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The story of Sr_2RuO_4

F. Lichtenberg

*Experimentalphysik VI, Center for Electronic Correlations and Magnetism (EKM), Institute of Physics,
Augsburg University, D-86135 Augsburg, Germany*

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Abstract

This article reports on the experiments performed in the Sr–Ru–O system, the motivation behind them and their impact on basic research and device applications. It refers to the time from 1987 to 2003, with emphasis on the occurrences before the discovery of superconductivity in Sr_2RuO_4 in 1994. Apart from the title compound Sr_2RuO_4 itself and related ruthenates, it touches on many different topics like titanates, ferrates, high- T_c superconducting cuprates, crystal growth by floating zone melting and thin films as well as fundamental and applied research.

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Keywords: Ruthenates; High- T_c superconductors; Titanates; Ferrates; Perovskite-related crystal structures; Layered materials; Polycrystalline compounds; Crystal growth; Floating zone melting; Thin films; Electrical conductors; Superconductivity; Basic research; Applied research; Device applications

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E-mail address: frank.lichtenberg@physik.uni-augsburg.de (F. Lichtenberg).

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1. Introduction

In 1994, Maeno, Hashimoto et al. reported the discovery of superconductivity with $T_c \approx 1$ K in Sr_2RuO_4 [1]. Since that time, Sr_2RuO_4 has gained considerable attention and more than 400 papers have been published on Sr_2RuO_4 . It is an unconventional spin-triplet superconductor with intriguing superconducting properties. These are discussed in two excellent review articles, a very recent and comprehensive paper in April 2003 by Mackenzie and Maeno [2] and a publication in January 2001 by Maeno, Rice and Sigrist [3]. The superconductivity in Sr_2RuO_4 is a very active field of research and there are many open questions.

This article narrates the story of Sr_2RuO_4 from the materials research point of view. It is focused on that what took place from before 1994 and how that, on the one hand, led to a possible application of SrRuO_3 in the semiconductor industry and, on the other hand, contributed to the discovery of superconductivity in Sr_2RuO_4 . Also, a few results of studies on Sr_2RuO_4 from 1994 to 2003 are presented. In the following, the chronological order of the events is used as a guideline. To illustrate this story with its events and people involved, in some parts of this paper, a personal rather than formal style of writing is used.

2. 1987–1993

2.1. How the decision to work on ruthenates came about

In 1986, Bednorz and Müller discovered superconductivity with $T_c \approx 30$ K in $(\text{La}, \text{Ba})_2\text{CuO}_4$ [4]. This material represents the parent compound of the high- T_c superconducting cuprates. Is the presence of Cu necessary for the occurrence of high- T_c superconductivity in oxides? This question led to many studies of physical and structural properties of Cu-free oxides, e.g. titanates and ruthenates.

The story presented in this article originated during the author's Ph.D. work from 1989 to 1992 at the IBM Zurich Research Laboratory (Switzerland) in the group of Bednorz. Concerning this story, two things have to be mentioned: One of the author's fields of work was the synthesis and characterization of titanates LaTiO_x , and at the same time there were already some studies on ruthenates at the IBM Research Laboratory.

The titanates LaTiO_x were prepared by the floating zone melting technique, which often resulted in crystals. During that time, a collaboration with Reller and Williams from the Institute of Inorganic Chemistry of the University of Zurich was established. Williams investigated structural features of the LaTiO_x samples by transmission electron microscopy (TEM). The results on LaTiO_x were published in 1991 [5,6]. The oxygen content x was systematically varied between both known end members $\text{LaTiO}_{3.0}$ and $\text{LaTiO}_{3.5}$, and new compounds were found. All compounds in the LaTiO_x system were identified as members of the homologous series $\text{A}_n\text{B}_n\text{O}_{3n+2} = \text{ABO}_x$ with a cation ratio of $\text{A}/\text{B} = 1$ ($\text{A} = \text{La}$, $\text{B} = \text{Ti}$): $\text{LaTiO}_{3.00-3.20}$ ($n = \infty$), $\text{LaTiO}_{3.4}$ ($n = 5$) and $\text{LaTiO}_{3.5}$ ($n = 4$). Apart from the perovskite ($n = \infty$), the $n \neq \infty$ members of this series have a layered perovskite-related structure. For recent overview articles on $\text{A}_n\text{B}_n\text{O}_{3n+2}$ type materials see Ref. [7].

Polycrystalline ruthenates with a three-dimensional perovskite structure like $(\text{Ca}, \text{Sr}, \text{La})\text{RuO}_3$ were studied at the IBM Zurich Research Laboratory in 1987 by Bednorz and Poulet [8] as well as in 1988 by Maeno and Bednorz [9]. In the time from 1988 to 1989, Maeno spent one year as guest scientist at the IBM Zurich Research Laboratory in the group of Bednorz. In 1989, Reller made the author aware of an investigation of the structural and thermochemical properties of polycrystalline solid solutions $\text{Sr}_2\text{Ru}_{1-x}\text{Ti}_x\text{O}_4$ and $\text{SrRu}_{2-x}\text{Ti}_x\text{O}_3$ at the University of Zurich. The results were published by Oswald, Felder-Casagrande and Reller in 1993 [10].

The author's interest was primarily in layered materials, and at IBM ruthenates with mainly three-dimensional structure were investigated. Therefore, the author looked for ruthenates with a layered structure. The layered titanates $\text{La}_n\text{Ti}_n\text{O}_{3n+2} = \text{LaTiO}_x$ involve a cation ratio of $\text{La}/\text{Ti} = 1$, but oxides with a cation ratio of $\text{A}/\text{B} \neq 1$ were also contemplated. Thereby, the perovskite-related layered materials of the type $\text{A}_{m+2}\text{B}_{m+1}\text{O}_{3m+4}$ gained attention. This so-called Ruddlesden–Popper series was established by Ruddlesden and Popper in 1957 and 1958 in the Sr–Ti–O system [11,12]. Fig. 1 shows the crystal structure of the members of the Ruddlesden–Popper series $\text{A}_{m+2}\text{B}_{m+1}\text{O}_{3m+4}$. Bulk compounds of this type are known for many B cations including $\text{B} = \text{Ru}$. In 1989, the author found two ruthenates of the Sr–Ru–O system in the JCPDS (ICDD) database, Sr_2RuO_4 ($m = 0$) and SrRuO_3 ($m = \infty$), and assumed that these are the only known Sr–Ru–O compounds. Similar to the approach in LaTiO_x , the author decided to try the preparation of materials with composition between the known end members Sr_2RuO_4 ($m = 0$) and SrRuO_3 ($m = \infty$), i.e. compounds with $0 < m < \infty$. The existence of such members of the Ruddlesden–Popper series, like the $m = 1$ or $m = 2$ type, was known from other systems, e.g. in Sr–Ti–O, as shown in Fig. 1. Analogous to the synthesis of LaTiO_x , the author also attempted to synthesize crystals of Sr–Ru–O compounds using the floating zone melting technique.

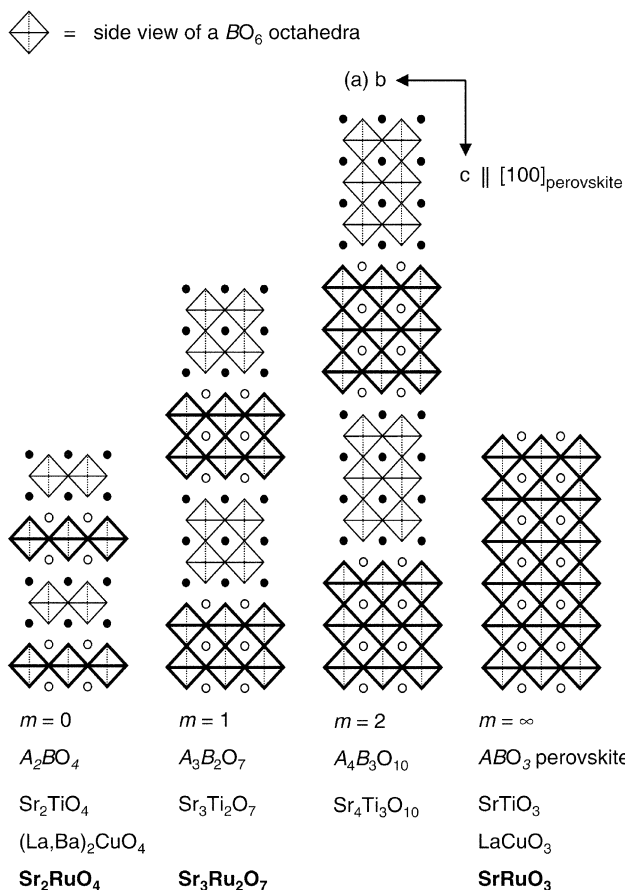


Fig. 1. Sketch of the crystal structure of the $m = 0, 1, 2$ and ∞ members of the perovskite-related layered homologous series $A_{m+2}B_{m+1}O_{3m+4}$ projected along the a - (or b -) axis. Circles represent the A cations. The layers are formed by corner-shared BO_6 octahedra within the ab -plane. Along the c -axis, the layers are $m + 1$ octahedra thick; thus, the thickness of the layers rises with increasing m . For $m = \infty$, the three-dimensional perovskite structure ABO_3 is realized. Light and heavy drawing of the BO_6 octahedra as well as filled and open circles indicate a height difference perpendicular to the drawing plane. Compositional examples are taken from the systems Sr–Ru–O, (La, Ba)–Cu–O and Sr–Ti–O.

