{C}$


Niobium wire (1)


Niobium foil (2)

Image sources: (1) http://www.chemistrylearner.com/wp-content/uploads/2017/11/Niobium-Wire.jpg
(2) https://5.imimg.com/data5/SELLER/Default/2021/4/KH/PN/UC/583179/niobium-foil.jpg

Such flexible manifestations does not exist for oxides because oxides are brittle ceramic materials ...
(Superconducting) Materials - Metals or metallic alloys versus oxides

## Examples of manifestations of oxides



Crystals

Thin film, thickness e.g. 120 nm


Thin films and heterostructures


Powder


Polycrystalline parts made of powder which was pressed or molded, sintered, and, if necessary, machined


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## Superconductivity - Applications

Areas of applications depend on the chemical and mechanical properties of the superconducting material (raw materials, preparation, processing ...) and the specific features of the superconducting state
Examples of already realized or potential applications of superconductors:

- Measurement and sensor technology: Detection of very weak magnetic fields, e.g. for materials testing, searching for ores, medicine
- Motors (e.g. for ship propulsion)
- Magnetic levitation trains
- Strong electromagnets (e.g. for separation of ores)
- Cables for current transport
- Electronics or superconducting electronics in general
- Microwave filters
- Generators
- Cables for current transport
- Computer technology
- Electrical engineering in general

Examples of papers:

- Search for New Very High Temperature Superconductors From an Applications Perspective, M. R. Beasley, IEEE Transactions on Applied Superconductivity $\underline{23}$ (2013) , http://dx.doi.org/10.1109/TASC.2013.2241173
- High-Temperature Cuprate Superconductors Get to Work, A. P. Malozemoff, J. Mannhart, and D. Scalapino, Physics Today 4 (2005) 41 - 47


## Superconductivity - Applications

An example of applications of classical low- $T_{c}$ superconductors is a so-called SQUID magnetometer which is used for the measurement of magnetic properties of materials. SQUID stands for Superconducting QUantum Inteference Device and it allows the detection of small magnetic moments of a sample which is placed in an external magnetic field.


SQUID magnetometer MPMS3 from the company Quantum Design in a lab of the Department of Materials of the ETH Zurich. Image from https://dx.doi.org/10.3929/ethz-a-010817148

Among others a SQUID magnetometer comprises a superconducting magnet which generates the external magnetic field and a SQUID. These both components are made of the chemical element niobium ( Nb ) which is a metal and superconducting below $9 \mathrm{~K}\left(-264{ }^{\circ} \mathrm{C}\right)$. Therefore the superconducting magnet and the SQUID are cooled by liquid helium whose temperature is $4 \mathrm{~K}\left(-269{ }^{\circ} \mathrm{C}\right)$. The SQUID magnetometer which is shown in the picture is extensively presented in part 13 of a publication whose doi link is provided on the left

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## Superconductivity - A quantum physical phenomenon

- Superconductivity does not only mean DC resistance $\mathrm{R}=0$ but comprises other phenomena, e.g. special magnetic properties like the so-called Meissner effect (see part 1.4 ), which cannot be explained solely by $\mathrm{R}=0$
- For the verification of superconductivity see part 1.4
- Peculiar quantum physical state of the so-called conduction electrons
- Conduction electrons: delocalized - responsible for the metallic behavior of the electrical resistivity - energetically located in close vicinity to the highest occupied states / energies, i.e. in the vicinity of the so-called Fermi energy
- Conduction electrons form pairs, so-called Cooper pairs, which consist of 2 electrons
- Cooper pairs form a coherent state (Bose-Einstein condensation) so that the electrons have a strong tendency to behave in the same manner or to stay in the same state
- Pair formation requires an attractive interaction between the electrons which usually repel each other because of their negative electric charge ...


## Superconductivity - A quantum physical phenomenon

- Attractive interaction under special conditions which are realized in some materials
- e.g. via the so-called electron-phonon interaction, i.e. the interaction between negatively charged electrons and the oscillations of the positively charged ions of the crystal lattice
- Another possibility via electron-electron interactions at the so-called excitonic superconductivity, see part 2.3.3
- Another suggestion: Superconductivity as a condensate of ordered zero-point oscillations of the conduction electrons

See paper by B. V. Vasiliev, published in arxiv.org as arXiv:1009.2293v5 [physics.gen-ph] 13 October 2011: https://arxiv.org/PS_cache/arxiv/pdf/1009/1009.2293v5.pdf
See also https://arxiv.org/abs/1009.2293 and an article published in Physica C 471 (2011) 277.
Thanks to Dr. Felix Scholkmann for the communication of this paper

- For many superconductors, escpecially for the Cu-based high- $T_{\mathrm{c}}$ superconductors, it is not yet clarified how the superconductivity comes about

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The verification of superconductivity: The first of two essential features

## Zero resistance

DC current I through sample: Measurement of voltage drop $U$ at various temperatures

resistance $R=\frac{U}{I}$
specific resistance or resistivity $\rho=R \frac{A}{L}$

current density $j=\frac{I}{A} \quad L=$ length $\quad A=$ cross sectional area
Notes: For I > $\mathrm{I}_{\mathrm{c}}$ or $\mathrm{j}>\mathrm{j}_{\mathrm{c}}$ the superconductivity disappears
$\mathrm{I}_{\mathrm{c}}$ or $\mathrm{j}_{\mathrm{c}}$ is the so-called critical current or critical current density
For example, for $\mathrm{YBa}_{2} \mathrm{Cu}_{3} \mathrm{O}_{7-\delta}$ the critical current density $\mathrm{j}_{\mathrm{c}}$
at $\mathrm{T}=77 \mathrm{~K}\left(-196{ }^{\circ} \mathrm{C}\right)$ is of the order of $10^{6} \mathrm{~A} / \mathrm{cm}^{2}$

## The verification of superconductivity: The second of two essential features

## Meissner effect

Cooling down of the sample in an external static magnetic field H : Below $\mathrm{T}_{\mathrm{c}}$ superconducting currents emerge in a thin surface layer of the sample. These currents create a negative magnetic moment M , i.e. M is antiparallel to H which is called diamagnetic behavior. This magnetic moment M generates an associated magnetic field which is exactly opposite to H
 so that the total interior field of the sample vanishes. This so-called Meissner effect results from a peculiar quantum physical state of the conduction electrons and cannot be explained solely by a DC resistance $\mathrm{R}=0$
Notes:

- The levitation of a superconductor above a magnet or vice versa, see pages 1, 10, and 24-32, is due to the fact that a superconductor is a strong diamagnet. Levitation in static magnetic fields without supply of energy is possible by a diamagnetic body in a spatially inhomogeneous magnetic field. See, for example, the paper "Levitation in Physics" by E. H. Brandt in Science $\underline{243}$ (1989) 349 - 355
- For $\mathrm{H}>\mathrm{H}_{\mathrm{c}}$ or $\mathrm{H}_{\mathrm{c} 2}$ the superconductivity disappears. $\mathrm{H}_{\mathrm{c}}$ (for so-called type I superconductors) or $\mathrm{H}_{\mathrm{c} 2}$ (for so-called type II superconductors) is the so-called critical field. For example, for $\mathrm{YBa}_{2} \mathrm{Cu}_{3} \mathrm{O}_{7-\delta}$ the critical field $\mathrm{H}_{\mathrm{c} 2}$ at $\mathrm{T}=-196{ }^{\circ} \mathrm{C}$ is of the order of 10 Tesla. For comparison: The earth's magnetic field is of the order of $5 \times 10^{-5}$ Tesla $=0.5$ Gauss ( 1 Tesla $=10^{4}$ Gauss)


## The Meissner effect / strong diamagnetism and the so-called flux pinning

 allows a superconductor to levitate in an inhomogenous magnetic field

Text on the right and images from Levitation in physics, E. H. Brandt, Science 243 (1989) 349 - 355 https://doi.org/10.1126/science.243.4889.349

Disks (12 mm in diameter) of the oxide superconductor $\mathrm{YBa}_{2} \mathrm{Cu}_{3} \mathrm{O}_{7-\delta}$ levitate above a permanent magnet with one central north pole and four south pole sections. The vertical and horizontal inhomogeneity of the magnetic field in connection with the pinning of magnetic flux lines inside the superconductor causes strong friction that damps oscillation and rotation of the disk and holds it rigidly levitated within a continuous range of possible stable positions and orientations.

The Meissner effect / strong diamagnetism (and so-called flux pinning) allows a superconductor to levitate in an inhomogenous magnetic field


Text on the right and images from Levitation in physics, E. H. Brandt,
Science 243 (1989) 349 - 355
https://doi.org/10.1126/science.243.4889.349

Top: Levitation of a type I superconductor in the perfect Meissner state above permanent magnets of cylindrical or other symmetry. A type I superconductor has only one stable equilibrium position and may oscillate or orbit about it without damping. Bottom: Levitation of a type II superconductor above or below the same permanent magnet. A range of stable equilibrium positions and orientations exists as a result of hysteresis effects caused by flux-line pinning. The levitated sample expels part of the magnetic flux (internal field $\mathrm{H}_{\text {int }}<$ external field H ). The suspended sample attracts magnetic field lines because some flux is trapped in it $\left(\mathrm{H}_{\text {int }}>\mathrm{H}\right)$ in an inhomogenous magnetic field


Pouring liquid nitrogen ( $\mathrm{T}=77 \mathrm{~K}=-196{ }^{\circ} \mathrm{C}$ ) into a polysterene box

Image source: Screenshot from the video "Superconductors and Magnets: Introduction to the Superconductor": https://www.youtube.com/watch?v=n0bf4hSFt7E
See also playlist "UC San Diego Physics: Superconductors and Magnets": https://www.youtube.com/playlist?list=PLyCuHjHss4f0hN1DIcZAJ2kiLG7KrSoe7

## Levitation / suspension of a superconductor in an inhomogenous magnetic field



Putting a disk into the polysterene box. The disk is made of a so-called high- $T_{c}$ superconductor with $\mathrm{T}_{\mathrm{c}}>77 \mathrm{~K}$, for example $\mathrm{YBa}_{2} \mathrm{Cu}_{3} \mathrm{O}_{7-\delta}$

Image source: Screenshot from the video "Superconductors and Magnets: Introduction to the Superconductor": https://www.youtube.com/watch?v=n0bf4hSFt7E
See also playlist "UC San Diego Physics: Superconductors and Magnets": https://www.youtube.com/playlist?list=PLyCuHjHss4f0hN1DlcZAJ2kiLG7KrSoe7 in an inhomogenous magnetic field


Removing the liquid nitrogen cooled superconductor from the polysterene box

Image source: Screenshot from the video "Superconductors and Magnets: Introduction to the Superconductor": https://www.youtube.com/watch?v=n0bf4hSFt7E
See also playlist "UC San Diego Physics: Superconductors and Magnets": https://www.youtube.com/playlist?list=PLyCuHjHss4f0hN1DlcZAJ2kiLG7KrSoe7

Levitation / suspension of a superconductor in an inhomogenous magnetic field


Superconductor levitates in an inhomogeneous magnetic field which is generated by an array of six permanent magnets

Image source: Screenshot from the video "Superconductors and Magnets: Introduction to the Superconductor": https://www.youtube.com/watch?v=n0bf4hSFt7E
See also playlist "UC San Diego Physics: Superconductors and Magnets": https://www.youtube.com/playlist?list=PLyCuHjHss4f0hN1DlcZAJ2kiLG7KrSoe7

## Levitation / suspension of a superconductor in an inhomogenous magnetic field



Turning the array of six permanent magnets by 90 degree results in a situation where the superconductor is suspended from the side

Image source: Screenshot from the video "Superconductors and Magnets: Introduction to the Superconductor": https://www.youtube.com/watch?v=n0bf4hSFt7E
See also playlist "UC San Diego Physics: Superconductors and Magnets": https://www.youtube.com/playlist?list=PLyCuHjHss4f0hN1DlcZAJ2kiLG7KrSoe7

## Levitation / suspension of a superconductor in an inhomogenous magnetic field



Turning the array of six permanent magnets by further 90 degree results in a situation where the superconductor is suspended from above

Image source: Screenshot from the video "Superconductors and Magnets: Introduction to the Superconductor": https://www.youtube.com/watch?v=n0bf4hSFt7E
See also playlist "UC San Diego Physics: Superconductors and Magnets": https://www.youtube.com/playlist?list=PLyCuHjHss4f0hN1DIcZAJ2kiLG7KrSoe7 in an inhomogenous magnetic field

## superconductor positions if suspended...


from below

from the side

from above

$$
\begin{gathered}
\text { Magnetic Force }=F_{\text {mag }} \\
\text { Gravitational Force }=F_{g}
\end{gathered}
$$

Image source: Screenshot from the video "Superconductors and Magnets: Introduction to the Superconductor": https://www.youtube.com/watch?v=n0bf4hSFt7E See also playlist "UC San Diego Physics: Superconductors and Magnets": https://www.youtube.com/playlist?list=PLyCuHjHss4f0hN1DIcZAJ2kiLG7KrSoe7

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## Superconducting materials with a relatively high transition temperature $T_{c}$

- The Cu -based oxide material $\mathrm{Hg}_{0.8} \mathrm{Tl}_{0.2} \mathrm{Ba}_{2} \mathrm{Ca}_{2} \mathrm{Cu}_{3} \mathrm{O}_{8+\delta}$ has a layered crystal structure and a superconducting transition temperature $\mathrm{T}_{\mathrm{c}}=138 \mathrm{~K}\left(-135^{\circ} \mathrm{C}\right)$ P. Dai et al., Physica C $\underline{243}$ (1995) 201-206, https://doi.org/10.1016/0921-4534\(94\)02461-8 See also A. Schilling et al., Nature 363 (1993) 56 - 58 , https://doi.org/10.1038/363056a0 Presently (September 2023) this is still that material with the highest established $T_{c}$
- Indications for superconductivity with $\mathrm{T}_{\mathrm{c}} \approx 90 \mathrm{~K}\left(-183^{\circ} \mathrm{C}\right)$ in the system $\mathrm{Na}-\mathrm{W}-\mathrm{O}$ : Superconducting islands on the surface of Na -doped $\mathrm{WO}_{3}$
S. Reich and Y. Tsabba, The European Physical Journal B $\underline{9}$ (1999) 1
A. Shengelaya et al., The European Physical Journal B 12 (1999) 13
S. Reich et al., Journal of Superconductivity 13 (2000) 855
- Strong experimental evidence for high- $T_{c}$ superconductivity without Cu
- In spite of many efforts the superconducting phase could not be identified
- Related to the publications about Na -doped $\mathrm{WO}_{3}$ : Indications for filamentary superconductivity - which implies a small volume fraction - with $\mathrm{T}_{\mathrm{c}}=80 \mathrm{~K}$ in $\mathrm{WO}_{2.9}$ which is a Magneli phase $\mathrm{W}_{20} \mathrm{O}_{58}$ and $\mathrm{T}_{\mathrm{c}}=94 \mathrm{~K}$ in Li-intercalated $\mathrm{WO}_{2.9}$
A. Shengelaya, K. Conder, and K. A. Müller, Journal of Superconductivity and Novel Magnetism 33 (2020) 301
- $\mathrm{GdFeAsO}_{1-\mathrm{y}}$ is a $\mathrm{Cu}-$ free superconductor with $\mathrm{T}_{\mathrm{c}}=53 \mathrm{~K}\left(-220^{\circ} \mathrm{C}\right)$.