2.2. Polycrystalline Sr–Ru–O compositions

To prepare the abovementioned samples, appropriate mixtures of $SrCO_3$ and RuO_2 powders were pressed into pellets and treated at high temperatures under air and at ambient pressure. Structural investigations were performed by powder X-ray diffraction (XRD) and TEM. In addition to the known ruthenates Sr_2RuO_4 ($m = 0$) and $SrRuO_3$ ($m = \infty$), the compound $Sr_3Ru_2O_7$ ($m = 1$) was readily

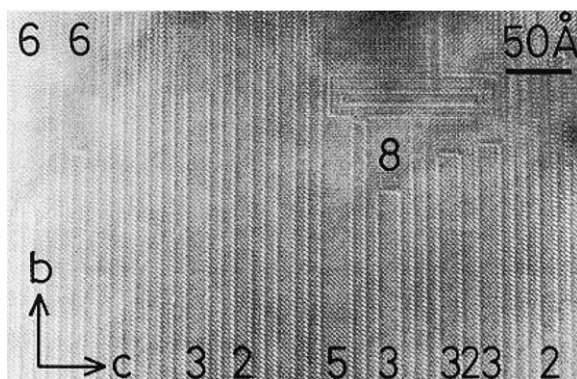


Fig. 2. TEM image from a tiny disordered crystal of a polycrystalline sample with nominal $m = 2$ composition $\text{Sr}_4\text{Ru}_3\text{O}_{10}$. In addition to the $m = 1$ majority $\text{Sr}_3\text{Ru}_2\text{O}_7$, other higher members like $m = 2, 3, 5, 6$ and 8 are present. (After Williams, Lichtenberg, Reller, Bednorz [13: p. 768]. Reprinted with the kind permission of Elsevier. ©1991 by Elsevier.)

obtained [13]. The next higher series member composition $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ ($m = 2$) could not be synthesized as single phase material as shown in Fig. 2. Therefore, it was concluded that single phase bulk materials exist only as $m = 0, 1, \infty$ types, at least under the preparation conditions used.

On the polycrystalline samples, resistivity measurements were performed between room temperature and 4 K in a four-point configuration. Fig. 3 displays the results for Sr_2RuO_4 ($m = 0$), $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($m = 1$) and SrRuO_3 ($m = \infty$). Note that SrRuO_3 is known as a ferromagnetic metal with a ferromagnetic transition temperature $T_c = 160$ K [15,16]. It is an itinerant ferromagnet, i.e. the ferromagnetic ordering is

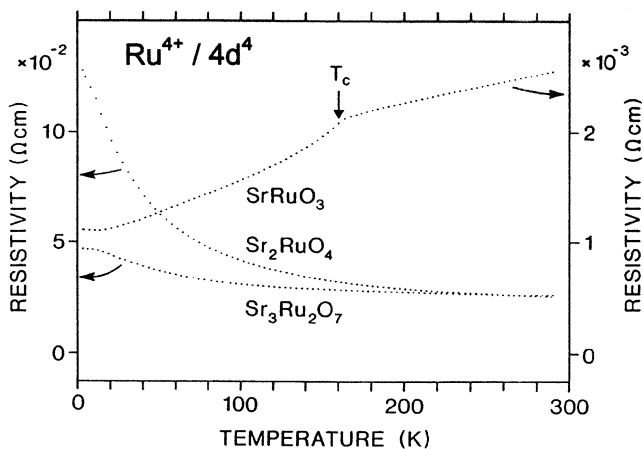


Fig. 3. Resistivity as a function of temperature of polycrystalline Sr–Ru–O compounds. The oxidation state of the Ru ions is the same for all of these compounds, namely $\text{Ru}^{4+}/4d^4$. The position of the ferromagnetic transition temperature T_c of SrRuO_3 is indicated by an arrow. After Lichtenberg [14].

due to delocalized electrons. It represents one of the very few ferromagnetic materials without a 3d or 4f element. The resistivity behavior of SrRuO_3 shown in Fig. 3 is in accordance with the data published by Bouchard and Gillson in 1972 [15]. For the layered Sr_2RuO_4 and $\text{Sr}_3\text{Ru}_2\text{O}_7$, it seemed likely that the true resistivity behavior differs from that shown in Fig. 3, because the polycrystalline nature of the samples hides their anisotropic features along and perpendicular to the layers. Also, grain boundaries were expected to influence the resistivity behavior. Of course, measurements on single crystals, if available, are preferable.

The polycrystalline samples were also investigated by magnetic measurements. The magnetic moment was measured as a function of temperature. However, for Sr_2RuO_4 and $\text{Sr}_3\text{Ru}_2\text{O}_7$, a strong increase of magnetic moment was observed below 160 K. This indicates the presence of small amounts of ferromagnetic SrRuO_3 as an impurity phase below the detection limit of powder XRD. Therefore, the magnetic measurements were not meaningful below 160 K.

2.3. Attempts to grow crystals of Sr–Ru–O compounds by floating zone melting

The crystal growth experiments were carried out in the following manner [14,17]. An appropriate mixture of SrCO_3 and RuO_2 powder was pressed into two rods and sintered at high temperatures in air and at ambient pressure. An example of two sintered polycrystalline rods is shown in Fig. 4. An optically heated floating zone melting furnace loaded with these rods is displayed in Fig. 5. An image from the floating zone melting process is shown in Fig. 6. During the floating zone melting, the long rod acts as feed material, whereas the short rod is used as seed and counterpart on which the melt solidifies. In general, crystals grow readily from the melt if the composition solidifies congruently or almost congruently (a solidification or melting is called congruent if the chemical composition of the melt and the solid is the same, i.e. if there is no decomposition into several phases). The floating zone melting was performed in a flow of synthetic air at ambient pressure.

In the first experiment, the growth of crystals of $\text{Sr}_3\text{Ru}_2\text{O}_7$ was attempted. Even during this attempt the following two observations were made, which are representative for all other Sr–Ru–O compositions used [14,17]:

1. The floating zone melting turned out to be difficult due to the relatively strong evaporation of RuO_2 . Thereby, a black layer was deposited within the quartz glass tube, which diminished the absorption of the radiation from the lamps. Therefore, to maintain the molten zone, a steady increase of the lamp power was necessary. Because 90% of the maximum lamp power was already required to melt the rods, the upper limit was reached soon and the experiment had to be stopped. Thus, only relatively small lengths of as-grown samples could be obtained. Furthermore, for all compositions used, the surface of the cylindrical as-grown samples had a rough polycrystalline appearance, probably due to the evaporation of RuO_2 . After crushing the as-grown samples, crystals were often found in the inner part. These pieces from the inner part were structurally investigated by powder XRD.

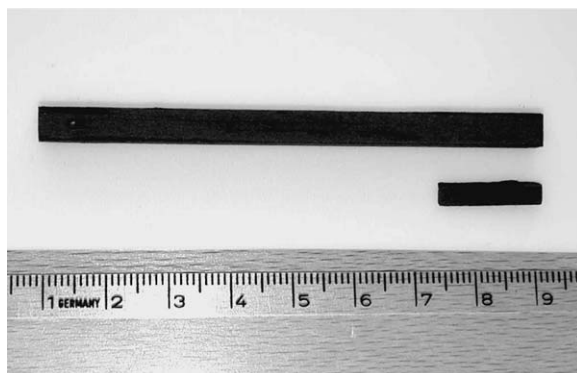


Fig. 4. Photograph of two sintered polycrystalline rods. The length of the long rod is 8 cm.



Fig. 5. Photograph of an optically heated floating zone melting furnace with opened elliptical reflectors and loaded with a long and a short polycrystalline sintered rod. The rods are separated from the environment in a gas-tight manner by a quartz glass tube, which acts as sample chamber. The process atmosphere can be chosen by a flow of an appropriate gas through the quartz glass tube. A lamp is located at the outer focus of each of the elliptical reflectors. During operation, the reflectors are closed, i.e. they surround the quartz glass tube completely. Thereby, the radiation from the lamps is concentrated on the inner focus, where the ends of the rods are located. By using a sufficiently high lamp power, the material located in the inner focus can be melted as shown in Fig. 6.

2. A strong tendency of formation of Sr_2RuO_4 was found, almost independent of the ratio Sr/Ru in the starting materials.

The attempts to grow crystals of $\text{Sr}_3\text{Ru}_2\text{O}_7$ were unsuccessful. The result was always a multiphase product with Sr_2RuO_4 as the dominant phase (today it is known that $\text{Sr}_3\text{Ru}_2\text{O}_7$ crystals can be obtained by floating zone melting under a high pressure of 10 bar).

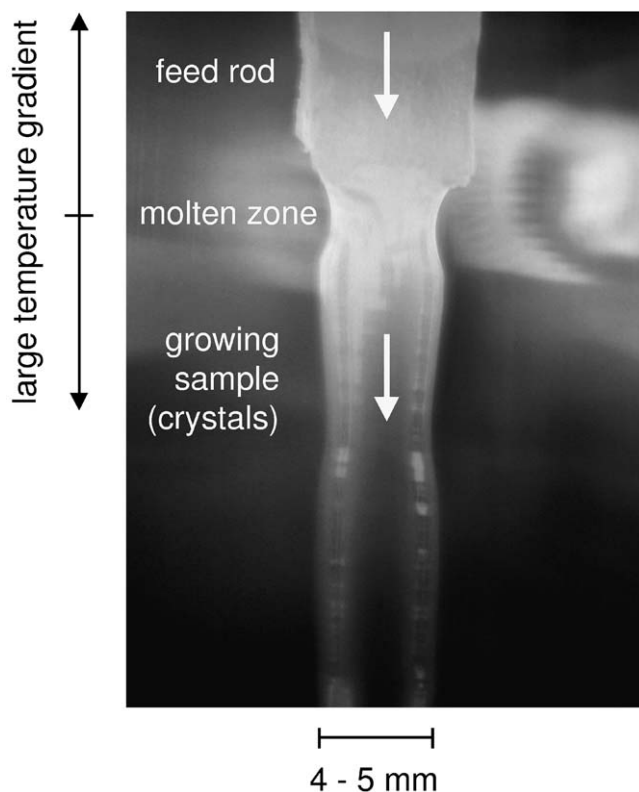


Fig. 6. Image of a floating zone melting process. It shows the bottom part of the feed rod, the molten zone and the growing sample. The latter evolves by solidification from the melt. The growing sample moves slowly (zone speed) in the same direction as the feed rod, which is indicated by the arrows. Thus, in the course of time, the feed rod is spent and converted via the melt into a melt-grown sample. The short seed rod is not visible in this picture: it is located below the bottom boundary. For the purpose of homogenization the growing sample is rotated, which results in a cylindrical shape. The as-grown sample may, for example, consist of a single crystal, many single crystals or a multiphase polycrystalline solid, depending on the chemical composition of the rods and growth conditions such as atmosphere and zone speed.

After the realization that the synthesis of $\text{Sr}_3\text{Ru}_2\text{O}_7$ crystals does not work (at ambient pressure), the author concentrated his efforts on Sr_2RuO_4 . An excess of RuO_2 in the starting materials was used to compensate for the loss due to evaporation. In the inner part of the as-grown samples, a single phase composition consisting of several single crystals could be achieved. The best crystals were obtained by using a ratio of $\text{Sr}/\text{Ru} \approx 2.1$ in the starting materials [14,17]. The largest crystals had a size in the range of $(2-3) \times (1-2) \times (0.1-0.3) \text{ mm}^3$. Fig. 7 shows an example. The Sr_2RuO_4 crystals can be cleaved easily, a feature which is typical for many layered materials. Regarding the as-grown samples, which have a cylindrical shape, the layers of the Sr_2RuO_4 crystals always grew parallel to the cylinder axis.



Fig. 7. Photograph of a Sr₂RuO₄ single crystal obtained by crushing the as-grown sample. The approximate size of this crystal is $2 \times 1 \times 0.2 \text{ mm}^3$.

The fact that Sr₂RuO₄ crystals can be grown by floating zone melting is remarkable and one may ask for the phase diagram of the SrO–RuO₂ system. To the best of the author's knowledge, this is not known even today, referring to the 1998 cumulative index of the phase equilibria diagrams [18]. Therefore, we use the SrO–TiO₂ system for comparison to discuss some items. Under oxidizing preparation conditions like air, the SrO–RuO₂ (Ru⁴⁺/4d⁴) and the SrO–TiO₂ (Ti⁴⁺/3d⁰) systems involve the same type of compounds as shown in Fig. 1. The SrO–TiO₂ phase diagram is known and presented in Fig. 8. The only compound which melts congruently is the perovskite SrTiO₃, as indicated by its continuous line from the solid to the liquid phase. The layered compounds Sr₂TiO₄ and Sr₃Ti₂O₇ melt incongruently. Attempts to grow Sr₂TiO₄ crystals by floating zone melting have so far not been successful even if a very low zone speed was used. This can be expected because Sr₂TiO₄ solidifies incongruently and shows a structural phase transition from the α -phase to the β -phase at $\approx 1525^\circ\text{C}$ (see Fig. 8). It looks, therefore, as if crystal growth by floating zone melting exhibits opposite behavior for SrO–RuO₂ and SrO–TiO₂: the layered compounds can be prepared for the ruthenates but not for the titanates, whereas the perovskite can be synthesized for the titanate but not for the ruthenate. It can also be said that the thermodynamically most stable compound of the titanates is the perovskite SrTiO₃ because it melts congruently, whereas for the ruthenates it is probably the layered Sr₂RuO₄ because of its strong tendency of formation. In general, in a system constituted by several elements with the presence of compounds, the thermodynamically most stable compounds are those which melt congruently. It can be supposed that Sr₂RuO₄ does not melt congruently in the strict sense, because of the intense evaporation of RuO₂. Therefore, the statement on thermodynamical stability refers to the experimentally observed strong tendency of formation.

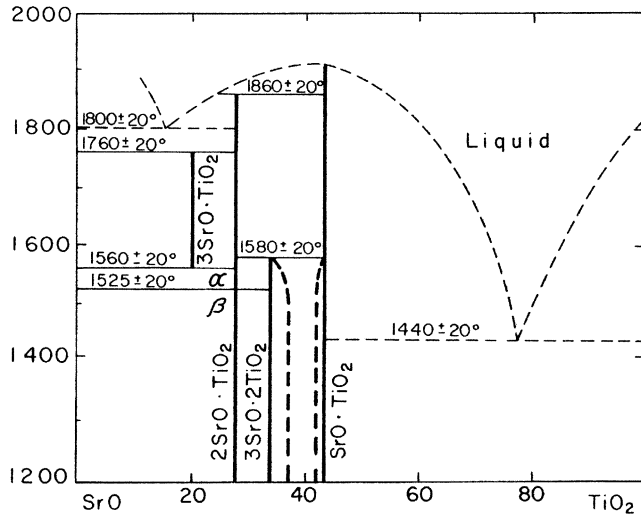


Fig. 8. Phase diagram of the system SrO–TiO₂. The vertical axis indicates the temperature in degrees Centigrade. The following compounds are given (see also Fig. 1): 2SrO · TiO₂ = Sr₂TiO₄ ($m = 0$), 3SrO · 2TiO₂ = Sr₃Ti₂O₇ ($m = 1$) and SrO · TiO₂ = SrTiO₃ ($m = \infty$). The only compound which melts congruently is SrTiO₃. (After Cocco and Massazza [19], which is presented in: *Phase Diagrams for Ceramists*, vol. II, p. 93, Fig. 2334, published by The American Ceramic Society (1969), ISBN 0-916094-05-7. Reprinted with the kind permission of The American Ceramic Society, <http://www.ceramics.org>. ©1969. All rights reserved.)

In this context, it is worth mentioning that recently single crystals of the solid solution Sr₂Ru_{1-x}Ti_xO₄ ($x < 0.25$) were grown by floating zone melting. This was done independent of each other by Ebbinghaus in Cava's group [20] as well as by Minakata in Maeno's group [21]. On these crystals, it was found by Minakata and Maeno [21] as well as by Pucher, Hemberger et al. [20] that for $x > 0$, the presence of non-magnetic Ti⁴⁺ induces a magnetic ordering with $T_c \approx 15$ K (the $x = 0$ compound Sr₂RuO₄ is paramagnetic).

2.4. The electrical resistivity of the Sr₂RuO₄ crystals

After the preparation of the Sr₂RuO₄ crystals, an interesting question was: How does the resistivity behave as a function of temperature? The resistivity was measured in a four-point configuration along and perpendicular to the layers between room temperature and 4 K [14,17]. The result is presented in Fig. 9. Along the layers, Sr₂RuO₄ is highly metallic, with $\rho_{ab} \approx 10^{-4} \Omega \text{ cm}$ at room temperature and $\rho_{ab} \approx 10^{-6} \Omega \text{ cm}$ at 4 K. The low value at 4 K is comparable to that of Cu at room temperature. The resistivity perpendicular to the layers is about 10^2 – 10^3 times larger than that along the layers. With decreasing temperature, it shows a semiconductor-to-metal transition at ≈ 120 K. The behavior displayed in Fig. 9 is qualitatively similar to that observed in the layered materials TaS₂ and graphite. Like Sr₂RuO₄, they are metallic along the layers and show a resistivity maximum

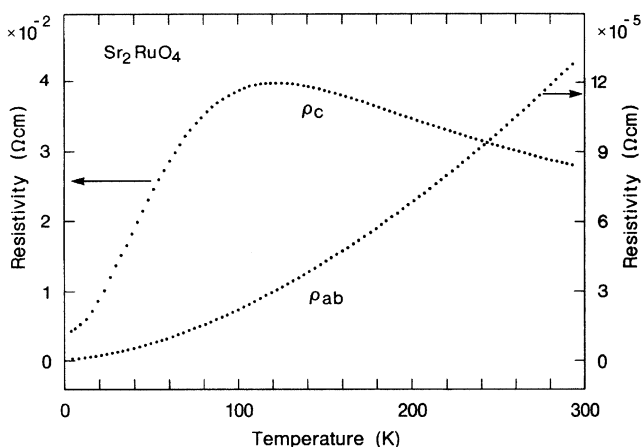


Fig. 9. Resistivity versus temperature of Sr_2RuO_4 along the layers, indicated by ρ_{ab} , and perpendicular to the layers, indicated by ρ_c . (After Lichtenberg, Catana, Mannhart and Schlom [17: p. 1139]. Reproduction kindly granted by the American Institute of Physics. ©1992 by the American Institute of Physics.)

between room temperature and 4 K perpendicular to the layers [22–24]. An explanation for the presence of a resistivity maximum in Sr_2RuO_4 was published by Maeno, Yoshida et al. in 1997 [25].