Its crystal structure is of the ZrCuSiAs type and consists of alternating Fe - As and Gd - O layers
J. Yang et al. , Superconducting Science and Technology 21 (2008) 1 - 3

Sometimes materials display a high (or higher) $\mathrm{T}_{\mathrm{c}}$ when they are put under a very high pressure

- Under a pressure of about $900 \mathrm{kbar} \mathrm{H}_{2} \mathrm{~S}$ transforms into a metal. At about 1400 kbar it becomes superconducting with $\mathrm{T}_{\mathrm{c}} \approx 200 \mathrm{~K}\left(-73^{\circ} \mathrm{C}\right)$. Probably $\mathrm{H}_{2} \mathrm{~S}$ decomposes under high pressure and the phase responsible for high- $\mathrm{T}_{\mathrm{c}}$ superconductivity is possibly $\mathrm{H}_{3} \mathrm{~S}$
A P. Drozdov et al. , Nature $\underline{523}$ (2015) 73-76, https://doi.org/10.1038/nature14964
- For $\mathrm{LaH}_{10}$ under a pressure of about 1700 kbar the reported $\mathrm{T}_{\mathrm{c}}$ is about $250 \mathrm{~K}\left(-23^{\circ} \mathrm{C}\right)$
A. P. Drozdov et al. , Nature $5 \underline{569}$ (2019) 528-531
https://doi.org/10.1038/s41586-019-1201-8
- For a N -doped Lu-hydride under a pressure of 10 kbar the reported max. $\mathrm{T}_{\mathrm{c}}$ is $294 \mathrm{~K}\left(+21^{\circ} \mathrm{C}\right)$
N. Dasenbrock-Gammon et al. , Nature $\underline{615}$ (2023) $244-250$
https://doi.org/10.1038/s41586-023-05742-0


## Superconducting materials with a relatively high transition temperature $T_{c}$

Critical papers by J. E. Hirsch in the Journal of Superconductivity and Novel Magnetism (2023) about reported superconductivity in hydrides under high pressure:

- Electrical Resistance of Hydrides Under High Pressure: Evidence of Superconductivity or Confirmation Bias ? https://doi.org/10.1007/s10948-023-06594-5
- Enormous Variation in Homogeneity and Other Anomalous Features of Room Temperature Superconductor Samples: A Comment on Nature 615, 244 (2023) https://doi.org/10.1007/s10948-023-06593-6

Often unverified reports or rumors about materials with high $T_{c}$, e.g. www.superconductors.org presents Cu - based oxides with very high $\mathrm{T}_{\mathrm{c}}$ values. However, the presented indications for superconductivity appear poor and their $\mathrm{T}_{\mathrm{c}}$ 's do not represent established values

In 2020 the journal Nature published a paper with the title "Room-temperature superconductivity in a carbonaceous sulfur hydride". In 2022 Nature has retracted that paper. https://doi.org/10.1038/s41586-020-2801-z

## Superconductivity - A vision, dream or wish

## Superconductivity at room temperature ! <br> For example a material with $\mathrm{T}_{\mathrm{c}}=380 \mathrm{~K}\left(+107^{\circ} \mathrm{C}\right)$

- No cooling required $\Rightarrow$ Applications possible in many areas
- Potentially - i.e. dependent on the properties of the material and the superconducting state - a revolution in technology including the possibility of the development of fundamentally new and entirely unexpected things
- Superconductivity in everyday life / in everyday devices !?


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## Do man-made room temperature superconductors already exist?

Special metal-hydrogen materials reported in two German patent applications:
"Offenlegungsschriften" (published patent applications) DE 10109973 A1 and DE 102008047334 A1 published in 2002 and 2010 (in German):
https://depatisnet.dpma.de/DepatisNet/depatisnet?action=pdf\&docid=DE000010109973A1
"Supraleiter mit Sprungtemperatur $\mathrm{T}_{\mathrm{c}}$ grösser 273 K " (superconductors with transition temperature $\mathrm{T}_{\mathrm{c}}$ above 273 K )
https://depatisnet.dpma.de/DepatisNet/depatisnet?action=pdf\&docid=DE102008047334A1

- Materials are described in the context of cold fusion
- Further information about these materials only for licensees
- So far no public reports of the presence of the Meissner effect (see part 1.4). Therefore it is presently not clear if these materials are really superconductors

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2.3 Carpy-Galy phases $A_{n} B_{n} O_{3 n+2}=A B O_{x}$
2.3.1 Crystal structure
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2.3.4 The O-deficient $n=5$ type Schückel-Müller-Buschbaum phase $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}=\mathrm{SrNbO}_{3.2}$ which was published in 1985 and related melt-grown Sr - and O-deficient materials which were published in 2020

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### 2.1 Introductory notes

## Examples of manifestations of solid matter such as oxides



Crystals

Thin film, thickness e.g. 120 nm


Thin films and heterostructures


Powder


Polycrystalline parts made of powder which was pressed or molded, sintered, and, if necessary, machined


### 2.1 Introductory notes

Among oxides there are many types of crystal structures and ranges of chemical compositions which might have a potential to create new high $-T_{c}$ superconductors. Materials can be prepared in several kinds of manifestations, namely as powder, polycrystalline sintered shapes, crystalline shapes or crystals, or as thin film grown on a substrate. And there are many techniques or approaches how to prepare materials.

The following parts 2.2 and 2.3. present examples from the research area of the author of this presentation, namely the synthesis of melt-grown oxides by the floating zone melting technique in a mirror furnace and the so-called Carpy-Galy phases $A_{n} B_{n} \mathrm{O}_{3 n+2}=A B \mathrm{O}_{x}$.

The author of this work is still convinced that the Carpy-Galy phases, which are perovskite-related layered oxides of the type $A_{n} B_{n} \mathrm{O}_{3 n+2}=A B O_{x}$, have a potential to create high $-T_{c}$ or room temperature superconductors, even if there are so far no indications for superconductivity among the known or published compositions. However, there are still many potential new or unexplored compositions and materials.

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### 2.2 Synthesis of melt-grown oxide materials

All following pages of part 2.2 are from Refs. [1] and [2] and sketch the preparation of crystalline oxides via a solidification from the melt by the floating zone melting technique in a mirror furnace. For further information and details see Refs. [1] and [2]
[1] Presentation of a laboratory for the synthesis and study of special oxides and melt-grown crystalline materials
Frank Lichtenberg
Published by the library of the ETH Zurich / ETH Research Collection in 2017 (438 pages)
https://dx.doi.org/10.3929/ethz-a-010817148
[2] Carpy-Galy phases $A_{n} B_{n} \mathrm{O}_{3 n+2}=A B \mathrm{O}_{x}$ : Overview, properties, special and hypothetical systems, and melt-grown synthesis of $A$ - and O-deficient $n=5$ types such as $\mathrm{Sr}_{19} \mathrm{Nb}_{19} \mathrm{WO}_{66}$ and $\mathrm{Sr}_{17} \mathrm{Ca}_{2} \mathrm{Nb}_{19} \mathrm{WO}_{64}$ and $n=6$ type $L n_{6} \mathrm{Ti}_{4} \mathrm{Fe}_{2} \mathrm{O}_{20}$ and $\mathrm{Ca}_{6} \mathrm{Nb}_{5} \mathrm{FeO}_{20}$
Frank Lichtenberg
Published by the library of the ETH Zurich / ETH Research Collection in July 2020 ( 477 pages)
https://dx.doi.org/10.3929/ethz-b-000424221

## Sketch of the sample preparation

1) $)$ It starts always with an idea about a known, new or apriori hypothetical oxide material, i.e. devise a chemical composition such as $\mathrm{La}_{6} \mathrm{Ti}_{4} \mathrm{Fe}_{2} \mathrm{O}_{20}$ or $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{17}$
2) Select appropriate starting materials from commercially available powders such as oxides $\mathrm{La}_{2} \mathrm{O}_{3}, \mathrm{TiO}_{2}, \mathrm{Fe}_{2} \mathrm{O}_{3}$ or $\mathrm{Nb}_{2} \mathrm{O}_{5}$, carbonates like $\mathrm{CaCO}_{3}$, and / or metals such as Nb
3) Calculate the amounts (mass, weight) of the selected starting materials according to the devised or desired chemical composition
4) Weighing the calculated amounts of the starting materials by a spatula, weighing paper, and an analytical balance
5) Mingle the weighed starting materials by a mortar and pestle. If steps 6-8 are omitted, then a part of the as-mingled startimg materials is pressed into two rods and it is continued with step 9
6) Pre-reaction in air: Heat the mingled starting materials in a laboratory chamber furnace to elevated temperatures

## Sketch of the sample preparation

7) Grind the pre-reacted starting materials into powder and mingle it by a mortar and pestle - in some cases another starting material is added to the pre-reacted starting materials
8) Press a part of the powder obtained in step 7 into two rods
9) Sinter the as-pressed rods at elevated temperatures under an appropriate atmosphere such as under air in a laboratory chamber furnace or under argon in a tube furnace or molybdenum furnace
10) Try to synthesize the devised or desired oxide material in a crystalline form via a solidification from the melt by processing the sintered rods by floating zone melting in a mirror furnace under an appropriate atmosphere such as air or argon. In some cases reduced mixed-valence titanates or niobates can be prepared by processing sintered rods with a fully oxidized composition by floating zone melting under argon plus hydrogen

## Examples of commercially available starting materials


$\mathrm{Fe}_{2} \mathrm{O}_{3}$ powder

$\mathrm{WO}_{3}$ powder

$\mathrm{SrCO}_{3}$ powder

$\mathrm{Nd}_{2} \mathrm{O}_{3}$ powder


Nb powder

Storage of starting materials in an alumina crucible in a desiccator $\mathrm{Mn}_{2} \mathrm{O}_{3}$ powder in this example


## Preparation and handling of powder mixtures



Spatula and


Analytical balance


High temperature ceramics:
Various types of crucibles and discs / lids made of alumina


Mingle the starting materials by a pestle in a mortar


Alumina crucible filled with powder


High temperature ceramics:
Various types of boats and boxes made of alumina

## Pressing dies for the preparation of rods for the mirror furnace

Custom-made pressing dies made of technical ceramics


Type C with square punch for other samples

Type B with rectangular punch for seed rods with length 35 mm and width $3,5 \mathrm{~mm}$

Type A with rectangular punch for feed rods with length 85 mm and width $4,5 \mathrm{~mm}$
Yellow parts made of magnesia stabilized zirconia (FRIATEC FRIALIT FZM) by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland) https://dx.doi.org/10.3929/ethz-a-0010817148
Metal frames made in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth and M. Elsener

## Several types of lower punches on which the powder is pressed

Lower punches for the pressing die type A (feed rod), type B (seed rod) and type C


Lower punches made of alumina (FRIATEC FRIALIT F 99,7)

- usable up to $1950{ }^{\circ} \mathrm{C}$


Lower punches made of yttria stabilized zirconia (FRIATEC DEGUSSIT FZY)

- usable up to $1500^{\circ} \mathrm{C}$

Made by FRIATEC AG (Germany), purchased and delivered from stone-ware gmbh (Switzerland) https://dx.doi.org/10.3929/ethz-a-010817148

## Example of an as-pressed feed rod for the mirror furnace



3 Rectangular rod with a continuous hole - made of pressed powder Chemical composition of the pressed powder in this example: $0,6 \mathrm{Nb}+0,2 \mathrm{Nb}_{2} \mathrm{O}_{5}$
2 Lower punch - made of alumina (FRIATEC FRIALIT F 99,7)
1 Base plate - made of magnesia stabilized zirconia (FRIATEC FRIALIT FZM)
The powder was pressed with a pressing force of 1 kN . The as-pressed rod is mechanically not stable. If it is touched in a not very careful way, then it becomes damaged or destroyed. However, the rod is needed in a mechanically stable form. Therefore the lower punch and the pressed rod will be placed into an alumina box and heated to an appropriate high temperature under a suitable atmosphere which results in sintering and chemical solid state reactions

## Feed rod and seed rod for the mirror furnace before and after sintering



Pressed rods on their lower alumina punch in an alumina box before sintering

Chemical composition of the powder in this example: $0,6 \mathrm{Nb}+0,2 \mathrm{Nb}_{2} \mathrm{O}_{5}$

Pressed rods on their lower alumina punch in an alumina box after sintering them for 1 h at $1150^{\circ} \mathrm{C}$ under argon

The color change of the rods from white-grey to black is due to chemical solid state reactions like $0,6 \mathrm{Nb}+0,2 \mathrm{Nb}_{2} \mathrm{O}_{5} \rightarrow \mathrm{NbO}$


## Another pressing dies for the preparation of rods for the mirror furnace

Custom-made pressing dies made of glass


Type A2 with rectangular punch for feed rods with length 90 mm and width 5 mm

Glass parts purchased and delivered from EMATAG AG (Switzerland)
Metal frames, trays and other metal parts made in the metal workshop of the Department of Materials of the ETH Zurich by C. Roth and M. Elsener

## Example of an as-pressed feed rod for the mirror furnace



An as-pressed rod inside the pressing die when the metal frame is removed. The applied pressing force was 1 kN

View when the side panels are removed:

As-pressed rod (1) on a lower punch (2) which is made of sapphire. The lower punch (2) is located on the base plate (3) which is made of quartz glass

## Cyberstar mirror furnace



1 Mirror furnace
2 Monitor and keyboard of the video recording and processing system which is equipped with the software HIRIS from R\&D Vision

3 Second monitor
4 Control cabinet
5 Movable control unit for lamp power and fast motion of seed and feed rod

6 Turbo pumping station

Cyberstar mirror furnace - Casing open and mirrors M1 and M2 locked


## Cyberstar mirror furnace - Mirrors unlocked



1 Elliptical and gold-coated mirror

2 Lamp

$$
P_{\max }=1000 \mathrm{~W}
$$

3 Quartz glass tube
4 Upper shaft
5 Lower shaft

Mirrors and lamps are cooled by cooling water and a flow of compressed air

- Mirrors focus radiation from lamps into a small volume. If a material is located at that volume, then it can be molten if the lamp power is high enough
- Heating-up and melting of a material takes mainly place by its infrared absorption
- Mirrors are gold-coated because that enhances their infrared reflectivity

Synthesis of crystalline materials by a mirror furnace requires the desired chemical composition in form of two rods


Example of two polycrystalline sintered rods with same chemical composition such as $\mathrm{La}_{2} \mathrm{Ti}_{2} \mathrm{O}_{7}$

Fixation of the rods at the lower and upper shaft by special sample holders ...

Cyberstar mirror furnace equipped with rods and quartz glass tube



Digital video camera (7) at the rear side

Synthesis of melt-grown oxides by a mirror furnace - Sketch of a run


Single phase crystalline material emerges readily if the solidification is (nearly) time congruent, i.e. if the melt and the solidified material have (nearly) the same chemical composition. If this is true depends on the chemical composition and is often not known or predictable, especially for unexplored chemical compositions

## Synthesis of melt-grown oxides by the Cyberstar mirror furnace

Example of a snap shot of a
floating zone melting process
The polycrystalline feed rod is converted via the melt into a crystalline material which is created by a solidification from the melt

2 Slow downwards motion of the feed rod, e.g. $10 \mathrm{~mm} / \mathrm{h}$

1 Slow downward motion of the seed rod, e.g. $8 \mathrm{~mm} / \mathrm{h}$

The crystalline material grows onto the upper part of the seed rod which is not visible in this image. The seed rod is located below the bottom boundary of this picture


Example of a melt-grown oxide prepared by a mirror furnace

$$
\mathrm{Ca}_{4} \mathrm{EuNb}_{5} \mathrm{O}_{17} \quad \mathrm{Eu}^{2+} / 4 \mathrm{f}^{7} \text { and } \mathrm{Nb}^{4.8+} / 4 \mathrm{~d}^{0.2}
$$

Grown with $15 \mathrm{~mm} / \mathrm{h}$ in argon - Black-blue electrical conductor - Sample No. 510 Structure type $n=5$ of layered perovskite-related Carpy-Galy phases $A_{n} B_{n} \mathrm{O}_{3 n+2}$



Plate-like crystal obtained by crushing / cleaving the as-grown material

Prepared at the University of Augsburg by a GERO mirror furnace
Progress in Solid State Chemistry 36 (2008) 253

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### 2.3 Carpy-Galy phases $A_{n} B_{n} O_{3 n+2}=A B O_{x}$

All pages in the following part 2.3.1
part 2.3.2
part 2.3.3
part 2.3.4
are from Ref. [2]. For further information and details see Ref. [2]
[2] Carpy-Galy phases $A_{n} B_{n} \mathrm{O}_{3 n+2}=A B O_{x}$ : Overview, properties, special and hypothetical systems, and melt-grown synthesis of $A$ - and O-deficient $n=5$ types such as $\mathrm{Sr}_{19} \mathrm{Nb}_{19} \mathrm{WO}_{66}$ and $\mathrm{Sr}_{17} \mathrm{Ca}_{2} \mathrm{Nb}_{19} \mathrm{WO}_{64}$ and $n=6$ type $L n_{6} \mathrm{Ti}_{4} \mathrm{Fe}_{2} \mathrm{O}_{20}$ and $\mathrm{Ca}_{6} \mathrm{Nb}_{5} \mathrm{FeO}_{20}$

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Sketch of the perovskite-related structure of
$A_{n} B_{n} O_{3 n+2}=A B O_{x}$
$B=\mathrm{Ti}, \mathrm{Nb}, \mathrm{Ta}$

| $n=$ layer thickness |
| :---: |
| $=$ |
| $\quad$ number of $\mathrm{BO}_{6}$ |
|  |
| octahedra along |
| $c$-axis per layer |

Existence of non-integral series members such as $n=4.5$ with an ordered stacking sequence of layers with different thickness
$\boxtimes=B O_{6}$ octahedra (O located at corners, $B$ hidden in center)


$$
n=4
$$



$$
n=4.5
$$



$$
n=5
$$

$n=5$

$$
A B O_{3.44}
$$

$A B O_{3.40}$
$\mathrm{SrNbO}_{3.44} \quad \mathrm{SrNbO}_{3.40}$ quasi-1D metals


$$
n=\infty
$$

$$
A B O_{3.50}
$$

Compositional examples $\rightarrow \mathrm{SrNbO}_{3.50}$ Physical properties $\rightarrow$ ferroelectric
$\mathrm{ABO}_{3}$ perovskite $\mathrm{SrNbO}_{3}$ metal