2.5. Sr_2RuO_4 and high- T_c thin films

The results of the resistivity measurements of Sr_2RuO_4 (see Fig. 9) were discussed with Mannhart, Schlom and Bednorz. At that time, Mannhart was a research staff member and Schlom a postdoctoral scientist at the IBM Zurich Research Laboratory, both in the group of Bednorz. Their field of work was the preparation and characterization of field effect devices based on thin films of high- T_c superconductors like $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [26–28].

The most common substrate used for the growth of high- T_c thin films was the perovskite SrTiO_3 , which is an insulator. The only available electrically conductive substrate compatible with high- T_c thin films was Nb-doped SrTiO_3 (i.e. a small amount of Ti^{4+} is substituted by Nb^{5+} , which results in a mixed-valence $\text{Ti}^{4+}/\text{Ti}^{3+}$). However, its electrical conductivity is relatively low and it shows a tendency towards insulating behavior under oxidizing conditions. Materials which are intrinsically metallic and/or highly conducting and compatible with high- T_c thin films were not known. For device applications of high- T_c superconductors, it was desirable to find such materials, e.g. in thin film form for SNS heterostructures (S = superconductor, N = normal metal) or as bulk substrate with high thermal conductivity. This led us to the idea that maybe Sr_2RuO_4 could be a metal compatible with high- T_c thin films. There were two reasons for this. First, Sr_2RuO_4 is an intrinsic metal with high conductivity along the layers (ab -plane) and seemed to be a very stable compound. Second, the lattice constants of the ab -plane of Sr_2RuO_4

fit those of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ very well. They fit $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ even better than those of SrTiO_3 , as shown by the comparison of the lattice constants a and b :

$$\begin{aligned} \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}: a &= 3.82 \text{ \AA}, b = 3.89 \text{ \AA} \quad (a \neq b) \\ \text{SrTiO}_3: a &= 3.91 \text{ \AA}, b = 3.91 \text{ \AA} \quad (a = b) \\ \text{Sr}_2\text{RuO}_4: a &= 3.87 \text{ \AA}, b = 3.87 \text{ \AA} \quad (a = b) \end{aligned}$$

We decided to perform some experiments to find out whether Sr_2RuO_4 really represents a metallic substrate compatible with thin films of high- T_c superconductors. Mannhart and Schlom deposited thin films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by hollow cathode magnetron sputtering on freshly cleaved ab -planes of Sr_2RuO_4 single crystals. The experimental details are described in Ref. [17]. The superconducting properties of the films were investigated by measuring their resistance R in a four-point configuration as a function of temperature. Indeed, good superconducting features were found, as shown in Fig. 10. Note that the transition temperature of $T_c(R=0) = 86 \text{ K}$ has to be compared with $T_c(R=0) = 88 \text{ K}$ for comparable films on SrTiO_3 . At that time, 88 K was the standard $T_c(R=0)$ at the IBM Zurich Research Laboratory. Later, the preparation of thin films was further improved and the $T_c(R=0)$ approached the well-known value of 91 K for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

Having obtained encouraging results from the resistance measurements, the next question was: Does $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grow epitaxially on the ab -plane of Sr_2RuO_4 ? To answer this question, Schlom carried out four-circle XRD measurements of the samples [17]. Fig. 11 presents the results. The Θ - 2Θ scan in Fig. 11(a) shows that the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ film is oriented with its c -axis perpendicular to the ab -plane of

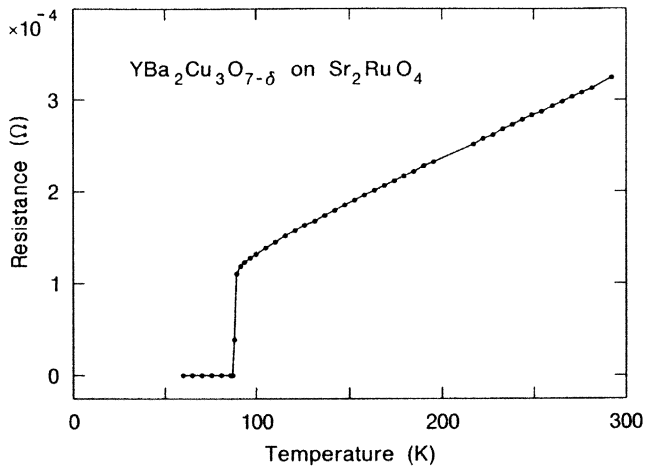


Fig. 10. Resistance R versus temperature T of a 120 nm thick film of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ deposited on the ab -plane of a Sr_2RuO_4 single crystal. The transition temperature of $T_c(R=0) = 86 \text{ K}$ with a transition width of $\Delta T = 1 \text{ K}$ indicates good superconducting properties. (After Lichtenberg, Catana, Mannhart and Schlom [17: p. 1139]. Reproduction kindly granted by the American Institute of Physics. ©1992 by the American Institute of Physics.)

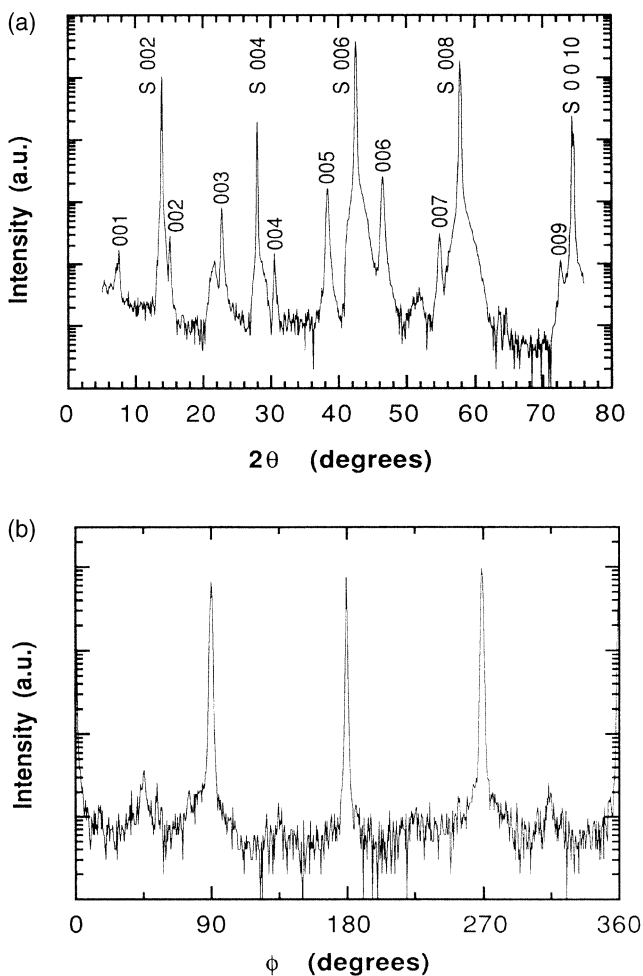


Fig. 11. XRD results from a thin film of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ deposited on the ab -plane of a Sr_2RuO_4 single crystal. (a) Θ – 2Θ scan aligned to the ab -plane of Sr_2RuO_4 . The label S denotes the peaks from Sr_2RuO_4 . (b) ϕ scan of the 103 reflection of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. $\phi \equiv 0$ is set parallel to the a -axis of Sr_2RuO_4 . (After Lichtenberg, Catana, Mannhart and Schlom [17: p. 1140]. Reproduction kindly granted by the American Institute of Physics. ©1992 by the American Institute of Physics.)

Sr_2RuO_4 . The ϕ scan of the 103 reflection of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ film in Fig. 11(b) indicates an epitaxial relationship between the film and the Sr_2RuO_4 substrate. This is because the appearance of peaks with a spacing of 90° points to an in-plane alignment of the perovskite axes of the film and substrate. Furthermore, in addition to the structural investigations by XRD, Catana studied the samples by TEM. At that time, he was a postdoctoral scientist at the IBM Zurich Research Laboratory. The TEM results of Catana also revealed an epitaxial relationship between the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ film and the Sr_2RuO_4 substrate [17].

Because of the properties just described, Sr_2RuO_4 was the first metallic substrate successfully employed for the epitaxial growth of high- T_c thin films. Therefore, we decided to apply for a patent concerning the use of Sr_2RuO_4 for this purpose [29]. We also considered the possibility of utilizing Sr_2RuO_4 in the form of thin films, e.g. deposited on a bulk substrate like SrTiO_3 [17,29]. An example of a potential use of Sr_2RuO_4 is shown in Fig. 12. It shows a field effect transistor (FET) involving a thin film of a high- T_c superconductor. More information on high- T_c FETs is given in Refs. [26–28].

We contemplated whether SrRuO_3 could also be a metal compatible with high- T_c thin films. Devices with high- T_c superconductors operate at temperatures at which SrRuO_3 is already in the ferromagnetic state. In general, the presence of a ferromagnet in the proximity of a superconductor disturbs the superconductivity. Therefore SrRuO_3 was not considered further.

2.6. Crystallographic investigations of Sr_2RuO_4

In collaboration with Walz, research scientist at the Daimler R&D Center in Ulm (Germany) and at the University of Ulm, a crystallographic study using single crystal XRD at room temperature and 100 K was performed.

Before Walz started with his crystallographic measurements, a literature research was carried out. We thereby became aware of a prior report by Müller-Buschbaum and Wilkens on crystals of Sr_2RuO_4 and also of $\text{Sr}_3\text{Ru}_2\text{O}_7$ [30]. It was published in 1990 and describes the preparation of Sr_2RuO_4 and $\text{Sr}_3\text{Ru}_2\text{O}_7$ crystals by the flux technique and the results of their crystallographic investigation by single crystal XRD at room temperature. In the case of Sr_2RuO_4 , Müller-Buschbaum and Wilkens obtained a few small needle-like single crystals, whereas they obtained irregular plate-like single crystals of $\text{Sr}_3\text{Ru}_2\text{O}_7$. In this context, it is worth mentioning that

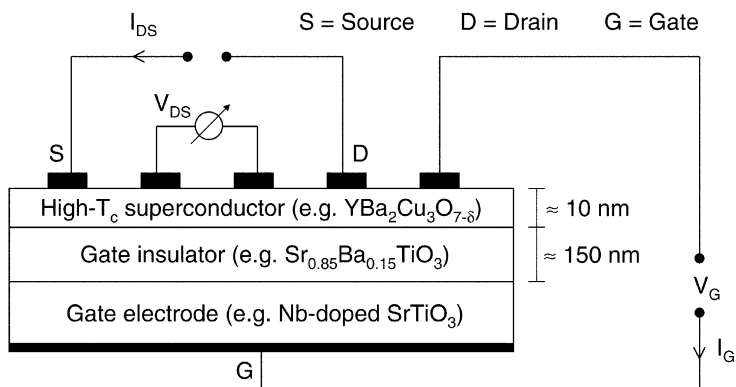


Fig. 12. Sketch of a high- T_c FET. The commonly used gate electrode material is Nb-doped SrTiO_3 . The use of Sr_2RuO_4 instead of Nb-doped SrTiO_3 was considered as advantageous [29].

the first paper on (polycrystalline) Sr_2RuO_4 was published by Randall and Ward in 1959 [31].

Walz performed the crystallographic measurements on appropriate crystals and determined the atomic coordinates at 295 and 100 K [32]. Two issues are worth mentioning:

- (I) Between 295 and 100 K, there were no indications for a structural phase transition, i.e. the structure remains tetragonal in this temperature range (later, in 1996, Ugadawa et al. and Gardner et al. revealed by Raman scattering on crystals from the same batch and by neutron diffraction on polycrystalline material that this is valid even down to 5 and 0.1 K, respectively [33,34]).
- (II) There is only a small temperature variation of the lattice constants which is compatible with that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

Both features favor the potential application of Sr_2RuO_4 for high- T_c devices.

2.7. Sr_2RuO_4 , high- T_c superconductors and layered ferrates

As the author often synthesized oxide materials by floating zone melting, Schlom became more and more interested in this method of crystal growth. Soon, Schlom started his own floating zone melting experiments. His main attention was directed towards the preparation of some special perovskite crystals, especially ferrates like LaFeO_3 , in order to employ them as substrate material for the growth of high- T_c thin films. The author was mainly interested in layered compounds and looked to find out whether layered ferrates were known. In the JCPDS (ICDD) database, the compound SrLaFeO_4 was listed, which has the same perovskite-related layered structure as Sr_2RuO_4 . SrLaFeO_4 represents an $m = 0$ and LaFeO_3 an $m = \infty$ type of the Ruddlesden–Popper series $\text{A}_{m+2}\text{B}_{m+1}\text{O}_{3m+4}$ (see Fig. 1). The Fe ions in these both ferrates are in the same oxidation state, namely $\text{Fe}^{3+}/3\text{d}^4$. The author decided to perform floating zone melting experiments with the compositions $\text{Sr}_{1+x}\text{La}_{1-x}\text{FeO}_4$ and found that good crystals could be prepared for $0 \leq x \leq 0.2$. A structural analysis by powder XRD showed that these crystals consisted of a single phase $m = 0$ type structure. Similar to Sr_2RuO_4 , they can easily be cleaved owing to their layered character. The (Sr, La) FeO_4 crystals were found to be electrically insulating. Concerning magnetic properties, Aso and Miyahara reported, in 1966, the absence of long range magnetic ordering in the temperature range from 800 to 4 K on polycrystalline SrLaFeO_4 [35]. SrLaFeO_4 has practically the same in-plane lattice constants as Sr_2RuO_4 . Therefore (Sr, La) FeO_4 could represent an insulator (I) which is maybe compatible with the high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (S) and the normal metal Sr_2RuO_4 (N). The following overview of the in-plane lattice constants a and b makes this clearer:

$$\begin{aligned} \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \text{ (S): } & a = 3.82 \text{ \AA}, b = 3.89 \text{ \AA} \quad (a \neq b) \\ \text{SrLaFeO}_4 \text{ (I): } & a = 3.87 \text{ \AA}, b = 3.87 \text{ \AA} \quad (a = b) \\ \text{Sr}_2\text{RuO}_4 \text{ (N): } & a = 3.87 \text{ \AA}, b = 3.87 \text{ \AA} \quad (a = b) \end{aligned}$$

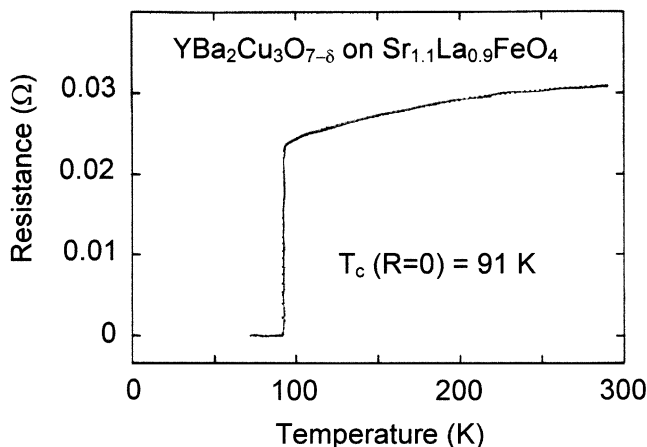


Fig. 13. Resistance versus temperature of a 100 nm thick film of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ deposited on the *ab*-plane of a $\text{Sr}_{1.1}\text{La}_{0.9}\text{FeO}_4$ single crystal. The transition temperature of $T_c(R=0) = 91$ K indicates good superconducting properties. After Lichtenberg, Schlom, Mannhart and Bednorz [36].

To find out whether $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is really compatible with $(\text{Sr}, \text{La})\text{FeO}_4$, Schlom and Mannhart deposited thin films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ on the *ab*-plane of freshly cleaved crystals of $\text{Sr}_{1.1}\text{La}_{0.9}\text{FeO}_4$ and measured the resistance of the films as a function of temperature [36]. Fig. 13 shows the result, which indicates good superconducting properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ on $\text{Sr}_{1.1}\text{La}_{0.9}\text{FeO}_4$. Therefore, the materials $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (S), $(\text{Sr}, \text{La})\text{FeO}_4$ (I) and Sr_2RuO_4 (S) were considered as a promising system for high- T_c SIN heterostructures which are exclusively built of oxides with a layered crystal structure.

3. 1992–1999: From Sr_2RuO_4 crystals to SrRuO_3 thin films

Our finding that Sr_2RuO_4 can be used as a metallic substrate for the epitaxial growth of thin films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was published in 1992 [17]. Our paper stimulated other groups to perform further work on ruthenates. The first subsequent report, also in 1992, came from Eom, Cava et al. at the AT&T Bell Laboratories [37]: a text excerpt is shown in Fig. 14. They studied the properties of epitaxial thin films of metallic $\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$ ($0 \leq x \leq 1$) on SrTiO_3 substrates. These films exhibited low resistivities, excellent chemical and thermal stability, good surface smoothness and high crystalline quality [37]. The CaRuO_3 films did not show any magnetic transition [37], whereas antiferromagnetism with $T_c \approx 110$ K was reported for CaRuO_3 in bulk form [15]. The metallic $\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$ films, and their multilayers with other oxide materials, can be used not only in superconducting but also in ferroelectric, magneto-optic and electro-optic devices [37]. These results from Eom, Cava et al. were an important step because they pointed to potential applications of ruthenates beyond the field of high- T_c superconductivity.