High-resolution transmission electron microscopy image from the $n=4.5$ type quasi-1D metal $\mathrm{SrNbO}_{3.45}(c \approx 59 \AA$ )


TEM image made by Tim Williams
T. Williams et al., Journal of Solid State Chemistry 103 (1993) 375 • F. Lichtenberg et al., Zeitschrift für Physik B Condensed Matter 84 (1991) 369 and Progress in Solid State Chemistry 29 (2001) 1 • D. H. Lu et al., Physica C 282-287 (1997) 995 • C. A. Kuntscher et al., Physical Review B $\underline{70}$ (2004) 245123 and B $\underline{61}$ (2000) 1876
$B \mathrm{O}_{6}$ octahedra (O located at corners, $B$ hidden in center) $=\boxtimes \boxtimes$

Sketch of the pronounced structural anisotropy of
$A_{n} B_{n} O_{3 n+2}=A B O_{x}$ by using $n=5$ as example
$B$ - O linkage:

- zig-zag along $b$-axis
- chains along a-axis
- interruptions along $c$-axis
$\rightarrow$ layered crystal structure


Progress in Solid State Chemistry $\underline{29}$ (2001) 1 and $\underline{36}$ (2008) 253

$$
n=5 \text { type } A_{5} B_{5} \mathrm{O}_{17}=A B O_{3.4}
$$

Sketch of the
perovskite-related structure of
An}\mp@subsup{B}{n}{}\mp@subsup{O}{3n+2}{\prime}=AB\mp@subsup{O}{x}{
An}\mp@subsup{B}{n}{}\mp@subsup{O}{3n+2}{\prime}=AB\mp@subsup{O}{x}{

$n=4$
$n=4.5$

$A B O_{3.5}$

$A B O_{3.44}$

$n=5$ (II)
$n=\infty$
$A B O_{3.2}$

$\mathrm{ABO}_{3}$

## Sketch of the perovskite-related structure of

| $A_{n} B_{n} \mathrm{O}_{3 n+2}=A B \mathrm{O}_{\mathrm{x}}$ | Examples from the system $\mathrm{SrNbO}_{x}$ <br> with $\mathrm{Nb}^{5+}\left(4 \mathrm{~d}^{0}\right)$ and $/$ or $\mathrm{Nb}^{4+}\left(4 \mathrm{~d}^{1}\right)$ |
| :--- | :--- |


$n=4$
$\mathrm{ABO}_{3.5}$
$\mathrm{SrNbO}_{3.5}$ non-centrosym. ferroelectric $\qquad$
$n=5$ (I)
$A B O_{3.4}$
$\mathrm{SrNbO}_{3.4}$


$n=4.5$
$A B O_{3.44}$
$\mathrm{SrNbO}_{3.44}$ centrosymmetric quasi-1D metals


C

$n=5$ (II)
$\mathrm{ABO}_{3.2}$
$\mathrm{SrNbO}_{3.2}$
non-centrosym.
quasi-1D metal?

$n=\infty$
$\mathrm{ABO}_{3}$
$\mathrm{SrNbO}_{3}$
centrosym. metal

Progress in Solid State Chemistry $\underline{36}$ (2008) 253 and references therein • Zeitschrift für Anorganische und Allgemeine Chemie $\underline{528}$ (1985) 91 • https://dx.doi.org/10.3929/ethz-b-000424221

## Sketch of the

 perovskite-related structure of$A_{n} B_{n} O_{3 n+2}=A B O_{x}$

$n=4$
$A B O_{3.5}$





## Approximate lattice parameters of oxides of the type $A_{n} B_{n} O_{3 n+2}=A B O_{x}$

| Lattice parameters |  | Structure type $n$ |
| :---: | :---: | :---: |
| $a(\AA)$ | $\sim 3.9$ or $\sim 2 \times 3.9=7.8$ | all $n$ |
| $b(\AA)$ | $\sim 5.5$ | all $n$ |
| $c(\AA)$ | $\sim 44$ | $n=7$ |
|  | $\sim 19$ or $\sim 2 \times 19=38$ | $n=6$ |
|  | $\sim 31$ | $n=5$ |
|  | $\sim 58$ | $n=4.5$ |
|  | $\sim 83$ | $n=4.33$ |
|  | $\sim 13$ or $\sim 2 \times 13=26$ | $n=4$ |
|  | $\sim 20$ | $n=3$ |
|  | $\sim 7.5$ or $\sim 2 \times 7.5=15$ | $n=2$ |
| $\beta\left({ }^{\circ}\right)$ | 90 (orthorhombic) or $\sim 96$ (monoclinic) | all $n$ |

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## $A_{n} B_{n} \mathrm{O}_{3 n+2}=A B O_{x}$ type insulators and ferroelectrics $\left(B=\mathrm{Ti}^{4+}, \mathrm{Nb}^{5+}, \mathrm{Ta}^{5+}\right)$

- The highest- $T_{\mathrm{c}}$ ferroelectrics are $n=4$ type oxides, e.g. $\mathrm{LaTiO}_{3.50}$ with $T_{\mathrm{c}}=1770 \mathrm{~K}$ and $\mathrm{CaNbO}_{3.50}$ which is ferroelectric up to its melting point of 1850 K !
S. Nanamatsu et al., Ferroelectrics $\underline{8}$ (1974) 511 • S. Nanamatsu and M. Kimura, J. Phys. Soc. Jpn. $\underline{36}$ (1974) 1495

Definition of highest- $T_{\mathrm{c}}$ ferroelectrics: Compounds with $T_{\mathrm{c}}>T_{\mathrm{c}}\left(\mathrm{LiNbO}_{3}\right)=1480 \mathrm{~K}$

- Ferroelectrics $\rightarrow n$ is an even number like $n=2,4,6$ (non-centrosymmetric) Antiferroelectrics $\rightarrow n$ is an odd number like $n=3,5,7$ (centrosymmetric)
- Compounds with non-integral $n$
e.g. $\mathrm{CaNb}_{0.89} \mathrm{Ti}_{0.11} \mathrm{O}_{3.44}(n=4.5) \mathrm{M}$. Nanot et al., Journal of Solid State Chemistry $\underline{28}(1979) 137$
- Single phase bulk materials known for $n=2,3,4,4.33,4.5,5,6,7$
- Complex structural details like incommensurate modulations e.g. in $\mathrm{SrNbO}_{3.50}(n=4)$ P. Daniels et al. , Acta Crystallographica Section B 58 (2002) 970
- Another ions $B^{c}=\mathrm{Al}^{3+}, \mathrm{Fe}^{3+} \ldots$ can occupy the $B$ site: $B=(\mathrm{Ti}, \mathrm{Nb}, \mathrm{Ta})_{1-\mathrm{y}} B_{\mathrm{y}}^{\prime}$ whereby so far $\mathrm{y} \leq 0.33$

Examples of melt-grown $A_{n} B_{n} \mathrm{O}_{3 n+2}=A B O_{x}$ type insulators with $B=\mathrm{Nb}^{5+}$ Crystalline pieces from the as-grown materials which were grown under synth. air

$\mathrm{Sr}_{4} \mathrm{Nb}_{4} \mathrm{O}_{14}=\mathrm{Sr}_{2} \mathrm{Nb}_{2} \mathrm{O}_{7}=\mathrm{SrNbO}_{3.5}$

## Sample No. 169

White transparent ferroelectric insulator with $T_{\mathrm{c}}=1615 \mathrm{~K}$
J. Phys. Soc. Jpn. 38 (1975) 817

Structure type $n=4$

Prog. Solid State Chem. $2 \underline{9}$ (2001) 1 • As-grown materials prepared at the University of Augsburg with a GERO mirror furnace - Photos taken at the ETH Zurich

$\mathrm{Ca}_{4} \mathrm{Nb}_{4} \mathrm{O}_{14}=\mathrm{Ca}_{2} \mathrm{Nb}_{2} \mathrm{O}_{7}$
$=\mathrm{CaNbO}_{3.5}$
Sample No. 84
White transparent insulator which is ferroelectric up to the melting point of 1850 K
J. Phys. Soc. Jpn. $\underline{36}$ (1974) 1495

Structure type $n=4$

Ferroelectric $\boldsymbol{n}=4$ type $\mathrm{Sr}_{4} \mathrm{Nb}_{4} \mathrm{O}_{14}=\mathrm{Sr}_{2} \mathrm{Nb}_{2} \mathrm{O}_{7}=\mathrm{SrNbO}_{3.5}$
$T_{c}=1340^{\circ} \mathrm{C}$

Crystallographic and Dielectric
Properties of Ferroelectric $\mathrm{A}_{2} \mathrm{~B}_{2} \mathrm{O}_{7}$
( $\mathrm{A}=\mathrm{Sr}, \mathrm{B}=\mathrm{Ta}, \mathrm{Nb}$ ) Crystals and
Their Solid Solutions
Satoshi Nanamatsu, Masakazu
Kimura, and Tsutomu Kawamura
Journal of the Physical Society of Japan 38 (1975) 817-824
https://doi.org/10.1143/JPSJ.38.817


## $A_{n} B_{n} \mathrm{O}_{3 n+2}=A B O_{x}$ type electrical conductors

No publications before 1991 apart from the following structural study on conducting $\mathrm{CaNbO}_{x}(3.4 \leq x<3.5)$ in which no physical properties are not reported:
M. Hervieu et al. , Journal of Solid State Chemistry $\underline{22}$ (1977) 273

## Systematic study of

$A_{n} B_{n} \mathrm{O}_{3 n+2}=A B O_{x}$ electronic conductors started with a study of melt-grown $\mathrm{La}_{n} \mathrm{Ti}_{n} \mathrm{O}_{3 n+2}=\mathrm{LaTiO}_{x}$

Synthesis and study of $\mathrm{LaTiO}_{x}$ between the end members $\mathrm{LaTiO}_{3}$ and $\mathrm{LaTiO}_{3.5}$ which were already known
F. Lichtenberg, Dissertation, University of Zurich (1991)
F. Lichtenberg et al., Zeitschrift für Physik B Condensed Matter 82 (1991) 211
T. Williams et al., Journal of Solid State Chemistry 93 (1991) 534 and 103 (1993) 375
F. Lichtenberg et al., Progress in

Solid State Chemistry $\underline{29}$ (2001) 1
C. A. Kuntscher et al., Physical

Review B 67 (2003) 035105

## Pictures from melt-grown $\mathrm{LaTiO}_{x}$


$n=\infty$ type $\mathrm{LaTiO}_{3}$ Sample No. 442
Pieces from the as-grown material which was prepared by processing rods with the composition $\mathrm{LaTiO}_{3}$ under Ar in a GERO mirror furnace at the University of Augsburg

Photo taken at the ETH Zurich
Physical Review B 68 (2003) 245108

$n=5$ type $\mathrm{LaTiO}_{3.4}$ Sample No. Z 187
Pieces from the as-grown material which was prepared by processing rods with the composition $\mathrm{LaTiO}_{3.4}$ under Ar in an IBM mirror furnace at the IBM Zurich Research Laboratory

Photos taken at the ETH Zurich
Zeitschrift für Physik B Condensed Matter 82 (1991) 211

## Pictures from melt-grown $\mathrm{LaTiO}_{x}$


$n=5$ type $\mathrm{LaTiO}_{3.41}$ Sample No. 353
A piece from the as-grown material which was prepared by processing rods with the fully oxidized composition $\mathrm{LaTiO}_{3.5}$ under $98 \%$ Ar plus $2 \% \mathrm{H}_{2}$ in a GERO mirror furnace at the University of Augsburg

Photo taken at the ETH Zurich
Progress in Solid State Chemistry 29 (2001) 1
Table 35 in Progress in Solid State Chemistry
36 (2008) 253 and references therein

$n=4$ type $\mathrm{LaTiO}_{3.5}$ Sample No. 168
Pieces from the as-grown material which was prepared by processing rods with the composition $\mathrm{LaTiO}_{3.5}$ under air in a GERO mirror furnace at the University of Augsburg

Photo taken at the ETH Zurich
Progress in Solid State Chemistry $\underline{29}$ (2001) 1

## Electrical contacts for resistivity measurements on plate-like crystals



A crystal prepared for four-point resistivity measurements along two different directions within the ab-plane, usually along the $a$ - and $b$-axis. The size of this crystal is $(1.7 \mathrm{~mm}) \times(1.7 \mathrm{~mm}) \times(0.3 \mathrm{~mm})$. At the four sides the current leads, $50 \mu \mathrm{~m}$ diameter Au wires, are attached with silver paint. On the top there are six voltage contacts, $25 \mu \mathrm{~m}$ diameter Al wires, which were mechanically fixed by ultrasonic bonding. Although one current direction requires only two voltage contacts, the presence of more contacts can be very useful, e.g. if one of them fails.

The same crystal as shown above but now with contacts for a four-point resistivity measurement perpendicular to the layers. Shown is one of the both sides with two contacts which were prepared by silver paint and $50 \mu \mathrm{~m}$ diameter Au wires. The U-like shape is used as current contact and the other in the middle as voltage contact. There are two corresponding contacts on the other side of the crystal.

## The monoclinic $n=5$ titanate $\mathrm{La}_{5} \mathrm{Ti}_{5} \mathrm{O}_{17}=\mathrm{LaTiO}_{3.4}\left(\mathrm{Ti}^{3.8+}, 3 \mathrm{~d}^{0.2}\right)$

https://dx.doi.org/10.3929/ethz-b-000424221


Resistivity $\rho(T)$ along $a$ - and $b$-axis and $\perp$ ab-plane


Optical reflectivity vs. frequency along $a$ - and $b$-axis


Highly anisotropic conductor and quasi-1D metal - At $T \approx 100 \mathrm{~K}$ metal-to-semiconductor transition / indications for a phase transition - Below $T \approx 100 \mathrm{~K}$ very small energy gap of $\approx 6 \mathrm{meV}$ along a-axis • Indications for strong electron-phonon coupling • Crystal structure detemined by single crystal x-ray diffraction - Studies under high pressure indicate a stable structure up to 18 GPa , a sluggish structural phase transition from 18 to 24 GPa , and near 15 GPa an onset of a dimensional crossover from a quasi-1D to a quasi-2D metal
F. Lichtenberg et al: Progress in Solid State Chemistry $\underline{36}$ (2008) 253 and $\underline{29}$ (2001) 1 and Zeitschrift für Physik B Condensed Matter 84 (1991) 369 • C. A. Kuntscher et al: Physical Review B 74 (2006) 054105 and 67 (2003) 035105

- I. Loa et al., Physical Review B 69 (2004) 224105 • P. Daniels et al., Acta Crystallographica Section C 59 (2003) i15


## The $n=5$ quasi-1D metal $\operatorname{La}_{5} \mathrm{Ti}_{5} \mathrm{O}_{17}\left(\mathrm{Ti}^{3.8+}, 3 \mathrm{~d}^{0.2}\right)$



## Melt-grown $n=4$ type $\mathrm{SrNbO}_{3.5}$ and $\mathrm{Sr}_{0.8} \mathrm{La}_{0.2} \mathrm{NbO}_{3.5}$


$\mathrm{Sr}_{4} \mathrm{Nb}_{4} \mathrm{O}_{14}=\mathrm{SrNbO}_{3.50}$
$\mathrm{Nb}^{5+} / 4 \mathrm{~d}^{0}$ Sample No. 169
White transparent high- $T_{c}$ ferroelectric insulator with $T_{\mathrm{c}}=1615 \mathrm{~K}$
C. A. Kuntscher et al., Physical Review B $\underline{70}$ (2004) 245123
V. Bobnar et al., Physical Review B $\underline{65}$ (2002) 155115
F. Lichtenberg et al., Progress in Solid State Chemistry
$\underline{29}$ (2001) 1 and $\underline{36}$ (2008) 253
Satoshi Nanamatsu et al., Journal of the Physical Society of Japan 38 (1975) 817

$\mathrm{Sr}_{3.2} \mathrm{La}_{0.8} \mathrm{Nb}_{4} \mathrm{O}_{14}=\mathrm{Sr}_{0.8} \mathrm{La}_{0.2} \mathrm{NbO}_{3.50}$
$\mathrm{Nb}^{4.8+} / 4 \mathrm{~d}^{0.2}$ Sample No. 72
Black-blue electrical conductor

- Optical spectroscopy, angle-resolved photoelectron spectroscopy and resistivity measurements $\rightarrow$ Weakly pronounced quasi-1D metal
- Optical spectroscopy indicates presence of ferroelectric soft mode $\rightarrow$ Is this a polar or ferroelectric metal ?

Melt-grown $n=4$ type $\mathrm{SrNbO}_{3.5}$ and $n=5$ type $\mathrm{SrNbO}_{3.4}$
Examples of crystalline pieces from the as-grown materials

$\mathrm{Sr}_{4} \mathrm{Nb}_{4} \mathrm{O}_{14}=\mathrm{SrNbO}_{3.50}$
$\mathrm{Nb}^{5+} / 4 \mathrm{~d}^{0}$ Sample No. 169
Grown under synthetic air White transparent high- $T_{c}$ ferroelectric insulator with $T_{\mathrm{c}}=1615 \mathrm{~K}$ Structure type $n=4$

$\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{17.05}=\mathrm{SrNbO}_{3.41}$
$\mathrm{Nb}^{4.82+} / 4 \mathrm{~d}^{0.18}$ Sample No. 71
Grown under argon
Black-blue quasi-1D metal
Structure type $n=5$

Progress in Solid State Chemistry $\underline{29}$ (2001) 1 and $\underline{36}$ (2008) 253
Physical Review B $6 \underline{5}$ (2002) 155115 and B $\underline{70}$ (2004) 245123
Physical Review Letters 89 (2002) 236403
Journal of the Physical Society of Japan 38 (1975) 817
Samples prepared at the University of Augsburg
Photo of $\mathrm{Sr}_{4} \mathrm{Nb}_{4} \mathrm{O}_{14}=\mathrm{SrNbO}_{3.5}$ taken at the ETH Zurich

## Resistivity $\rho(T)$ of some $A_{n} \mathrm{Nb}_{n} \mathrm{O}_{3 n+2}=A \mathrm{NbO}_{\mathrm{x}}$ along the $a-, b$ - and $c$-axis





- Highly anisotropic conductors

Progress in Solid State Chemistry
29 (2001) 1

- Quasi-1D metals along a-axis. The quasi-1D metallic behavior is confirmed or revealed by angle-resolved photoemission (ARPES) and optical spectroscopy. For references see the previous pages and the pages after the next two pages
- Metal-to-semiconductor transition at low $T$ https://dx.doi.org/10.3929/ethz-b-000424221


## Resistivity $\rho(T)$ of the $n=5$ type $\mathrm{SrNbO}_{3.41}$

 and the Sr - and O-deficient $n=5$ type $\mathrm{Sr}_{0.95} \mathrm{NbO}_{3.37}$
F. Lichtenberg et al., Progress in Solid State Chemistry $\underline{29}$ (2001) 1
https://dx.doi.org/10.3929/ethz-b-000424221

# Resistivity $\rho(T)$ of the $n=5$ type $\mathrm{SrNbO}_{3.41}$ 

and the Sr - and O -deficient $n=5$ type $\mathrm{Sr}_{0.95} \mathrm{NbO}_{3.37}$

F. Lichtenberg et al., Progress in Solid State Chemistry $\underline{29}$ (2001) 1

## Resistivity $\rho(T)$ of the $n=5$ type $\mathrm{SrNbO}_{3.41}$ and the Sr - and O -deficient $\boldsymbol{n}=5$ type $\mathrm{Sr}_{0.95} \mathrm{NbO}_{3.37}$



Optical spectroscopy confirmed or revealed that both materials are quasi-1D metals
$\mathrm{SrNbO}_{3.41}$ :
C. A. Kuntscher et al., Physical Review Letters 89 (2002) 236403 and Physical Review B 70 (2004) 245123
$\mathrm{Sr}_{0.95} \mathrm{NbO}_{3.37}$ :
Teguh Citra Asmara et al., to be published in Communications Physics (2020).
F. Lichtenberg et al., Progress in Solid State Chemistry $\underline{29}$ (2001) 1

Comprehensive studies on $A_{n} \mathrm{Nb}_{n} \mathrm{O}_{3 n+2}=A \mathrm{NbO}_{\mathrm{x}}$ by angle-resolved photoemission (ARPES) and optical spectroscopy: Example $\boldsymbol{n}=5$ type $\mathrm{SrNbO}_{3.41}$

ARPES probes occupied electronic states and their dispersion $E(k), k=k(\theta)$


Binding energy (eV)
Inset: Reflectivity $R(v)$

$T=75 \mathrm{~K}$

Binding energy (eV)
Band with dispersion,
i.e. $E(k) \neq$ constant,
only along a-axis

- Metal-to-semiconductor transition at $T<100 \mathrm{~K}$
- High-resolution ARPES at 25 K , resistivity $\rho(T)$ \& optical conductivity $\rightarrow$ Semiconducting state with extremely small energy gap $\Delta \approx 5 \mathrm{meV}$, the smallest $\Delta$ of all known quasi-1D metals
- Experimental findings appear inconsistent with Peierls or 1D Mott-Hubbard picture
C. A. Kuntscher et al.: Phys. Rev. B $\underline{61}(2000) 1876$ \& $\underline{70}$ (2004) 245123 and Phys. Rev. Lett. $\underline{89}$ (2002) 236403

Comprehensive studies on $A_{n} \mathrm{Nb}_{n} \mathrm{O}_{3 n+2}=A N b \mathrm{O}_{\mathrm{x}}$ by ARPES，optical spectroscopy， resistivity measurements，and electronic band structure calculations
\(\left.\left.$$
\begin{array}{lll}n=4 & \mathrm{Sr}_{0.8} \mathrm{La}_{0.2} \mathrm{NbO}_{3.50} & 4 \mathrm{~d}^{0.20} \\
n=4.5 & \mathrm{SrNbO}_{3.45} & 4 \mathrm{~d}^{0.10} \\
n=5 & \mathrm{SrNbO}_{3.41} & 4 \mathrm{~d}^{0.18} \\
n=5 & \mathrm{Sr}_{0.9} \mathrm{La}_{0.1} \mathrm{NbO}_{3.4} & 4 \mathrm{~d}^{0.3}\end{array}
$$\right\} \begin{array}{l}Weakly pronounced quasi－1D metal <br>

No energy gap at low T along a －axis\end{array}\right\}\)| Quasi－1D metals |
| :--- |
| Small energy gap at low $T$ along a－axis |


|  |  | $\downarrow$ |
| :---: | :---: | :---: |
| $\stackrel{\prime \prime}{\prime \prime} \times \square$ |  | Special role of layers which |
| C |  | are $5 \mathrm{NbO}_{6}$ octahedra thick： |
| ${ }^{\circ}$ ® $^{\circ}$ 区 ${ }^{\circ}$ ® $^{\circ}$ 区 23 |  | are $5 \mathrm{NbO}_{6}$ Octahedra thick： |
|  | $\rightarrow$ | Electrons from the Nb ions |
|  |  |  |
|  |  | located in the central and |
| 23 ه○区 ○区○区 |  | nearly undistorted |
| $\uparrow \quad n=4 \quad n=4.5$ |  | octahedra contribute most |
| L typical distortions of $\mathrm{NbO}_{6}$ octahedra（\％）${ }^{\text {a }}$ |  | to the metallic character |

C．A．Kuntscher et al．：Physical Review B $\underline{61}$（2000） 1876 and $\underline{70}$（2004） 245123 as well as Physical Review Letters $\underline{89}$（2002） 236403 • F．Lichtenberg et al．：Progress in Solid State Chemistry $\underline{29}$（2001） 1 and $\underline{36}$（2008） 253

## LDA calculations of the

 electronic band structure of the $n=5$ quasi-1D metal $\mathrm{SrNbO}_{3.41}$Good agreement with results from angleresolved photoelectron spectroscopy (ARPES) with respect to lowest band



Nb atoms of least distorted
octahedra contribute most to the electronic density of states (DOS) at the Fermi energy $E_{F}$
Quasi-1D features along a-axis related to octahedra distortions

LDA predicts further bands around $E_{F}$ which disperse along $a$ - and $b$-axis, but they are not observed by ARPES: Subtle structural details? Electronic correlations ? ARPES resolution ?
C. A. Kuntscher et al.

Phys. Rev. B
61 (2000) 1876
H. Winter et al.
J. Phys. Cond. Matter

12 (2000) 1735
S. C. Abrahams et al.

Acta Cryst. B
$\underline{54}$ (1998) 399
F. Lichtenberg et al.

Prog. Solid State Chem. $\underline{29}$ (2001) 1

## A special feature of the $A_{n} B_{n} \mathrm{O}_{3 n+2}=A B O_{\mathrm{x}}$ type quasi-1D metals

Structural, compositional and electronical proximity to (anti)ferroelectric insulators !

This distinguishes them from all other known quasi-1D metals such as $\mathrm{K}_{0.3} \mathrm{MoO}_{3}$, $\mathrm{Li}_{0.9} \mathrm{Mo}_{6} \mathrm{O}_{17}, \mathrm{NbSe}_{3},(\mathrm{SN})_{y}$ and organic conductors like TTF-TCNQ

## Examples:

$n=4$ : Ferroelectric $\mathrm{SrNbO}_{3.5}\left(4 \mathrm{~d}^{0}\right) \rightarrow$ Poor quasi-1D metal $\mathrm{Sr}_{0.8} \mathrm{La}_{0.2} \mathrm{NbO}_{3.5}\left(4 \mathrm{~d}^{0.2}\right)$ $n=5$ : Antiferroelectric $\mathrm{SrNb}_{0.8} \mathrm{Ti}_{0.2} \mathrm{O}_{3.4}\left(4 \mathrm{~d}^{0}\right) \rightarrow$ Quasi-1D metal $\mathrm{SrNbO}_{3.4}\left(4 \mathrm{~d}^{0.2}\right)$

Intrinsic coexistence of metallic conductivity and large dielectric polarizability in $A_{n} B_{n} \mathrm{O}_{3 n+2}$ type systems !?

Usually these both features exclude each other
Intrinsic coexistence of these both features might be useful for the creation of superconductors

The following experimental observations support the presence of such an intrinsic coexistence ...


## Is the $n=4$ type $\mathrm{Sr}_{0.8} \mathrm{La}_{0.2} \mathrm{NbO}_{3.50}$ a polar or ferroelectric metal ?


$\mathrm{Sr}_{4} \mathrm{Nb}_{4} \mathrm{O}_{14}=\mathrm{SrNbO}_{3.50}$
$\mathrm{Nb}^{5+} / 4 \mathrm{~d}^{0}$ Sample No. 169
White transparent high- $T_{\mathrm{c}}$ ferroelectric insulator with $T_{\mathrm{c}}=1615 \mathrm{~K}$
C. A. Kuntscher et al., Physical Review B $\underline{70}$ (2004) 245123
V. Bobnar et al., Physical Review B $\underline{65}$ (2002) 155115
F. Lichtenberg et al., Progress in Solid State Chemistry
$\underline{29}$ (2001) 1 and and $\underline{36}$ (2008) 253
Satoshi Nanamatsu et al., Journal of the Physical Society of Japan 38 (1975) 817

Examples of $n=4$ type crystalline pieces from the as-grown materials
Grown under synth. air (left) or argon (right) at the University of Augsburg. Photos taken at the ETH Zurich

Replacing
$\mathrm{Sr}^{2+}$ partly
by $\mathrm{La}^{3+}$

$\mathrm{Sr}_{3.2} \mathrm{La}_{0.8} \mathrm{Nb}_{4} \mathrm{O}_{14}=\mathrm{Sr}_{0.8} \mathrm{La}_{0.2} \mathrm{NbO}_{3.50}$ $\mathrm{Nb}^{4.8+} / 4 \mathrm{~d}^{0.2}$ Sample No. 72
Black-blue electrical conductor

- Optical spectroscopy, angle-resolved photoelectron spectroscopy and resistivity measurements $\rightarrow$ Weakly pronounced quasi-1D metal
- Optical spectroscopy indicates presence of ferroelectric soft mode $\rightarrow$ Is this a polar or ferroelectric metal ?


Ferroelectric insulator $\mathrm{SrNbO}_{3.5}(n=4)$ and quasi-1D metal $\mathrm{SrNbO}_{3.4}(n=5)$
Examples of crystalline pieces from the as-grown materials

$\mathrm{Sr}_{4} \mathrm{Nb}_{4} \mathrm{O}_{14}=\mathrm{SrNbO}_{3.50}$
$\mathrm{Nb}^{5+} / 4 \mathrm{~d}^{0}$ Sample No. 169
Grown under synthetic air White transparent high- $T_{c}$ ferroelectric insulator with $T_{\mathrm{c}}=1615 \mathrm{~K}$
Structure type $n=4$

$\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{17.05}=\mathrm{SrNbO}_{3.41}$
$\mathrm{Nb}^{4.82+} / 4 \mathrm{~d}^{0.18}$ Sample No. 71
Grown under argon
Black-blue quasi-1D metal
Structure type $n=5$

Progress in Solid State Chemistry $\underline{29}$ (2001) 1 and $\underline{36}$ (2008) 253
Physical Review B $6 \underline{5}$ (2002) 155115 and B $\underline{70}$ (2004) 245123
Physical Review Letters 89 (2002) 236403
Journal of the Physical Society of Japan 38 (1975) 817
Samples prepared at the University of Augsburg
Photo of $\mathrm{Sr}_{4} \mathrm{Nb}_{4} \mathrm{O}_{14}=\mathrm{SrNbO}_{3.5}$ taken at the ETH Zurich

Intrinsic high-frequency dielectric permittivity of the $\boldsymbol{n}=5$ quasi-1D metal $\mathrm{SrNbO}_{3.41}$ along the $\boldsymbol{c}$-axis


Large permittivity: $\varepsilon_{\mathrm{c} \infty} \approx 100$
$T>70 \mathrm{~K}$ : Measurement prevented by too high conductivity
V. Bobnar et al.

Physical Review B $\underline{65}$ (2002) 155115
$T \approx 70 \mathrm{~K}$ : Metallic along a-axis according to ARPES and resistivity $\rho(T)$
C. A. Kuntscher et al., Physical Review B $\underline{70}$ (2004) 245123
F. Lichtenberg et al., Progress in Solid State Chemistry $\underline{29}$ (2001) 1

Coexistence of large intrinsic high-frequency dielectric permittivity $\varepsilon_{c \infty}$ along $c$-axis and metallic behavior along a-axis

Note: Largest possible intrinsic dielectric permittivity in non-ferroelectrics of the order of $\varepsilon_{\infty} \approx 100!? \quad$ P. Lunkenheimer et al., Physical Review B 66 (2002) 052105

2 Searching for new superconductors among oxides
2.1 Introductory notes
2.2 Synthesis of melt-grown oxide materials
2.3 Carpy-Galy phases $A_{n} B_{n} O_{3 n+2}=A B O_{x}$
2.3.1 Crystal structure
2.3.2 Physical and structural properties
2.3.3 Why they might have a potential to create high $-\mathrm{T}_{\mathrm{c}}$ or room temperature superconductors
2.3.4 The O-deficient $n=5$ type Schückel-Müller-Buschbaum phase $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}=\mathrm{SrNbO}_{3.2}$ which was published in 1985 and related melt-grown Sr - and O-deficient materials which were published in 2020

## Potential for high $-\mathrm{T}_{\mathrm{c}}$ superconductivity in $A_{n} B_{n} \mathrm{O}_{3 n+2}=A B O_{x}$ quasi-1D metals from the perspective of so-called excitonic superconductivity

A hypothetical possibility to realize superconductivity at room temperature is given by the so-called excitonic mechanism of superconductivity (electron-electron mediated):

- Original proposal by W. A. Little for hypothetical quasi-1D organic conductors:

Conducting chains surrounded by electronically polarizable side branches

- In: Novel Superconductivity, Plenum Press (1987) 341
- Journal de Physique Colloque C3 Supplement No 6 (1983) 819
- Int. Journal of Quantum Chemistry (Quantum Chemistry Symposium) 15 (1981) 545
- Scientific American 212 (1965) 21
- Physical Review 134 (1964) A1416
- Original proposal by V. L. Ginzburg for quasi-2D systems:

Thin metallic sheet surrounded by two dielectric layers

- Soviet Physics Uspekhi $7 \underline{2}$ (1970) 335

The results of the studies on $\mathrm{La}_{5} \mathrm{Ti}_{5} \mathrm{O}_{17}=\mathrm{LaTiO}_{3.4}$ and $(\mathrm{Sr}, \mathrm{La}) \mathrm{NbO}_{x}$ which are presented in part 2.3.2 suggest the following scenario ...

## Potential for high $-T_{c}$ superconductivity in $A_{n} B_{n} O_{3 n+2}=A B O_{x}$ quasi-1D metals from the perspective of so-called excitonic superconductivity

For example, the types $n=4.5$ and $n=5$ seem to be interesting from Little's and from Ginzburg's point of view: - Quasi-2D crystal structure - Electronically quasi-1D by $B-O$ chains and delocalized electrons along $a$-axis • Electronically polarizable units by electronic band structure, fluctuating valence states of rare earth ions at $A$ site ... ?