**Single-Crystal Epitaxial Thin Films of the Isotropic
Metallic Oxides $\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$ ($0 \leq x \leq 1$)**

C. B. Eom,* R. J. Cava, R. M. Fleming, Julia M. Phillips,
R. B. van Dover, J. H. Marshall, J. W. P. Hsu, J. J. Krajewski,
W. F. Peck, Jr.

Recently, Lichtenberg *et al.* reported the epitaxial growth of $\text{YBa}_2\text{Cu}_3\text{O}_7$ thin films on metallic substrates of Sr_2RuO_4 single crystals (10). This substrate material is a paramagnetic conductor with the K_2NiF_4 structure. Because of its layered structure, Sr_2RuO_4 exhibits metallic behavior parallel to the layers but is semiconducting perpendicular to the layers. This anisotropic resistivity might be a problem for making devices.

In this report, we present results on $\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$ epitaxial thin films. These films exhibit physical properties that may make them useful in some of these applications. These materials are pseudocubic perovskites (11–13) with essentially isotropic properties.

Fig. 14. Text excerpt from the paper of Eom, Cava, Fleming, Phillips, van Dover, Marshall, Hsu, Krajewski and Peck Jr [37: p. 1766].

Owing to its excellent physical and chemical properties, SrRuO_3 developed into a frequently used material for thin films and is used today for ferroelectric and dielectric devices. It is even expected that SrRuO_3 will be used as electrode material for $(\text{Ba}, \text{Sr})\text{TiO}_3$ capacitors in DRAMs (dynamic random access memory) in the semiconductor industry. This is presented in Fig. 15, referring to *The International Technology Roadmap for Semiconductors 1999*. Thin film capacitors consist of a bottom electrode, an insulating layer with a high dielectric constant κ and an upper electrode. According to Fig. 15, it is expected that SrRuO_3 will take over the role of the metals W, Pt, Ru, RuO_2 and IrO_2 in the bottom electrode.

Using published papers as reference, Fig. 16 presents the route from the Sr_2RuO_4 crystals grown by floating zone melting to the SrRuO_3 thin films which are expected to be used in DRAMs in the semiconductor industry.

In this context, the following is worth mentioning. The experimental attempts to grow thin films of ruthenates revealed that SrRuO_3 does form more readily than Sr_2RuO_4 . The low tendency of formation of Sr_2RuO_4 in thin film form is contrary to its bulk behavior, where the preparation via the melt indicated a strong tendency of formation.

4. 1994: The discovery of superconductivity in Sr_2RuO_4

In 1994, Maeno and Hashimoto from the University of Hiroshima (Japan) searched for superconductivity in Sr_2RuO_4 at low temperatures below 4 K. At first, the studies at low temperatures were performed on polycrystalline samples. Fig. 17

Year Technology Node	1999 180 nm	2002 130 nm	2005 100 nm	2008 70 nm	2011 50 nm	2014 35 nm
Upper Electrode (A)	poly-Si	TiON TiN	metal			
High κ Dielectric	ON	Ta ₂ O ₅	BST, STO	Epi-BST	super high κ	
Bottom Electrode (A,B)	poly-Si	metal		perovskite	tbd	

(A) Metal : W, Pt, Ru, RuO₂, IrO₂

(B) Perovskite : SrRuO₃³⁰

DRAM Stack Capacitor Films Potential Solutions

Fig. 15. Figure from p. 137 of The International Technology Roadmap for Semiconductors 1999. It shows, for the years 1999–2014, the potential materials which constitute the three different layers of which capacitors in DRAMs are built, namely upper electrode, insulator with high dielectric constant κ and bottom electrode. Here, “poly” means polycrystalline and “Epi” stands for epitaxial. “BST” and “STO” are the abbreviations for (Ba, Sr)TiO₃ and SrTiO₃, respectively. The terms “metal” and “perovskite” are explained below the table: “metal” means W, Pt, Ru, RuO₂, IrO₂ and “perovskite” stands for SrRuO₃. The cited reference for SrRuO₃, indicated by a small 30, is given in Fig. 16 as second from the top. (Reproduced with the kind permission of International SEMATECH, Semiconductor Industry Association. The International Technology Roadmap for Semiconductors, 1999 edition. International SEMATECH, Austin, TX, 1999. ©1999 by the Semiconductor Industry Association.)

shows the results of the magnetic susceptibility and resistivity measurements which were presented by Hashimoto in his master thesis in 1995 [38]. The magnetic susceptibility shows a drop below 1 K and the resistivity decreases below 2 K, which is indicative of a transition into a superconducting state. However, this behavior does not prove the presence of superconductivity beyond doubt because zero resistivity was not achieved. Therefore, an investigation of the low temperature properties on single crystals was suggested. Then, Maeno sent these intriguing results of the polycrystalline specimen to Bednorz and asked for some of the Sr₂RuO₄ crystals which were grown by the author in 1990. These crystals were stored in a sample cabinet of the IBM Zurich Research Laboratory. Bednorz was very interested and sent some of these crystals to Maeno. The low temperature measurements on the single crystals were performed at the University of Hiroshima and revealed the presence of superconductivity with $T_c = 0.93$ K in an unambiguous way, as shown in Fig. 18 [1].

The discovery of superconductivity in Sr₂RuO₄ by Maeno, Hashimoto et al. in 1994 was very remarkable. Its low $T_c = 0.93$ K is certainly not spectacular. However, since the discovery of superconductivity in perovskite-related layered (La, Ba)₂CuO₄ with $T_c \approx 30$ K in 1986 by Bednorz and Müller, Sr₂RuO₄ was the first

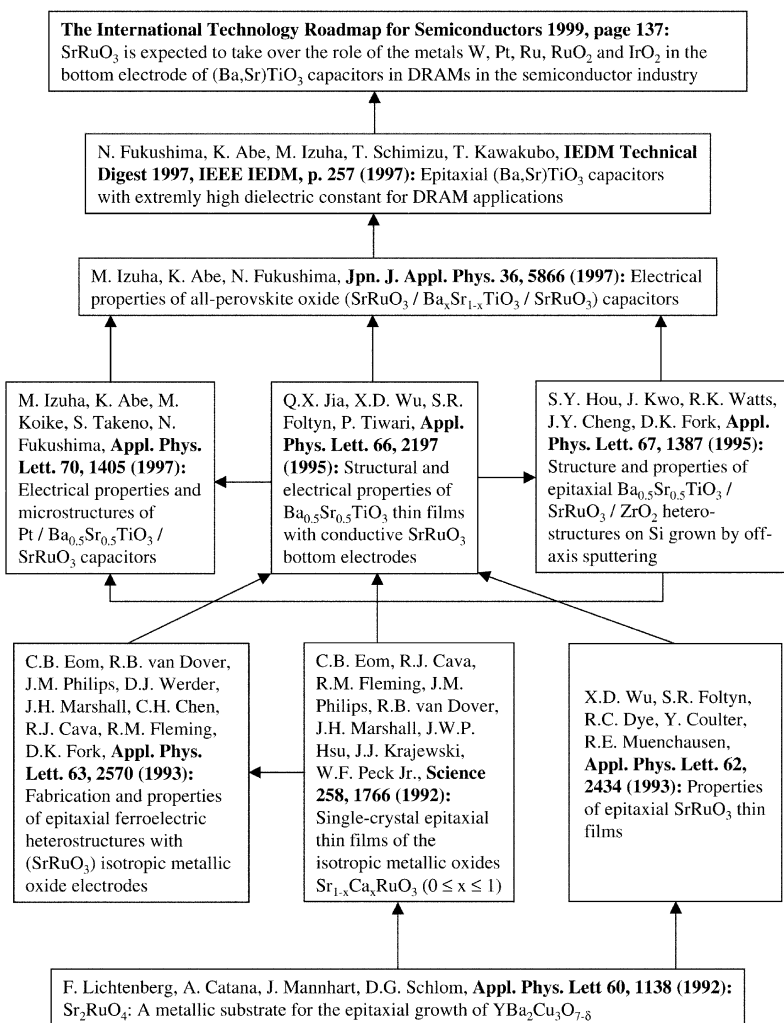


Fig. 16. Sketch of the evolution from Sr₂RuO₄ crystals grown by floating zone melting to a possible application of SrRuO₃ thin films in DRAMs in the semiconductor industry. This evolution is shown in terms of published reports.

Cu-free superconductor with a perovskite-related layered structure [1]. Even today, Sr₂RuO₄ represents the only non-cuprate superconductor isostructural with (La, Ba)₂CuO₄ as well as the only superconducting ruthenate. It was expected that a detailed study of the physical and structural properties of Sr₂RuO₄, and its comparison with the results obtained from (La, Ba)₂CuO₄, could lead to a more profound understanding of superconductivity in perovskite-related layered oxides.