- Metal-insulator-like interfaces within the unit cell
$n=4.5$
- Electronically not 2D but 1D concerning Ginzburg's concept
- Also quasi-2D metals among $A_{n} B_{n} \mathrm{O}_{3 n+2}$ type oxides ?

Searching for high $-T_{\mathrm{c}}$ and room temperature superconductors

- Excitonic superconductivity only in a very small region of the compositional parameter space (W. A. Little, V. L. Ginzburg)
- "Therefore, synthesizing a room temperature superconductor, one must pay attention to its structure: the "distance" between failure and success can be as small as $0.01 \AA$ in the lattice constant".

Cited from Andrei Mourachkine‘s book "Room-Temperature Superconductivity", 2004 (ISBN 1-904602-27-4), pages 292 and 293

2 Searching for new superconductors among oxides
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2.3.4 The O-deficient $n=5$ type Schückel-Müller-Buschbaum phase $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}=\mathrm{SrNbO}_{3.2}$ which was published in 1985 and related melt-grown Sr - and O-deficient materials which were published in 2020

## The Schückel-Müller-Buschbaum phase $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}$

In 1985 K. Schückel and Hk. Müller-Buschbaum have published the following paper about the synthesis of $\mathrm{SrNbO}_{3.2}=\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}=\mathrm{Sr}_{20} \mathrm{Nb}_{20} \mathrm{O}_{64}$ and its structure determination by single crystal x-ray diffraction:

Ein weiteres gemischtvalentes Oxoniobat: $\mathrm{Sr}_{5} \mathrm{Nb}_{3}{ }^{4+} \mathrm{Nb}_{2}{ }^{5+} \mathrm{O}_{16}$ K. Schückel and Hk. Müller-Buschbaum

Zeitschrift für anorganische und allgemeine Chemie $5 \underline{528}$ (1985) 91-97 https://doi.org/10.1002/zaac. 19855280909 Paper in German but title and abstract also in English

Title: About a Mixed Valence Oxoniobate: $\mathrm{Sr}_{5} \mathrm{Nb}_{3}{ }^{4+} \mathrm{Nb}_{2}{ }^{5+} \mathrm{O}_{16}$
Abstract: The hitherto unknown compound $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}$ was prepared and examined by X-ray single crystal work. It crystallizes with orthorhombic symmetry (space group $\mathrm{D}_{2 \mathrm{~h}}{ }^{7}-\mathrm{Pmn} 2_{1}$, $a=3.992(1)$, $b=5.677(2), c=32.476(10), Z=2) . \mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}$ consists of stacked perovskite-like blocks cut by a plane perpendicular to the cube face diagonal of the perovskite structure. The coordination relations of the intersections between those blocks and the distribution of $\mathrm{Nb}^{5+}$ and $\mathrm{Nb}^{4+}$ are discussed. Compared to the original text $b$ and $c$ are swapped so that they correspond to the assignment used in this work

## The Schückel-Müller-Buschbaum phase $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}$

In 1985 K. Schückel and Hk. Müller-Buschbaum have published the following paper about the synthesis of $\mathrm{SrNbO}_{3.2}=\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}=\mathrm{Sr}_{20} \mathrm{Nb}_{20} \mathrm{O}_{64}$ and its structure determination by single crystal x-ray diffraction:

Ein weiteres gemischtvalentes Oxoniobat: $\mathrm{Sr}_{5} \mathrm{Nb}_{3}{ }^{4+} \mathrm{Nb}_{2}{ }^{5+} \mathrm{O}_{16}$ K. Schückel and Hk. Müller-Buschbaum

Zeitschrift für anorganische und allgemeine Chemie $5 \underline{528}$ (1985) 91-97 https://doi.org/10.1002/zaac. 19855280909 Paper in German but title and abstract also in English

## Notes

- Physical properties are not reported / were not studied
- Oxides of the type $A_{n} B_{n} \mathrm{O}_{3 n+2}$ and a relationship to the structure type $n=5$ are not mentioned
- In the paper https://dx.doi.org/10.3929/ethz-b-000424221 the name Schückel-Müller-Buschbaum phase is suggested and introduced for $\mathrm{SrNbO}_{3.2}=\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}=\mathrm{Sr}_{20} \mathrm{Nb}_{20} \mathrm{O}_{64}$ and its reported crystal structure


## The Schückel-Müller-Buschbaum phase $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathbf{O}_{16}$

As already communicated in

## Progress in Solid State Chemistry 36 (2008) 253

- the crystal structure of the non-centrosymmetric $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}$ can be considered as an oxygen-deficient variant of the $n=5$ type and centrosymmetric quasi-1D metal $\mathrm{SrNbO}_{3.4}=\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{17}=\mathrm{Sr}_{20} \mathrm{Nb}_{20} \mathrm{O}_{68}$ with fully ordered oxygen vacancies
- attempts to prepare the Schückel-Müller-Buschbaum phase $\mathrm{SrNbO}_{3.2}=\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}=\mathrm{Sr}_{20} \mathrm{Nb}_{20} \mathrm{O}_{64}$ via the melt were unsuccessful In contrast to the quasi-1D metal $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{17}$ a layer or slab of $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}$ comprises along the $c$-axis an asymmetric distribution of the
- $\mathrm{Nb}^{4+}\left(4 \mathrm{~d}^{1}\right)$ and $\mathrm{Nb}^{5+}\left(4 \mathrm{~d}^{0}\right)$ ions
- Nb - O polyhedra distortions

Maybe these particular details of this structure type and its reported non-centrosymmetricity can bring forth special physical properties.

## The crystal structure of $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}$ and the $n=5$ type $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{17}$

P

## $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}$ and the $\boldsymbol{n}=5$ type $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{17}$

| Composition |  | $\begin{gathered} \mathrm{SrNbO}_{3.2}=\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16} \\ =\mathrm{Sr}_{20} \mathrm{Nb}_{20} \mathrm{O}_{64} \end{gathered}$ | $\begin{gathered} \mathrm{SrNbO}_{3.4}=\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{17} \\ =\mathrm{Sr}_{20} \mathrm{Nb}_{20} \mathrm{O}_{68} \end{gathered}$ |
| :---: | :---: | :---: | :---: |
| Synthesis approach |  | $2 \mathrm{SrO}+\mathrm{Nb}_{2} \mathrm{O}_{5}$ with Nb on surface was heated in a $\mathrm{H}_{2}$ / H plasma $\rightarrow$ Small crystals. Synthesis via melt did not work (incongruent melting) | Floating zone melting of the composition $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{17}$ under Ar |
| Structure type |  | Schückel-Müller-Buschbaum phase Oxygen-deficient $n=5$ type with fully ordered oxygen vacancies | $n=5$ type Carpy-Galy phase $A B O_{x}=A_{n} B_{n} O_{3 n+2}$ |
| Space group |  | Pmn2 ${ }_{1}$ / Non-centrosymmetric | Pnnm / Centrosymmetric |
| Published / actual or assumed orthorhombic lattice parameters | $a(\AA)$ | 3.99 / $2 \times 3.99$ | $4.00 / 2 \times 4$ |
|  | $b(\AA)$ | 5.68 | 5.67 |
|  | $c(\AA)$ | 32.48 | 32.46 |
| Number of 4d electrons from $\mathrm{Nb}^{4+} / 4 \mathrm{~d}^{1}$ per unit cell |  | 12 | 4 |
| Physical properties |  | ? | Quasi-1D metal |
| References |  | Z. Anorg. Allg. Chem. 528 (1985) 91 Prog. Solid State Chem. 36 (2008) 253 | See part 2.3.2 |

## The Schückel-Müller-Buschbaum phase $\mathrm{SrNbO}_{3.2}=\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}=\mathrm{Sr}_{20} \mathrm{Nb}_{20} \mathrm{O}_{64}$

Comments and open questions

- In contrast to the quasi-1D metal $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{17}$ a layer or slab of $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}$ comprises along the $c$-axis an asymmetric distribution of the $\mathrm{Nb}^{4+}\left(4 \mathrm{~d}^{1}\right)$ and $\mathrm{Nb}^{5+}\left(4 \mathrm{~d}^{0}\right)$ ions and $\mathrm{Nb}-\mathrm{O}$ polyhedra distortions. Maybe these particular details of the $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}$ type structure can bring forth special physical properties
- What are its physical properties ?
- Is it a quasi-1D metal like the related $n=5$ type $\mathrm{SrNbO}_{3.4}=\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{17}$ ? If yes, is $\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}$ because if its non-centrosymmetric structure a polar or ferroelectric metal?
- Are there related materials which can be prepared via the melt ?
- If yes, then larger amounts of crystalline material / larger crystals could be obtained. That would facilitate the study of the physical properties
- Can the crystal structure reported by K. Schückel and Hk. Müller-Buschbaum be confirmed?


## The Schückel-Müller-Buschbaum phase $\mathrm{SrNbO}_{3.2}=\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}=\mathrm{Sr}_{20} \mathrm{Nb}_{20} \mathrm{O}_{64}$

Comments and open questions

- Its reported crystal structure can be considered as an oxygen-deficient $n=5$ type structure with fully ordered oxygen vacancies. Therefore the Schückel-Müller-Buschbaum phase and potential related compounds with the same type of crystal structure, i.e. Schückel-Müller-Buschbaum type phases, represent a special subset of the Carpy-Galy phases $A_{n} B_{n} O_{3 n+2}=A B O_{x}$
- The oxygen-deficient $n=5$ type structure of $\mathrm{SrNbO}_{3.2}$ is perovskite-related and layered and its composition is close to that of the non-layered $n=\infty$ type perovskite $\mathrm{SrNbO}_{3}$

For comparison: In the system $\mathrm{LaTiO}_{x}$ the $n=\infty$ type perovskite structure has a large homogeneity range, namely $3.00 \leq x \leq 3.20$, i.e. it extends up to the composition $\mathrm{LaTiO}_{3.2}$ (see page 80)

## The Schückel-Müller-Buschbaum phase $\mathrm{SrNbO}_{3.2}=\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{16}=\mathrm{Sr}_{20} \mathrm{Nb}_{20} \mathrm{O}_{64}$

Comments and open questions

- The overall homogeneity range of $n=5$ type $\mathrm{SrNbO}_{x}$ seems to be $3.20 \leq x \leq 3.42$ whereby $x=3.40$ corresponds to the stoichiometric composition
- When having prepared a series of niobates $\mathrm{SrNbO}_{x}$ with an oxygen content ranging from $x=3.40$ to $x=3.20$ : Is there a specific oxygen content $x_{\mathrm{c}}$ or a two-phase oxygen content range which separates the two single phases
- centrosymmetric / non-centrosymmetric
- symmetric / asymmetric distribution of the $\mathrm{Nb}^{4+}$ and $\mathrm{Nb}^{5+}$ ions
- symmetric / asymmetric distribution of the $\mathrm{Nb}-\mathrm{O}$ polyhedra distortions ?
- For $x \approx 3.33$ basically an $n=6$ type phase could arise but for $\mathrm{SrNbO}_{x}$ there are no indications for that. An example for an $n=6$ type material is the ferrorelectric insulator $\mathrm{SrNb}_{0.67} \mathrm{Ti}_{0.33} \mathrm{O}_{3.33}\left(\mathrm{Nb}^{5+} / 4 \mathrm{~d}^{0}\right.$ and $\left.\mathrm{Ti}^{4+} / 3 \mathrm{~d}^{0}\right)$


## Melt-grown Sr- and O-deficient $\boldsymbol{n}=5$ type materials

## $(\mathrm{Sr}, \mathrm{Ca}, \mathrm{Ba})_{19} \mathrm{Nb}_{19} \mathrm{WO}_{x}(64 \leq x \leq 66)$ which were published in July 2020

The above-mentioned materials such as $\mathrm{Sr}_{17} \mathrm{Ca}_{2} \mathrm{Nb}_{19} \mathrm{WO}_{64}$ are reported in the paper https://dx.doi.org/10.3929/ethz-b-000424221. Those with an oxygen content of 64 represent Sr -deficient Schückel-Müller-Buschbaum type phases.

The temperature dependence of the magnetic moment M of the above-mentioned compounds was measured by a SQUID magnetometer. The resulting $\mathrm{M}(\mathrm{T})$ curves suggest that these materials are potentially quasi-1D metals like the related $n=5$ type quasi-1D metal $\mathrm{Sr}_{20} \mathrm{Nb}_{20} \mathrm{O}_{69}=\mathrm{Sr}_{5} \mathrm{Nb}_{5} \mathrm{O}_{17}$.

The reported materials do not display indications for the presence of superconductivity. Nevertheless, other Schückel-Müller-Buschbaum type phases with another compositions might have a potential to create superconductors.

The following pages present some pictures and results from one of the reported compounds, namely of $\mathrm{Sr}_{17} \mathrm{Ca}_{2} \mathrm{Nb}_{19} \mathrm{WO}_{64}$

As-grown crystalline $\mathrm{Sr}_{17} \mathrm{Ca}_{2} \mathrm{Nb}_{19} \mathrm{WO}_{69.5-y}$ and polycrystalline rods Run / Sample No. 826


5 cm long as-grown crystalline material (1) plus polycrystalline seed rod (2) and remaining part of the polycrystalline feed rod (3)

Prepared at the ETH Zurich in 2019

As-grown crystalline material $\mathrm{Sr}_{17} \mathrm{Ca}_{\mathbf{2}} \mathrm{Nb}_{19} \mathrm{WO}_{69.5-y}$ Sample No. 826


5 cm long as-grown crystalline material

## As-grown crystalline material $\mathrm{Sr}_{17} \mathrm{Ca}_{\mathbf{2}} \mathrm{Nb}_{19} \mathrm{WO}_{69.5-y}$

 Sample No. 826

Another view from the 5 cm long as-grown crystalline material

As-grown crystalline material $\mathrm{Sr}_{17} \mathrm{Ca}_{\mathbf{2}} \mathrm{Nb}_{19} \mathrm{WO}_{69.5-y}$ Sample No. 826


A section from the 5 cm long as-grown crystalline material

As-grown crystalline material $\mathrm{Sr}_{17} \mathrm{Ca}_{\mathbf{2}} \mathrm{Nb}_{19} \mathrm{WO}_{69.5-y}$ Sample No. 826


5 cm long as-grown crystalline material

As-grown crystalline material $\mathrm{Sr}_{17} \mathrm{Ca}_{\mathbf{2}} \mathrm{Nb}_{19} \mathrm{WO}_{69.5-y}$ Sample No. 826


Crystalline pieces from section C8 of the as-grown material

## As-grown crystalline material $\mathrm{Sr}_{17} \mathrm{Ca}_{\mathbf{2}} \mathrm{Nb}_{19} \mathrm{WO}_{69.5-y}$ Sample No. 826



Crystalline piece C6-1 with $\mathrm{m}=221 \mathrm{mg}$ from section C6 of the as-grown material

This piece was used to study its magnetic properties by a SQUID magnetometer

## 826 C6 $\mathbf{S r}_{17} \mathrm{Ca}_{2} \mathbf{N b}_{19} \mathbf{W O}_{x} \quad$ Thermogravimetry

Thermogravimetric oxidation in flowing synth. air up to the fully oxidized composition with $x=x_{F}=69.5$ for the determination of the oxygen content $x=69.5-y$ by using a thermogravimetric analyzer NETZSCH TG 209 F1 Libra Pulverized crystalline material from section C6 of the as-grown sample $\rightarrow x=63.97$

TG /mg
https://dx.doi.org/10.3929/ethz-b-000424221
Temp. $/{ }^{\circ} \mathrm{C}$


Valence or oxidation states of the Nb and W ions in $\mathrm{Sr}_{17} \mathrm{Ca}_{2} \mathrm{Nb}_{19} \mathrm{WO}_{63.97}$

The most likely scenario is $\mathrm{W}^{4+} / 5 \mathrm{~d}^{2}$


Charge neutrality and $\mathrm{Sr}^{2+}, \mathrm{Ca}^{2+}$, and $\mathrm{O}^{2-} \rightarrow \mathrm{Nb}^{4.52+} / 4 \mathrm{~d}^{0.48}$
$2(5 d)+19 \times 0.48(4 d)=11.1$ d-electrons per formula and assumed size of the unit cell
$826 \mathrm{C} 6 \quad \mathrm{Sr}_{17} \mathrm{Ca}_{\mathbf{2}} \mathrm{Nb}_{19} \mathrm{WO}_{64} \quad$ Powder x-ray diffraction
Powder x-ray diffraction pattern of pulverized crystalline material from section C6 Square root - linear plot - Background subtracted
All observed peaks fit to an orthorhombic $n=5$ type structure


|  | Observed <br> peak <br> position <br> $\left({ }^{\circ} 2 \theta\right)$ | d-spacing <br> $(\AA)$ | Relative <br> intensity <br> $(\%)$ | h k I <br> from lattice <br> parameter <br> refinement |
| :--- | :---: | :---: | :---: | :---: |
| Lowest angle peak | 5.41 | 16.31 | 5 | 002 | | Its position indicates |
| :--- |
| the structure type of |
| $A_{n} B_{n} O_{3 n+2}$, namely |
| $n=5$ in this case |$\quad$| Highest intensity peak |
| :--- |