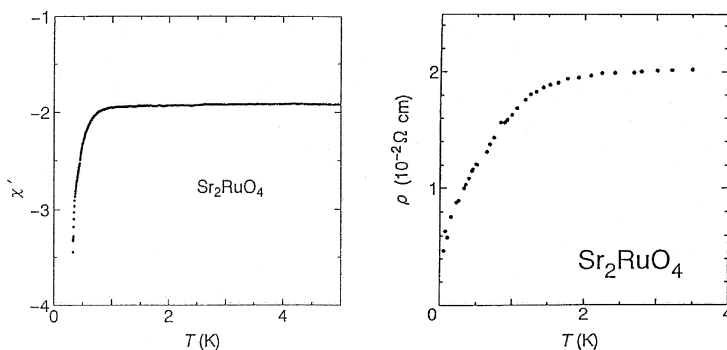


Fig. 17. Magnetic susceptibility χ' in arbitrary units (left) and resistivity ρ (right) of polycrystalline Sr_2RuO_4 as function of temperature below 5 K. After Hashimoto [38]. Reproduced with the kind permission of H. Hashimoto.

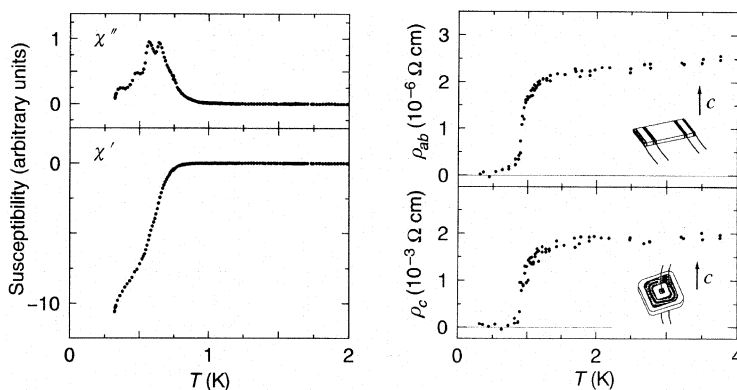


Fig. 18. Low temperature behavior of Sr_2RuO_4 single crystals. Left: Real part χ' and imaginary part χ'' of the magnetic susceptibility. Right: Resistivity ρ_c and ρ_{ab} perpendicular to and along the layers, respectively. Note that $\rho_c \approx 10^3 \times \rho_{ab}$. It clearly displays the existence of superconductivity with $T_c = 0.93$ K. These results were obtained in 1994 with crystals grown by the author in 1990. (After Maeno, Hashimoto, Yoshida, Nishizaki, Fujita, Bednorz and Lichtenberg [1: p. 533]. Reprinted with the kind permission of Nature, <http://www.nature.com/nature>. ©1994 by Macmillan Magazines Limited.)

5. 1995–2003: Some results of studies on Sr_2RuO_4

5.1. General remarks

Since the discovery of superconductivity in 1994, many papers on Sr_2RuO_4 have been published. It is beyond the scope of this article to give an overview of all studies and their results. The following reports briefly on some investigations which are related to the author's personal story of Sr_2RuO_4 and on a few further topics which are worth mentioning from the materials research point of view.

5.2. Normal state electronic properties at temperatures above T_c

It is very interesting that Sr_2RuO_4 is not only a metallic substrate for the epitaxial growth of high- T_c thin films, but is itself a (low- T_c) superconductor. At a conference of the German Physical Society in Berlin in 1995, the author reported on Sr_2RuO_4 and its properties. After this short post-deadline talk, Schmidt asked for some crystals to investigate the electronic states by near-edge X-ray absorption fine structure (NEXAFS) and photoemission spectroscopy. At that time, Schmidt was performing his Ph.D. work in the electron spectroscopy group of Schuppler at the Forschungszentrum Karlsruhe (Germany).

Schmidt, Cummins et al. studied the Sr_2RuO_4 crystals by NEXAFS, photoemission spectroscopy and angle-resolved photoemission spectroscopy (ARPES) and identified the orbital character and symmetry of the electronic states near the Fermi level E_F [39]. In total, the character at E_F can be estimated to be 80% Ru 4d derived and 20% O 2p derived—in contrast to the high- T_c superconducting cuprates, where the corresponding states are oxygen dominated. Also, the density of states at E_F is higher for Sr_2RuO_4 than in the cuprates. Furthermore, clear signatures for correlation effects could be found in Sr_2RuO_4 .

Subsequent ARPES performed with higher energy resolution enabled Lu, Schmidt et al. to map the Fermi surfaces (FS) as shown in Fig. 19 [40]. Although similar results had been obtained independently and published two months earlier by Yokoya, Chainani et al. [41], that group (at first) observed only two of the three FS. Fig. 20 displays the three FS obtained from recent ARPES studies by Damascelli, Lu et al. [42]. Comparison with Fig. 19 shows some differences, mainly in the shape of the γ band (this shape change, it should be noted, corresponds to only small modifications in energy positions of this nearly half-filled band). As possible explanations, the presence of a surface reconstruction as well as the difference in photon energies used (apparently leading to different surface contributions) have been suggested.

Maeno, Yoshida et al. performed resistivity, magnetic and specific heat measurements on many Sr_2RuO_4 crystals taken from several batches grown by Maeno's group in 1995 and 1996 and by the author in 1990 [25]. For low temperatures, it was found that Sr_2RuO_4 behaves like a highly anisotropic (two-dimensional) Fermi liquid [25]. For example, at temperatures T below 25 K, the resistivity along (ρ_{ab}) and perpendicular (ρ_c) to the layers is proportional to T^2 , whereby $\rho_c \approx 10^3 \times \rho_{ab}$. Such a temperature dependence is predicted by a theoretical model in which only contributions of the electron–electron interaction to the resistivity are considered and the interacting electrons are described as quasiparticles (Fermi liquid).

5.3. Progress in crystal growth

At the time of the discovery of superconductivity in Sr_2RuO_4 in 1994, the only crystals available were those which the author had grown in 1990. But soon, Maeno's and other groups started their own attempts to grow crystals by floating zone melting. Finally, many experimental efforts revealed the conditions for the preparation

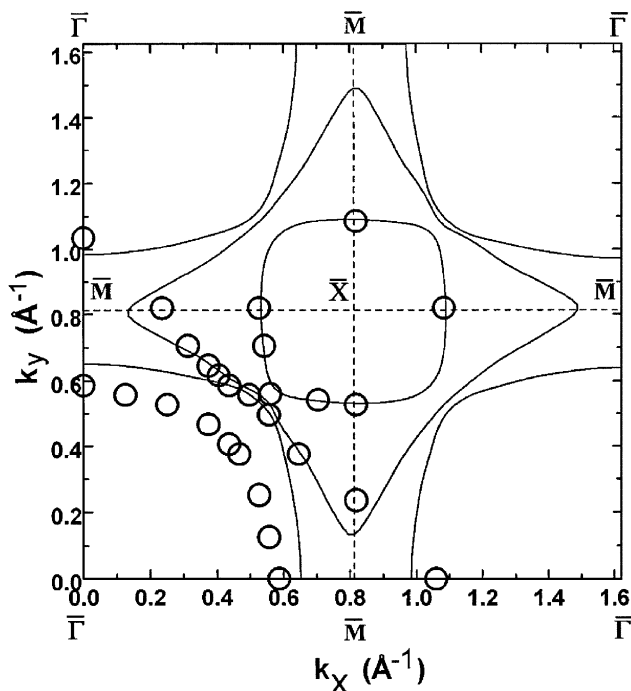


Fig. 19. Cross-section view of the three two-dimensional Fermi surfaces (FS) of Sr_2RuO_4 , i.e. three Fermi lines in the two-dimensional reciprocal k -space. The two axes of the k -space, denoted as k_x and k_y , are parallel to the high-symmetry lines which correspond in real space to the a - and b -axis within the layers. The open circles denote the FS crossings which correspond in ARPES measurements. The solid lines denote the FS derived from band structure calculations of Singh [43] by shifting the Fermi level by 77 meV. These results were obtained in 1995 with crystals grown by the author in 1990. (After Lu, Schmidt, Cummins, Schuppler, Lichtenberg and Bednorz et al. [40: p. 4847]. Reproduced with the kind permission of the American Physical Society. ©1996 by the American Physical Society.)

of large single crystals of high quality. A detailed description had been presented by Mao, Maeno and Fukazawa [44]. Fig. 21 shows an example. Large single crystals of high quality were also synthesized by Servant et al. of the CRTBT-CNRS in Grenoble (France) [45].