## $826 \mathrm{C} 6 \quad \mathrm{Sr}_{17} \mathrm{Ca}_{2} \mathbf{N b}_{19} \mathrm{WO}_{64} \quad$ Powder x-ray diffraction

Results of lattice parameter refinement with $(\mathrm{hkI})_{\max }=\left(\begin{array}{lll}10 & 10 & 20\end{array}\right)$

| Number of observed peaks | 97 |
| ---: | :---: |
| Number of indexed peaks | 97 |
| Number of unindexed peaks | 0 |
| Crystal structure type | $n=5$ of $A_{n} B_{n} \mathrm{O}_{3 n+2}$ |
| Crystal system | Orthorhombic |
| Bravais lattice | P |
| $\mathrm{a}(\AA)$ | 7.96 |
| $\mathrm{~b} \mathrm{( } \AA)$ | 5.67 |
| $\mathrm{c}(\AA)$ | 32.46 |
| $\mathrm{~V}\left(\AA^{3}\right)$ | 1465 |
| $\left\|2 \theta_{\text {obs }}-2 \theta_{\text {calc }}\right\|$ for all observed and calculated peaks | $\leq 0.071^{\circ}$ |
| Figure of merit of the refinement or fit | 16.8 |
| Chi square of the refinement or fit | $4.4 \times 10^{-6}$ |

DC magnetic moment $M(T)$ measured by a Quantum Design SQUID magnetometer MPMS3 11.1 d-electrons from $\mathrm{Nb}^{4+} / 4 \mathrm{~d}^{1}$ and $\mathrm{W}^{4+} / 5 \mathrm{~d}^{2}$


The behavior of $\chi(T)$ in the range from 390 K to 70 K is similar to that of $A_{n} B_{n} \mathrm{O}_{3 n+2}$ type quasi-1D metals. Thus this $n=5$ type material is potentially also a quasi-1D metal

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3.2 The tripartition of the chemical elements
3.3 Global Scaling - A holistic approach in science
3.3.1 Introduction into Global Scaling
3.3.2 Another examples of Fundamental Fractals
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The atomic number of the chemical element Nb is 41 , i.e. it comprises 41 protons and 41 electrons per Nb atom. The element Nb displays several special features [3]:

- Among the $81=3 \times 3 \times 3 \times 3$ stable chemical elements the element Nb is located at a central position, i.e. if 81 elements are arranged with equal distance in form of a one-dimensional chain or in form of a two-dimensional $9 \times 9$ square lattice, then element No. 41 is located at the central position
- Nb has only 1 naturally occuring istope
- The atomic number of Nb is 41 which is a prime number
- Among all superconducting chemical elements Nb 41 has the highest superconducting transition temperature $\mathrm{T}_{\mathrm{c}}$, namely $\mathrm{T}_{\mathrm{c}} \approx 9 \mathrm{~K}=-264{ }^{\circ} \mathrm{C}$, see e.g. http://hyperphysics.phy-astr.gsu.edu/HBase/tables/supcon.html
[3] The tripartition of the chemical elements: Observations, considerations and hypotheses about the chemical elements and the number 3 : https://novam-research.com/resources/Chem-elements-and-number-3.pdf


## The chemical element Nb (niobium)

The special features of Nb which are described on the previous page might suggest the following hypothesis [3]:

Hypothesis: Superconductivity at room temperature can be achieved by a special material which contains Nb as crucial chemical element. Of course, such a material requires another specific features.

As a concrete example we refer to a special class of materials, namely oxides of the type $A_{n} B_{n} \mathrm{O}_{3 n+2}=A B \mathrm{O}_{x}$ (Carpy-Galy phases) which are presented in part 2.3. Some of their specific features suggest that they might have a potential to create room temperature superconductors and they are also known for $B=\mathrm{Nb}$, see part 2.3
[3] The tripartition of the chemical elements: Observations, considerations and hypotheses about the chemical elements and the number 3 : https://novam-research.com/resources/Chem-elements-and-number-3.pdf

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On the following page we present a tripartition of the 81 stable chemical elements and on the subsequent pages some associated hypotheses [3]. The tripartition of the chemical elements can be derived in two different ways [3] , namely

1) by Global Scaling which represents a holistic approach in science
2) by an assumed special role of the number 3
[3] The tripartition of the chemical elements: Observations, considerations and hypotheses about the chemical elements and the number 3: https://novam-research.com/resources/Chem-elements-and-number-3.pdf

The tripartition of the $81=3 \times 27=3 \times 3 \times 3 \times 3$ stable chemical elements $2 / 4$

Group $\mathbf{A 1}(-) \mathbf{1}, 4$ or $7 \quad$ Group $\mathbf{A 2}(+) \mathbf{2}, 5$ or 8

| $1(-)$ | 2 (+) | 3 (0) |
| :---: | :---: | :---: |
| $\mathrm{H}$ | $\mathrm{Be}$ | $\mathrm{N}_{7}$ |
| $\underset{10}{\mathrm{Ne}}$ | ${ }_{13}^{\mathrm{Al}}$ | ${ }_{16} \mathrm{~S}_{6}$ |
| ${ }_{19}{ }^{\mathrm{K}}$ | ${ }_{22} \mathrm{Ti}_{8}$ | $\underset{25}{\mathrm{Mn}}$ |
| $\begin{gathered} \mathrm{Ni} \\ 28 \quad 10 \end{gathered}$ | $\begin{gathered} \mathrm{Ga} \\ 31 \end{gathered}$ | $\begin{gathered} \mathrm{Se} \\ 34 \quad 12 \end{gathered}$ |
| $\begin{gathered} \mathrm{Rb} \\ 37 \end{gathered}$ | $\underset{40 \quad \mathrm{Zr}}{14}$ | 15 |
| $\begin{gathered} \mathrm{Pd} \\ 46 \quad 16 \end{gathered}$ | $\ln _{4917}$ | $\underset{52}{\mathrm{Te}}$ |
| $\begin{gathered} \mathrm{Cs} \\ 55 \end{gathered}$ | $\begin{gathered} \mathrm{Ce} \\ 5820 \end{gathered}$ | 21 |
| $\begin{gathered} \mathrm{Gd} \\ 64 \quad 22 \end{gathered}$ | Ho <br> 67 | $\begin{gathered} \mathrm{Yb} \\ 70 \quad 24 \end{gathered}$ |
| $\begin{gathered} \mathrm{Ta} \\ 73 \quad 25 \end{gathered}$ | $\begin{gathered} \mathrm{Os} \\ 76 \end{gathered}$ | $\begin{gathered} \mathrm{Au} \\ 79 \quad 27 \end{gathered}$ |
| $\begin{gathered} \mathrm{Pb} \\ 82 \quad 28 \end{gathered}$ |  |  |


| 1 (-) | 2 (+) | 3 (0) |
| :---: | :---: | :---: |
| $\mathrm{He}$ | ${ }_{5} \mathrm{~B}_{2}$ | $0$ |
| $\underset{11}{\mathrm{Na}}$ | $\begin{gathered} \mathrm{Si} \\ 14 \quad 5 \end{gathered}$ | $\underset{17}{\mathrm{Cl}}$ |
| $\underset{20}{\mathrm{Ca}}$ | $\begin{gathered} \mathrm{V} \\ 23 \end{gathered}$ | $\underset{26}{\mathrm{Fe}}$ |
| $\begin{gathered} \mathrm{Cu} \\ 29 \quad 10 \end{gathered}$ | $\begin{gathered} \mathrm{Ge} \\ 32 \end{gathered}$ | ${ }_{35} \mathrm{Br}_{12}$ |
| $\begin{gathered} \mathrm{Sr} \\ 38 \quad 13 \end{gathered}$ | $\begin{gathered} \mathrm{Nb} \\ 41 \quad 14 \end{gathered}$ | $\underset{44 \quad \mathrm{Ru}}{15}$ |
| $\underset{47}{\mathrm{Ag}}$ | $\begin{gathered} \mathrm{Sn} \\ 50 \quad 17 \end{gathered}$ | $\begin{gathered} 1 \\ 5318 \end{gathered}$ |
| $\begin{gathered} \mathrm{Ba} \\ 56 \quad 19 \end{gathered}$ | $\begin{gathered} \mathrm{Pr}_{59} \end{gathered}$ | $\underset{62}{\mathrm{Sm}}$ |
| $\begin{gathered} \mathrm{Tb} \\ 65 \quad 22 \end{gathered}$ | $\underset{68}{\mathrm{Er}}$ | $\begin{gathered} \quad \mathrm{Lu} \\ 71 \quad 24 \end{gathered}$ |
| $\begin{gathered} \text { W } \\ 7425 \end{gathered}$ | $\begin{gathered} \text { Ir } \\ 7726 \end{gathered}$ | $\underset{80 \quad \mathrm{Hg}}{27}$ |
| Bi | The atom group A1 |  |

Group A3 (0) 3, 6 or


Atomic number is a prime number group A1, A2, or A3 differ by an integer multiple of 3

Hypothesis 5a: The 3 groups A1, A2 and A3 which are presented on the previous page have a physical meaning and originate from the 3 states of an oscillation which can be called minus, plus, and zero (see Ref. [3] on page 133)

- Group A1 may be called or considered as the "minus group" because it comprises ( $3 \times 3 \times 3=27$ ) - 1 stable elements $=26$ stable elements. Note: The two empty boxes with number 15 and 21 (see previous page ) are not counted because they represent the unstable elements Tc 43 and Pm 61, respectively
- Group A2 may be called or considered as the "plus group" because it comprises $(3 \times 3 \times 3=27)+1$ stable elements $=28$ stable elements
- Group A3 may be called or considered as the "zero group" because it comprises $3 \times 3 \times 3=27$ stable elements

The atomic numbers of any chemical elements which belong exclusively to group A1 (minus) or group A2 (plus) or group A3 (zero) differ always by $3 k$ whereby $k$ is an integer, i.e. $k=1,2,3,4, \ldots$

Hypothesis 5b: The tripartition of the chemical elements can be used in various ways to obtain a selection or set of specific elements which could favor or enable special physical effects when they are used as components of a material, system, subsystem, or process. Of course, the generation of special physical effects requires another specific features of the corresponding material, system, subsystem, or process

The hypotheses 7a and 7b on the following two pages present some specific ways to obtain special selections or sets of chemical elements ...

The tripartition of the $81=3 \times 3 \times 3 \times 3$ stable chemical elements and the search for room temperature superconductors

Hypothesis 7a (see Ref. [3] on page 133):
The creation of high- $T_{c}$ superconductivity, especially at room temperature, is favored or enabled by a special material that comprises only or mainly chemical elements from group A1 (minus) or group A2 (plus) or group A3 (zero), i.e. their atomic numbers differ always or mainly by $3 k$ whereby is $k$ an integer, i.e. $k=1,2,3,4, \ldots$ This may be considered as a scenario which comprises in a pronounced manner the presence of the number 3

Of course, the creation of superconductivity at room temperature requires another special features of the material

The tripartition of the $81=3 \times 3 \times 3 \times 3$ stable chemical elements and the search for room temperature superconductors

Hypothesis 7b (see Ref. [3] on page 133):
The creation of high- $T_{c}$ superconductivity, especially at room temperature, is favored or enabled by a special material that comprises chemical elements from all three groups, i.e.
at least 1 element belongs to group A1 (minus),
at least 1 element belongs to group A2 (plus), and at least 1 element belongs to group A3 (zero).
This may be considered as a scenario which comprises in a pronounced manner the presence of all 3 aspects of an oscillation, namely minus, plus, and zero

Of course, the creation of superconductivity at room temperature requires another special features of the material

The tripartition of the $81=3 \times 3 \times 3 \times 3$ stable chemical elements and the search for room temperature superconductors

The hypothesis 7a or 7b can be used to isolate chemical compositions which might favor or enable the creation of superconductivity at room temperature

Example: Oxides of the type $A_{n} B_{n} \mathrm{O}_{3 n+2}=A B O_{x}$ (Carpy-Galy phases) which might have a potential to create room temperature superconductors, see part 2.3 . Here hypothesis 7a can be applied only to group A2 (see page 134) because in this example the considered materials are oxides and O (oxygen) belongs to group A2

Note: A possible view of the transition temperatures of superconductors and potential room temperature superconductors from a Global Scaling point of view is presented in part 3.3.3

The tripartition of the $81=3 \times 3 \times 3 \times 3$ stable chemical elements and high $-\mathrm{T}_{\mathrm{c}}$ superconductors

Among the presently known superconducting materials the highest superconducting transition temperatures $T_{c}$ under ambient pressure are achieved by layered oxides which contain copper $(\mathrm{Cu})$, oxygen $(\mathrm{O})$ and other elements. Examples are

| Compound | $\mathrm{T}_{\mathrm{c}}(\mathrm{K})$ |
| :--- | :---: |
| $\mathrm{La}_{1.85} \mathrm{Ba}_{0.15} \mathrm{CuO}_{4}$ | 30 |
| $\mathrm{YBa}_{2} \mathrm{Cu}_{3} \mathrm{O}_{7-\delta}$ | 92 |
| $\mathrm{Bi}_{2} \mathrm{Sr}_{2} \mathrm{Ca}_{2} \mathrm{Cu}_{3} \mathrm{O}_{10}$ | 110 |
| $(\mathrm{Ba}, \mathrm{Sr}) \mathrm{CuO}_{2}$ | 90 |
| $(\mathrm{Sr}, \mathrm{Ca})_{5} \mathrm{Cu}_{4} \mathrm{O}_{10}$ | 70 |
| $\mathrm{Hg}_{0.8} \mathrm{Tl}_{0.2} \mathrm{Ba}_{2} \mathrm{Ca}_{2} \mathrm{Cu}_{3} \mathrm{O}_{8+\delta}$ | 138 |

For references see for example

- https://www.nobelprize.org/uploads/2018/06/bednorz-muller-lecture.pdf
- http://hyperphysics.phy-astr.gsu.edu/hbase/solids/hitc.html
- P. Dai et al. , Physica C 243 (1995) 201-206 , https://doi.org/10.1016/0921-4534\(94\)02461-8
- https://flatworldknowledge.lardbucket.org/books/principles-of-general-chemistry-v1.0m/s16-07-superconductors.html

The tripartition of the $81=3 \times 3 \times 3 \times 3$ stable chemical elements and high $-\mathrm{T}_{\mathrm{c}}$ superconductors

Observation: The number of chemical elements per formula unit of all Cu-O-based superconductors are predominantly elements from group A2 (see page 134) such as $\mathrm{O}, \mathrm{Cu}, \mathrm{Sr}$, and Ba. Example:
$\mathrm{YBa}_{2} \mathrm{Cu}_{3} \mathrm{O}_{7-\delta}: 2 \times \mathrm{Ba}+3 \times \mathrm{Cu}+(7-\delta) \times \mathrm{O}=(12-\delta)$ elements from group A 2 and $1 \times Y=1$ element from group A3, see page 134

We note that the atomic number of the essential element Cu is a prime number, namely 29

Hypothesis: This is not accidental and related to hypothesis 7a which is presented on page 137

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## What is Global Scaling?

Global Scaling represents a holistic approach in science. Global Scaling and its founder Hartmut Mueller are controversial. The author of this presentation is convinced that Global Scaling comprises significant insights into the universe, nature, life, and many physical / scientific topics and invites everybody to an open-minded and critical consideration. Global Scaling is still in early stages, there are many open questions and further research is necessary

The following statements about / from Global Scaling are based on

- the author's participation in an overall 13 - day course in Global Scaling in 2005 lectured by Hartmut Mueller nearby Munich in Germany
- a German-language introduction into Global Scaling (1 MB pdf, 25 pages): https://www.novam-research.com/resources/Global-Scaling_Einfuehrung_V-2-dot-0_Maerz-2009.pdf an English version of this introduction (1 MB pdf, 23 pages): https://www.novam-research.com/resources/Global-Scaling_Introduction_V-2-dot-0_March-2009.pdf

Further information: Global Scaling website https://www.interscalar.com . A Global Scaling book from Hartmut Mueller (2018, New Heritage Publishers, ISBN 978-0-9981894-0-6) can be downloaded as pdf free of charge via the following link (file size 11 MB pdf): http://www.ptep-online.com/books/muller2018.pdf . Various information, links, and papers are listed in https://novam-research.com/global-scaling.php

## Global Scaling - How it came about and some keywords

- Global Scaling rests upon the results of very comprehensive studies of frequency distributions of many different physical, chemical and biological processes and phenomena such as radioactive decay and body masses of biological species. Such studies were, for example, performed by Prof. Simon E. Shnoll et al. These studies revealed the existence of formerly unexplored physical laws and effects
- Global Scaling was developed by Hartmut Mueller


Simon E. Shnoll


- Some keywords of Global Scaling:
scale invariance - logarithm - fractal - fractal structures - Fundamental Fractal
- continued fractions • (eigen) oscillations • nodes - gaps • resonance • proton resonance • vacuum resonance • synchronicity • frequency distributions • probability • compression • decompression • non-linear and fractal course of time


## Global Scaling - Some essential statements or hypotheses

- In the universe / nature / vacuum there is an everywhere present background field in form of oscillations (standing waves) which have a significant influence on the constitution of all processes, structures and systems in the universe, nature, and the design of workable and reliable technology
- Particles such as protons and electrons are considered as vacuum resonances, i.e. they are an oscillation state of the physical vacuum
- In the universe there is a synchronicity in which all particles and matter are intimately involved. There are indications that this can be revealed, for example, by noise spectra of electronic components which show at different locations simultaneously the same fine structure
- Every part of the universe, e.g. an atom, comprises the entire information of the universe


## Global Scaling - Another essential statement or hypothesis

On every physical scale $x$ - such as length, mass, time, frequency, temperature, amperage, and dimensionless numbers in terms of sets or ratios - there is an universal distribution of certain positions and zones which have a special meaning and a potential physical effect, e.g. a high or low resonance or oscillation capability. On the logarithmic scale this universal distribution is called the Fundamental Fractal (FF), see example below and examples on pages 148, 150, 152, 153, 155, and 158 . If, which and how many of these positions and zones actually unfold their corresponding effects depends on the details of the specific system or process and on external conditions.

FF example: Simplified sketch of a section of the Fundamental Temperature Fractal: Spectrum of discrete values on the so-called level $n_{0}$ on the logarithmic $z$-axis and linear $T$-axis whereby $T$ is any temperature and $T_{p}=m_{p} c^{2} / k=1.0888 \times 10^{13} \mathrm{~K}$, the so-called proton temperature, an assumed (universal) calibration unit for temperatures:


## Global Scaling - More about the Fundamental Fractal (on the level $n_{0}$ and $n_{1}$ )

The Fundamental Fractal is an universal distribution or pattern of certain positions and zones which have - on every physical scale - a special meaning and a potential effect
Consider a logarithmic scale: $z=\ln \frac{x}{x_{c}}$
$\mathrm{x}=$ physical quantity or dimensionless number (ratio or set) under consideration
$\mathrm{x}_{\mathrm{c}}=$ calibration unit of the considered physical scale
The positions of so-called nodes and sub-nodes - one of their potential effects is a high resonance or oscillation capability - are generated by a special continued fraction:
$z=\ln \frac{x}{x_{c}}=\frac{3 n_{0}}{2}+\frac{2}{n_{1}+\frac{2}{n_{2}+\ddots}}$

$$
\mathrm{n}_{0}= \pm \mathrm{k} \quad \mathrm{n}_{1}= \pm 3 \mathrm{j} \quad \mathrm{k}, \mathrm{j}=0,1,2,3 \ldots
$$

range of nodes and sub-nodes: $n_{0} \pm 1, n_{1} \pm 1$
Spectrum of discrete values on logarithmic $z$ - and linear $x$-axis


## Global Scaling - Micellaneous notes

- The continued fraction which is presented on the previous page comprises a striking presence of the number 3, i.e. Global Scaling implies a marked presence of the number 3
- Global Scaling phenomena are mainly a feature of complex and open systems or processes and are less or not at all apparent in "simple and isolated" systems or processes
- Global Scaling may allow an access to complex tasks / problems / systems and may be applied in many areas such as engineering, physics, biology, (holistic) medicine, architecture, economy, optimization, prognosis ...
- A Global Scaling analysis of an existing system or process may lead to a deepened understanding of its specific parameters, features and behavior


## Global Scaling - How it can be applied

Brief description of an approach when Global Scaling is applied with respect to the consideration or modification of an existing system or the creation of a new system:

If Global Scaling is assumed to be relevant for the corresponding task / process / system, then consider the positions of its associated physical quantities and numbers in the corresponding Fundamental Fractal(s) (FF) $\rightarrow$ Identify the adjustable and non-adjustable quantities or parameters of the corresponding task / process / system $\rightarrow$ To obtain a certain desirable result it is necessary to get an idea, hypothesis or intuition at which positions in the Fundamental Fractal(s) (FF) the adjustable quantities or parameters have to be placed Note: For any task or question in which Global Scaling is applied, "conventional" knowledge, experiences, results and ideas play an equal role

FF example: Simplified sketch of a section of the Fundamental Number Fractal on the level $n_{0}$ (number in terms of set or ratio), i.e. a spectrum of discrete values on the logarithmic $z$-axis and linear $x$-axis ( $x=$ number , $1=$ assumed calibration unit):


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Global Scaling - A section of the Fundamental Time Fractal on the level $n_{0}$

$$
\mathrm{z}=\ln \frac{\mathrm{t}}{\tau_{\mathrm{p}}}=\frac{3 \mathrm{n}_{0}}{2} \quad \mathrm{n}_{0}=0, \pm 1, \pm 2, \pm 3 \ldots
$$

$\mathrm{t}=$ time, e.g. elapsed time after the creation of an object or birth of a human being
$\tau_{\mathrm{p}}=1 / \mathrm{f}_{\mathrm{p}}=\lambda_{\mathrm{p}} / \mathrm{c}=7.01515 \times 10^{-25} \mathrm{~s}=$ assumed (universal) calibration unit for the time $f_{p}=$ proton frequency,$\lambda_{p}=h /\left(2 \pi c m_{p}\right)=$ reduced Compton wave length of the proton

Node positions $\mathrm{z}\left(\mathrm{n}_{0}\right)$ or $\mathrm{t}\left(\mathrm{n}_{0}\right)$ in the time fractal mark with high probability important points of change in the course of a process, independent of its nature


## Global Scaling - A representation or template of the Fundamental Fractal on level $n_{0}$ and $n_{1}$

$$
z=\ln \frac{x}{x_{c}}=\frac{3}{2} n_{0}+\frac{2}{n_{1}+\frac{2}{n_{2}+\ddots}} \quad n_{0}= \pm k \quad n_{1}= \pm 3 j \quad k, j=0,1,2,3 \ldots
$$

> so-called nodes: $n_{0}, z\left(n_{0}\right), x\left(n_{0}\right)$ so-called sub-nodes: $n_{1}, z\left(n_{1}\right), x\left(n_{1}\right)$
$x=$ physical quantity or number (ratio or set) under consideration
$\mathrm{X}_{\mathrm{c}}=$ calibration unit of the considered physical scale such as length
For further information see https://www.novam-research.com/resources/Global-Scaling_Introduction_V-2-dot-0_March-2009.pdf (in English) or https://www.novam-research.com/resources/Global-Scaling_Einfuehrung_V-2-dot-0_Maerz-2009.pdf (in German) and the previous pages about Global Scaling in this presentation


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Global Scaling - A section of the Fundamental Temperature Fractal on the level $n_{0}$ and a potential view of the (distribution of) transition temperatures of superconductors $\mathrm{z}=\ln \frac{T_{\mathrm{c}}}{T_{p}}=\frac{3 \mathrm{n}_{0}}{2} \quad \mathrm{n}_{0}=0, \pm 1, \pm 2, \pm 3 \ldots, \mathrm{~T}_{\mathrm{c}}=$ transition temperature $[\mathrm{K}], \mathrm{T}_{\mathrm{p}}=\mathrm{m}_{\mathrm{p}} \mathrm{c}^{2} / \mathrm{k}$ $=1.08882 \times 10^{13} \mathrm{~K}=$ assumed calibration unit for temperatures Node positions $z\left(n_{0}\right)$ or $T_{c}\left(n_{0}\right)$ : High probability of tendency change, event attractor Borders $z\left(n_{0} \pm 1\right)$ or $T_{c}\left(n_{0} \pm 1\right)$ of nodes: Development limit


A: Classical superconductors such as $\mathrm{Nb}_{3} \mathrm{Ge}$ or $\mathrm{MgB}_{2}$, typical (max.) $\mathrm{T}_{\mathrm{c}}$ 's $\approx 20$ (40) K
B: High- $T_{c}$ superconductors based on Cu and O such as $\mathrm{YBa}_{2} \mathrm{Cu}_{3} \mathrm{O}_{7-\delta}$, typical $\mathrm{T}_{\mathrm{c}}$ 's about 100 K . Also reports of indications for $\mathrm{T}_{\mathrm{c}} \approx 240 \mathrm{~K}$ but unverified because difficult to reproduce: 249 K upper $\mathrm{T}_{\mathrm{c}}$ limit of $\mathrm{Cu}-\mathrm{O}$-based superconductors ?
C: $T_{c}$ s of next generation superconductors ? Typical $T_{c} ‘ s$ about 400 K ?

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Hypothesis: Superconductivity at room temperature can be achieved by a resonance-like interaction between an everywhere present background field and a special material with an appropriate crystal structure and chemical composition

On the following page we present a brief outline of an useful appearing approach how Global Scaling can be used to isolate chemical compositions and crystal structure types which potentially favor the creation of superconductivity at room temperature ...

## Global Scaling and the search for room temperature superconductors

Brief description of an useful appearing approach: Prepare such materials whose readily accessible material parameters are located at special positions in the Fundamental Fractal (FF), see example below and examples on pages $147,148,150,152,153$, and 155 . For example, this could mean that some material parameters are placed at positions with a potentially high resonance or oscillation capability, whereas others are placed at positions with a potentially low resonance or oscillation capability. Examples of readily accessible material parameters are the number and mass of atoms in the crystallographic unit cell, the lattice parameters and the chemical composition. This approach may lead to a significant reduction of the number of useful appearing chemical compositions. Nevertheless, there are still many possibilities because there are various conceivable configurations of material parameters in the Fundamental Fractals which could favor the creation of room temperature superconductivity.

FF example: Simplified sketch of a section of the Fundamental Length Fractal: Spectrum of discrete values on the level $n_{0}$ on the logarithmic $z$-axis and linear $d$-axis whereby $d$ is any length and $\lambda_{\mathrm{p}}=\mathrm{h} /\left(2 \pi \mathrm{c} \mathrm{m}_{\mathrm{p}}\right)=2.10309 \times 10^{-16} \mathrm{~m}$, the so-called reduced Compton wave length of the proton, an assumed (universal) calibration unit for lengths:

nodes $d\left(n_{0}\right): 0.15 n m \quad 0.69 n m \quad 3.08 n m \quad 13.8 n m \quad 61.9 n m$

## Global Scaling and the search for room temperature superconductors

A tripartition of the chemical elements and associated hypotheses and observations are presented in part 3.2 and Ref. [3]. The tripartition of the chemical elements was first derived by Global Scaling and later also another way of its derivation was found. The tripartition of the chemical elements and associated hypotheses can be used to obtain a selection or set of specific chemical elements which favor or enable the occurence of superconductivity at room temperature. For further information see part 3.2 and Ref. [3]
[3] The tripartition of the chemical elements: Observations, considerations and hypotheses about the chemical elements and the number 3 : https://novam-research.com/resources/Chem-elements-and-number-3.pdf

Notes:

- For any task or question in which Global Scaling is applied, "conventional" knowledge, experiences, results and ideas play an equal role
- Global Scaling may also be applied to the search for room temperature superconductors among non-oxide materials such as organic conductors or metal-hydrogen compounds

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## Global Scaling - Examples of open questions

The following examples of open questions should be considered with respect to the following papers:
[4] https://www.novam-research.com/resources/Global-Scaling_Einfuehrung_V-2-dot-0_Maerz-2009.pdf (in German, 1 MB pdf, 25 pages)
[5] https://www.novam-research.com/resources/Global-Scaling_Introduction_V-2-dot-0_March-2009.pdf (in English, 1 MB pdf, 23 pages)

The papers [4] and [5] comprise for the Fundamental Fractal a list with calibration units which are mainly related to the properties of the proton

Further information about Global Scaling:

- Global Scaling website https://www.interscalar.com
- A Global Scaling book from Hartmut Mueller (2018, New Heritage Publishers, ISBN 978-0-9981894-0-6) can be downloaded as pdf free of charge via the following link (file size 11 MB ): http://www.ptep-online.com/books/muller2018.pdf
- Various information, links, and papers are listed in https://novam-research.com/global-scaling.php


## Global Scaling - Examples of open questions

- Does the Fundamental Fractal describe the (potential) effects of an everywhere present background field in an appropriate way and how universal is it?
- Are the pesently assumed calibration units appropriate and how universal are they?

Appropriate means if the Fundamental Fractal and the calibration units reflect or describe most appropriately the observed features of systems and processes in nature, biology, physics, universe, workable and reliable technology ...

- Is it possible to derive the Fundamental Fractal and the calibration units from a physical theory such as a specific type of unified field theory ?


## Global Scaling - Examples of open questions

About the calibration units
If the concept of the Fundamental Fractal and associated calibration units is basically correct, then the calibration units are specified by the underlying physics of the so-called empty space, vacuum, or ether and its inherent oscillations. Then it can be assumed that the calibration units are readable from some features of phenomena or physical appearances in nature and the universe, e.g. from something that is predominant and stable. The proton is a very stable elementary particle and the mass of the atoms is mainly given by the mass of the protons (the proton mass is 1836 times greater than that of the electron). The presently assumed calibration units are mainly quantities which are associated with the proton. For example, for masses the assumed (universal) calibration unit is the proton mass $m_{p}=1.67262 \times 10^{-27} \mathrm{~kg}$, for temperatures the assumed (universal) calibration unit is the so-called proton temperature $T_{p}=m_{p} c^{2} / k=1.0888 \times 10^{13} \mathrm{~K}$, and for lengths the assumed (universal) calibration unit is $\lambda_{p}=h /\left(2 \pi c m_{p}\right)=2.10309 \times 10^{-16} \mathrm{~m}$ which is the so-called reduced Compton wave length * of the proton.
Why just the reduced Compton wave length of the proton and not $\mathrm{h} /\left(\mathrm{c}_{\mathrm{p}}\right)=1.32141 \times 10^{-15} \mathrm{~m}$ which is the usual Compton wave length of the proton ? Why the Compton wave length at all and not, for example, the radius or diameter of the proton ? The electric charge radius of the proton was determined to $8.41 \times 10^{-16} \mathrm{~m}$, see e.g. https://www.psi.ch/en/media/our-research/proton-size-puzzle-reinforced . In comparison to masses, a well-defined and useful appearing calibration unit for lengths seems to be less obvious

[^0]
## Global Scaling - Examples of open questions

## About the calibration unit for angular momentum and spin

The angular momentum $L$ of a rigid body is defined by $L=I \omega$ whereby $I$ is the moment of inertia tensor and $\omega$ the angular velocity of the body. The angular momentum $L$ of a particle is defined by the vector product $L=\mathbf{r} \times \mathbf{p}$ whereby $\mathbf{r}$ is the position vector of the particle and $\mathbf{p}=\mathbf{m} \mathbf{v}$ is the momentum of the particle with mass $m$ and velocity $\mathbf{v}$. The intrinsic angular momentum of elementary particles such as the proton or electron is called spin. The physical unit of the angular momentum and spin is mass length ${ }^{2} /$ time such as $\mathrm{kg} \mathrm{m}^{2} / \mathrm{s}$.
When looking at the calibration units which are presented in Refs. [4] and [5] on page 162 , then it appears suggestive to obtain a calibration unit for the angular momentum and spin, $L_{p}$, in the following way:
$\mathrm{L}_{\mathrm{p}}=\mathrm{m}_{\mathrm{p}} \lambda_{\mathrm{p}}{ }^{2} / \tau_{\mathrm{p}}=\mathrm{h} / 2 \pi=\hbar=$ reduced Planck constant $=1.05457 \times 10^{-34} \mathrm{~kg} \mathrm{~m}^{2} / \mathrm{s}$ whereby $m_{p}$ is the proton mass, $\lambda_{p}=h /\left(2 \pi c m_{p}\right)$ the so-called reduced Compton wave length of the proton, and $\tau_{p}=\lambda_{p} / c=h /\left(2 \pi c^{2} m_{p}\right)$ the "proton time". On the other hand, it is known that the proton is a spin $1 / 2$ particle, i.e. its spin $S_{p}$ is $S_{p}=\hbar / 2=5.27286 \times 10^{-35} \mathrm{~kg} \mathrm{~m}^{2} / \mathrm{s}$ Is $L_{p}$ or $S_{p}$ an appropriate calibration unit for the spin and the angular momentum ? We suggest to consider $S_{p}$ as an appropriate calibration unit because it reflects the actual spin of the proton

## Global Scaling - Examples of open questions

About the calibration unit for magnetic moments
The physical unit of the magnetic moment is energy / magnetic flux density such as $\mathrm{J} / \mathrm{T}$ whereby $1 \mathrm{~J}=1 \mathrm{~kg} \mathrm{~m}^{2} / \mathrm{s}^{2}$ and $1 \mathrm{~T}($ Tesla $)=1 \mathrm{~kg} \mathrm{~A}^{-1} \mathrm{~s}^{-2}$. The latter reflects the physical unit of the magnetic flux density, namely mass current ${ }^{-1}$ time $^{-2}$
When looking at the calibration units which are presented in Refs. [4] and [5] on page 162 , then it appears suggestive to obtain a calibration unit for the magnetic moment, $v_{p}$, in the following way:
$v_{p}=E_{p} /\left(m_{p} I_{p}{ }^{-1} \tau_{p}{ }^{-2}\right)=e \hbar / m_{p}=1.01016 \times 10^{-26} \mathrm{~J} / \mathrm{T}$
whereby $E_{p}=m_{p} c^{2}$ is the proton energy, $m_{p}$ the proton mass, $I_{p}=e / \tau_{p}$ the "proton current", $\tau_{p}=\lambda_{\mathrm{p}} / \mathrm{c}=\mathrm{h} /\left(2 \pi \mathrm{c}^{2} \mathrm{~m}_{\mathrm{p}}\right)$ the "proton time", and $\mathrm{e}=1.602176 \times 10^{-19} \mathrm{~A} \mathrm{~s}$ the elementary charge.
On the other hand, the experimentally determined magnetic moment of the proton, $\mu_{\mathrm{p}}$, is
$\mu_{\mathrm{p}}=1.410607 \times 10^{-26} \mathrm{~J} / \mathrm{T}$
Is $v_{\mathrm{p}}$ or $\mu_{\mathrm{p}}$ an appropriate calibration unit for the magnetic moment? We suggest to consider $\mu_{\mathrm{p}}$ as an appropriate calibration unit because it reflects the actual magnetic moment of the proton

## Global Scaling - Examples of open questions

About the calibration unit for magnetic fields
The physical unit of the magnetic field or magnetic flux density is mass current ${ }^{-1}$ time $^{-2}$ such as $\mathrm{kg} \mathrm{A}^{-1} \mathrm{~s}^{-2}=\mathrm{T}$ (Tesla)

When looking at the calibration units which are presented in Refs. [4] and [5] on page 162 , then it appears suggestive to obtain a calibration unit for the magnetic field, $b_{p}$, in the following way:
$b_{p}=m_{p} I_{p}{ }^{-1} \tau_{p}{ }^{-2}=m_{p}{ }^{2} c^{2} /(e \hbar)=1.48816 \times 10^{16} \mathrm{~T}$
whereby $\mathrm{c}=299792458 \mathrm{~m} / \mathrm{s}$ is the speed of light. The other quantities are defined on the previous pages.

- Is the quantity $b_{p}$ really an appropriate calibration unit for the magnetic field?
- Is it possible to obtain another calibration unit for the magnetic field, for example via $\mu_{\mathrm{p}}=1.410607 \times 10^{-26} \mathrm{~J} / \mathrm{T}$ which is the experimentally determined magnetic moment of the proton?


## Global Scaling - Examples of open questions

About the calibration units
The following properties of the proton represent well-defined and experimentally determined quantities and therefore it seems to be obvious to consider them as welldefined and useful appearing calibration units for the corresponding physical scale:

- Proton mass: $m_{p}=1.67262 \times 10^{-27} \mathrm{~kg}$
- Electric charge of the proton (elementary charge): $\mathrm{e}=1.602176 \times 10^{-19} \mathrm{As}$
- Spin (intrinsic angular momentum) of the proton:

$$
S_{p}=\hbar / 2=5.27286 \times 10^{-35} \mathrm{~J} \mathrm{~s}
$$

- Magnetic moment of the proton: $\mu_{\mathrm{p}}=1.410607 \times 10^{-26} \mathrm{~J} / \mathrm{T}$
- Rest mass energy of the proton: $E_{p}=m_{p} c^{2}=1.503276 \times 10^{-10} \mathrm{~J}$

All other calibration units which are presented on the previous pages and in Refs. [4] and [5] on page 162 appear as "constructed" values that raise the following questions:

- Are they really appropriate calibration units ? When we consider e.g. The Fundamental Time Fractal on page 152 , then the assumed calibration unit for the time, the "proton time" $\tau_{\mathrm{p}}=\mathrm{h} /\left(2 \pi \mathrm{c}^{2} \mathrm{~m}_{\mathrm{p}}\right)$, seems to be appropriate because the corresponding values in the Fundamental Fractal reflect observed facts from our world
- Is there a clear explanation why $\tau_{\mathrm{p}}$ and other "constructed" calibration units are appropriate ?
- Is there perhaps a way to derive another and useful appearing calibration units from the above-mentioned, well-defined and experimentally determined quantities ?


## Global Scaling - Examples of open questions

The electron as a potential provider of another set of calibration units On the logarithmic $z$-axis the basic unit of The Fundamental Fractal repeats when z is displaced by $3 \mathrm{k} / 2=1.5 \mathrm{k}$ whereby $\mathrm{k}=0, \pm 1, \pm 2, \pm 3 \ldots$ Thus, if we neglect the absolute position on the logarithmic $z$-axis, then a calibration unit $x_{c}$ is equivalent to the following calibration units:
$\mathrm{x}_{\mathrm{c}}(\mathrm{k})=\mathrm{x}_{\mathrm{c}} \exp (1.5 \mathrm{k})$ whereby $\mathrm{k}=0, \pm 1, \pm 2, \pm 3 \ldots$
It is well-known that the proton mass $m_{p}$ is about 1836 times greater than the electron mass $\mathrm{m}_{\mathrm{e}}$ :
$m_{p}=1836.15 m_{e}=e^{7.515} m_{e}=m_{e} \exp (1.5 \times 5+0.015)!$
Thus, if the proton mass $m_{p}$ and the electron mass $m_{e}$ are considered as useful appearing calibration units, then both generate almost the same positions within the basic unit of The Fundamental Fractal. On the logarithmic $z$-axis they differ only by $0.015=1.5 \%$, in fact not only for masses but also on other physical scales when the associated calibration unit is a "constructed" quantity which comprises a mass such as the proton mass $m_{p}$ in the numerator or denominator, see previous pages and Refs. [4] and [5] on page 162. Is the electron mass $m_{e}$ or the proton mass $m_{p}$ the more appropriate calibration unit ? A detailed study is necessary to answer this question

4 Another extended / advanced / unconventional concepts in the context of superconductivity
4.1 Application of superconductivity in the area of entirely novel energy technologies
4.1.1 The cryogenic magnet motor of Walter Thurner
4.2 Superconductivity and ECE Theory

4 Another extended / advanced / unconventional concepts in the context of superconductivity
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## Superconductivity - Applications in the area of entirely novel energy technologies

Entirely novel energy technologies extract usable energy from an everywhere present space energy / space-time energy / vacuum energy / ether energy, see e.g. https://novam-research.com and https://novam-research.com/resources/information-document.pdf

Special configurations of physical fields such as magnetic, electric or gravitational fields allow the construction of self-running devices which can generate permanently usable energy by tapping the everywhere present space energy / space-time energy / vacuum energy / ether energy, see e.g. the above-mentioned links.

Magnetic fields are e.g. generated by permanent magnets or electromagnets but they can also be created by superconductors / superconducting coils / superconducting magnets. Therefore superconductors have an application potential in the area of entirely novel energy technologies. See for example section 5.1 in a paper from Prof. C. W. Turtur about the conversion of vacuum energy into mechanical energy, published in May 2009 in The General Science Journal: https://www.gsjournal.net/Science-Journals/Research\ Papers/View/2108 and https://www.gsjournal.net/Science-Journals/Research\ PapersQuantum\ Theory\ /\ Particle\ Physics/Download/2108

## Superconductivity - Applications in the area of entirely novel energy technologies

Experimental observation by several researchers and inventors:
A special geometrical array of permanent magnets results in an self-running acceleration of a magnetic slide or rotor

Example: The cryogenic magneti motor of Walter Thurner
It comprises a circular array of permanant magnets and a slide in form of a mechanical rotor. The array of permanent magnets is at some positions interrupted by diamagnets which are realized by high- $\mathrm{T}_{\mathrm{c}}$ superconductors that require a cooling by liquid nitrogen (superconductors are strong or ideal diamagnets). In case of an appropriate construction there is a permanent acceleration of the rotor. For a workable system, which represents an entirely novel energy or propulsion technology, it is necessary to develop a control system which limits the acceleration and speed. The cryogenic magneti motor of Walter Thurner is presented on the following pages ...

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The cryogenic magnet motor of the German engineer and inventor Walter Thurner is a nice example of a self-running system because its operation principle is published and comprehensible at the macroscopic scale. It can be understood just by considering the acting forces which operate in its design

Walter Thurner died on 12 February 2021 and meanwhile his former Germanlanguage website www.walter-thurner.de no longer exists and his former German-language pdf document www.walter-thurner.de/magnet.pdf is no longer available via his former website. However, his original pdf document is still available via https://novam-research.com/resources/Walter-Thurner_Kryo-Magnet-Motor.pdf. The author of this presentation thanks Walter Thurner for his remarkable work and his former pdf document whose essential parts are presented in English on the following pages. A German-language obituary is published on pages 63 and 64 in the May / June 2021 issue of the Germanlanguage NET-Journal (www.borderlands.de/inet.jrnl.php3) (ISSN 1420-9292).

Another German-language article about Walter Thurner: www.borderlands.de/net_pdf/NET0308S4-10 . This article is published on pages 4-10 in the March / April 2008 issue of the German-language NET-Journal. The cryogenic magnet motor is described on pages 8 and 9 .

An example of an embodiment of Walter Thurner`s idea is sketched on the following page in Fig. 1 and Fig. 2. His concept implies a linear or especially a circular array of magnets. One of such a magnet (1) is sketched in Fig. 1 and Fig. 2. Another magnet (3) is attached to a rod (4) which is connected with a shaft (5) so that the magnet (3) can move above (1). The sketched arrangement of the magnets (1) and (3) results in a motion of (3) towards the edge of (1). A repulsion arises between (3) and (1) when (3) approaches the edge of (1) and an attraction occurs when (3) goes away from (1). Thus at the edge of (1) the magnetic forces act against the direction of motion of (3).
That corresponds to a conventional or conservative system without any self-running motion

Sketch of an example of an embodiment of Walter Thurner`s idea from https://novam-
research.com/resources/Walter-Thurner_Kryo-Magnet-Motor.pdf (in German)


Fig. 1


Fig. 2
Image from https://novam-research.com/resources/Walter-
Thurner_Kryo-Magnet-Motor.pdf

Walter Thurner’s concept enables a self-running motion of the movable magnet (3) because strong diamagnets $(6,2)$ are placed at the edges of the magnet (1). The strong diamagnets $(6,2)$ are realized by high- $\mathrm{T}_{\mathrm{c}}$ superconductors such as $\mathrm{YBa}_{2} \mathrm{Cu}_{3} \mathrm{O}_{7-\delta}$ which is superconducting at the temperature of liquid nitrogen ( 77 K ). Thus Walter Thurner`s device requires a cooling by liquid nitrogen. The strong diamagnet, for example (2), generates an induced magnetic field whose direction is opposite to the external field of the magnets (1) and (3) and thus it attenuates / shields / modifies the magnetic fields / forces of and between (1) and (3) at the edge of (1). Therefore (3) can leave the edge of (1) in a non-decelerated way. If (3) approaches then the edge of another magnet of the type (1), then the strong diamagnet (6) attenuates or shields the repulsive force between (3) and (1) so that (3) crosses the edge of (1) in a non-decelerated manner. Thus a circular array of several units of the type (6)(1)(2) leads to a self-running and self-accelerating motion of the movable magnet (3) from one magnet (1) to another. An increase of the effect can be achieved when not only one but more movable magnets of the type (3) are used. For example, several magnets of the type (3) can be placed on or in a rotating disc. The self-running and self-accelerating motion implies a generation of usable energy. For example, the rotating shaft (5) can propel an electric generator

Important safety note: If the described device is constructed properly, then it is self-running and self-accelerating. Without appropriate measures the speed of rotation can increase continuously until the device does fly apart ! That is of course very dangerous and indeed it did happen with a constructed prototype!
Fortunately nobody was injured during that event. Pictures from components of the prototype before its self-destruction are shown on the right. The visible holes in the lower picture allow a supply of liquid nitrogen. A renewed construction of this device requires the development of appropriate measures which limit and control the speed of rotation!


Images from
https://novam-research.com/resources/Walter-
Thurner_Kryo-Magnet-Motor.pdf


The cryogenic magnet motor of Walter Thurner represents a nice example of a self-running system which can generate usable energy. Its operation principle appears comprehensible.
Once it is understood one has an idea how a self-running system can work concretely, at least at the macroscopic scale. Devising a self-running system by considering the existing macroscopic forces does not require to know the source of the generated energy. Nevertheless, it is of course an interesting question from where the generated energy comes from. The author of this presentation assumes that self-running devices imply at the subatomic level an extraction of usable energy from the everywhere present space energy, vacuum energy or ether energy via physical fields such as magnetic fields

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## Superconductivity and ECE Theory

The hypothesis on page 157 how superconductivity at room temperature may come about, namely
by a resonance-like interaction between an everywhere present background field and a special material with an appropriate crystal structure and chemical composition
seems to be supported by a statement from the so-called ECE Theory which is possibly related to the hypothesis above:
"... One of the important practical consequences is that a material can become a superconductor by absorption of the inhomogeneous and homogeneous currents of ECE space-time ..."

Cited from page 97 of the ECE uft paper No. 51
"ECE Generalization of the d'Alembert, Proca and Superconductivity Wave Equations: Electric Power from ECE Space-Time"
by M. W. Evans: www.aias.us/documents/uft/a51stpaper.pdf

## What is the ECE Theory?

- ECE stands for Einstein, Cartan and Evans and represents an unified field theory which allows a common description of the electromagnetic, gravitational, weak and strong nuclear forces
- Developed by Prof. Myron W. Evans by starting from Albert Einstein's Theory of General Relativity and the mathematic research work of the mathematician Elie Cartan


Myron W. Evans

- Some important statements:
- Gravitation is related to curvature of space-time
- Electromagnetism is related to torsion of space-time
- Coupling between electromagnetism and gravitation
- Extended electrodynamics with resonance phenomena via so-called spin connection $\Rightarrow$ Possibility of extracting usable energy from space-time
- Comprehensive information about ECE Theory in the website www.aias.us
- For an introduction into the ECE Theory see an article by H. Eckardt and L. G. Felker: www.aias.us/documents/eceArticle/ECE-Article_EN.pdf


# About the author 

and
Closing words

## About the author

- Name: Frank Lichtenberg
- Born 1962 in Bremen (Germany)
- 1983 - 1989: Study of physics at the University of Heidelberg (Germany)
- 1989 - 1992: Doctoral thesis in the division of Dr. J. Georg Bednorz at the IBM Zurich Research Laboratory (Switzerland). Doctorate / PhD at the University of Zurich in 1991. Field of work: Synthesis of oxides - especially in crystalline form via the melt - and study of their physical and structural properties
- 1992 - 1997: Research scientist in the nickel metal hydride technology department of Dr. Uwe Koehler at the research center of the battery company VARTA (Germany). Two months stay as guest scientist in Tokyo (Japan) at the TOSHIBA Battery Company within a collaboration between VARTA und TOSHIBA. Field of work: Hydrogen storage alloys and nickel metal hydride batteries
- 1997 - 2007: Research scientist in the department of Prof. Dr. Jochen Mannhart at the Institute of Physics of the University of Augsburg (Germany). Field of work: Setting up a new laboratory and synthesis of oxides - especially in crystalline form via the melt - and study of their physical and structural properties
- 2005: Participation in an 13 - day course in Global Scaling lectured by Hartmut Mueller in Germany
- 2007 - 2010: Freelance work, autonomous occupation with subjects in the area of physics and science. Creation of several presentations and papers and the website https://novam-research.com about entirely novel and environmentally friendly energy technologies and other new or little-known topics of science
- Since 2011: Research scientist in the division of Prof. Dr. Nicola Spaldin at the Department of Materials of the ETH Zurich (Switzerland). See personal ETH webpage and https://theory.mat.ethz.ch/lab.html .
Field of work: Setting up a new laboratory, synthesis of oxides - especially in crystalline form via the melt and study of their physical and structural properties, and teaching.
Secondary employment: Since 2015 consulting activities for the R \& D company Quantum Power Munich


## Closing words




[^0]:    * The Compton wave length of a particle with rest mass m corresponds to the wave length of a photon whose energy is equal to the energy $\mathrm{m} \mathrm{c}^{2}$ of the rest mass $m$