The crystals which were prepared by the author in 1990 had a superconducting transition temperature T_c in the range from 0.93 to 1.02 K [1,46]. Crystals with a very low concentration of impurities were prepared in the group of Maeno. The impurity concentration of the crystals can be traced by measurement of the residual resistivity ρ_0 at low temperatures. The lower the impurity concentration, the lower the residual resistivity ρ_0 . It was found by Mackenzie, Haselwimmer and coworkers that T_c increases with decreasing impurity concentration, as shown in Fig. 22 [47]. The highest T_c achieved is 1.5 K for $\rho_0 = 0.05 \mu\Omega \text{ cm}$ [44]. The results presented in Fig. 22 also show that T_c can be easily suppressed by non-magnetic

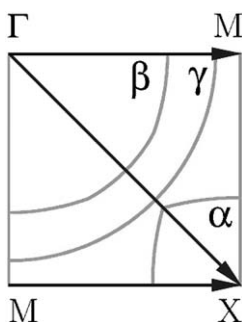


Fig. 20. Cross-section view of the three two-dimensional Fermi surfaces of Sr_2RuO_4 which are denoted as α , β and γ . This quadrant corresponds to the upper left of Fig. 19. These results were obtained in 2000 on crystals grown by Y. Maeno's group. (After Damascelli, Lu, Shen, Armitage, Ronning, Feng, Kim, Shen, Kimira, Tokura, Mao and Maeno [42: p. 5195]. Reproduced with the kind permission of the American Physical Society. ©2000 by the American Physical Society.)

impurities (such behavior hints at unconventional non-s-wave superconductivity, see Section 5.4.).

In this context, it is worth mentioning that so far there is no publication on the presence of superconductivity in thin films of Sr_2RuO_4 . It was reported by Zurbuchen, Jia et al. that minimizing the structural disorder in the films is important to achieve superconductivity, because their studies revealed structural defects in Sr_2RuO_4 films of a size comparable to the superconducting coherence length [48]. Furthermore, because the superconductivity in Sr_2RuO_4 is very sensitive to impurities, films of Sr_2RuO_4 certainly require a high degree of purity to attain superconductivity.

5.4. Unconventional superconductivity

In 1995, Rice and Sigrist argued on theoretical grounds that the superconductivity in Sr_2RuO_4 is an electronic analogue to superfluid ^3He , i.e. they suggested that Sr_2RuO_4 represents an unconventional p-wave spin-triplet superconductor [49]. To the best of the author's knowledge, the same was also proposed by Baskaran somewhat later in 1996 [50]. Superconductivity is called unconventional

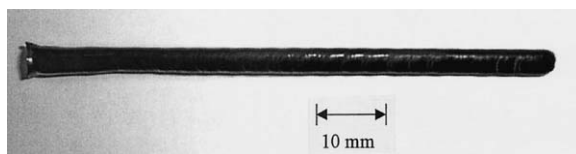


Fig. 21. Photograph of a large-size single crystal of Sr_2RuO_4 grown by floating zone melting. The crystal has its shortest dimension perpendicular to the paper surface, which is approximately the direction of the c -axis. (After Mao, Maeno and Fukazawa [44: p. 1815]. Reprinted with the kind permission of Elsevier. ©2000 by Elsevier.)

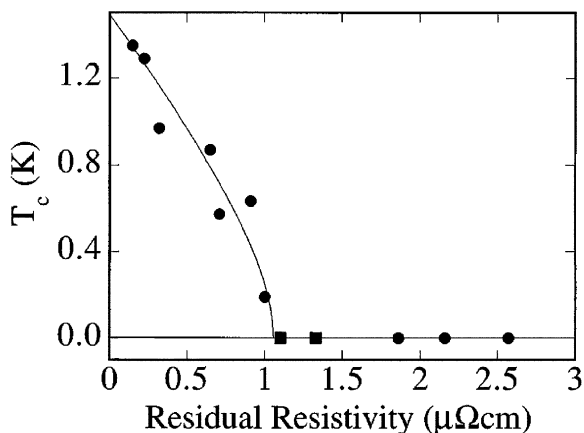


Fig. 22. Superconducting transition temperature T_c of Sr_2RuO_4 versus residual resistivity, which is a measure of the impurity concentration. These results with non-magnetic impurities were obtained in 1997 with crystals grown by Y. Maeno's group. (After Mackenzie, Haselwimmer, Tyler, Lonzarich, Mori, Nishizaki and Maeno [47: p. 163]. Reproduced with the kind permission of the American Physical Society. ©1998 by the American Physical Society.)

if the symmetry of the superconducting order parameter is less than the symmetry of the crystal structure, which usually implies a non-s-wave type. The terms s-wave, p-wave and d-wave denote the crystal analogs of the Cooper pair orbital angular momentum $L = 0, 1$ and 2 , respectively. The term spin-triplet means that a Cooper pair has a total spin $S = 1$. The high- T_c cuprates are also unconventional superconductors, but of d-wave (i.e. $L = 2$) and spin-singlet (i.e. $S = 0$) type. Meanwhile, there are many experimental results which indicate the presence of unconventional spin-triplet superconductivity in Sr_2RuO_4 . This kind of superconductivity is very unusual, and therefore Sr_2RuO_4 has gained more and more attention. The superconductivity in Sr_2RuO_4 is a very active field of research and there are many open questions. The intriguing superconducting properties of Sr_2RuO_4 are discussed in two excellent review articles, namely in a very recent and comprehensive paper, published in April 2003 by Mackenzie and Maeno [2], and in a publication in January 2001 by Maeno, Rice and Sigrist [3].

Some of the crystals which the author had grown in 1990 were used about 10 years later for some studies related to the unconventional superconductivity. In 1998, Goll, research scientist at the University of Karlsruhe (Germany) in the group of Löhneysen, asked Schuppler from the Forschungszentrum Karlsruhe and the author for Sr_2RuO_4 crystals (some of the crystals prepared by the author in 1990 were already in Schuppler's group). The idea was to perform point contact spectroscopy experiments in the superconducting state. From such measurements, it is possible to gain information on the symmetry of the superconducting order parameter. The point contact spectroscopy spectra were recorded by Laube, Goll et al. and the data analysis was supported by theoretical considerations of Fogel-

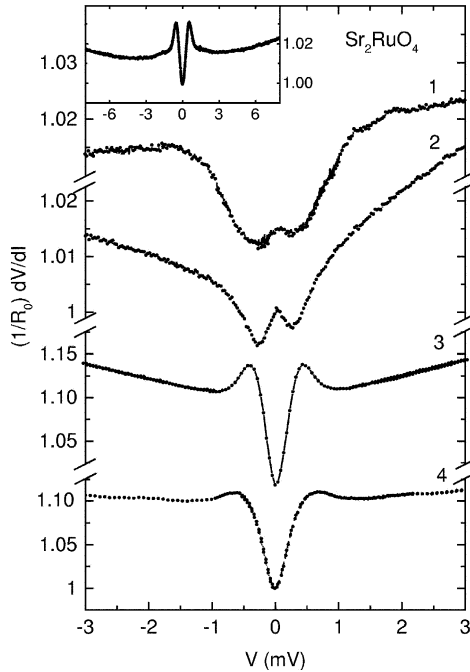


Fig. 23. Representative point contact spectra of Sr_2RuO_4 crystals at a low temperature of $T = 0.2 \text{ K} \ll T_c = 1.02 \text{ K}$. The S/N point contact consisted of $\text{Sr}_2\text{RuO}_4/\text{Pt}$ (S = superconductor, N = normal metal). The current I was injected predominantly along the layers. Shown is the normalized differential resistance dV/dI as a function of the bias voltage V for different zero-bias resistances $R_0 = 4.4 \text{ } \Omega$ (1), $5.0 \text{ } \Omega$ (2), $5.3 \text{ } \Omega$ (3) and $3.6 \text{ } \Omega$ (4). The inset displays dV/dI versus V with $R_0 = 7.6 \text{ } \Omega$. The results were obtained in 1999 with crystals prepared by the author in 1990. (After Laube, Goll, Löhneysen, Fogelström and Lichtenberg [46: p. 1596]. Reproduced with the kind permission of the American Physical Society. ©2000 by the American Physical Society.)

ström [46]. Some of the spectra are shown in Fig. 23. The results were confirmed on crystals with a T_c of 1.5 K from Maeno's group [51]. The differential resistance versus bias voltage (see Fig. 23), its temperature dependence (not shown) and associated theoretical considerations strongly support the presence of unconventional superconductivity of p-wave spin-triplet type in Sr_2RuO_4 [46,51]. Very recently, in 2003, Laube, Goll et al. presented results of point contact measurements in applied magnetic fields [52,53]. Two findings are especially worth mentioning. First, a field-induced insulating state at the surface of Sr_2RuO_4 was observed, which persists even above T_c up to several Kelvin [52]. The origin of this phenomenon is not yet understood. A field-induced structural instability at the surface seems to be the most probable reason, but further work is required for a definite assignment. Second, it was found that the excess current displays a linear dependence on the field and temperature over a surprisingly wide range [53]. A quantitative descrip-

tion of this behavior is obtained within a model in which the superconductivity is of p-wave spin-triplet type.

6. Other related ruthenates

The results obtained on Sr_2RuO_4 stimulated investigations on other related ruthenates of the Ruddlesden–Popper type (see Fig. 1), like $(\text{Sr}, \text{Ca})_2\text{RuO}_4$, $(\text{Sr}, \text{Ca})_3\text{Ru}_2\text{O}_7$ and $(\text{Sr}, \text{Ca})\text{RuO}_3$. Many interesting features were found in these $\text{Ru}^{4+}/4d^4$ oxides. Ca_2RuO_4 , for example, is an antiferromagnetic insulator [54] and $\text{Sr}_3\text{Ru}_2\text{O}_7$ a metal which shows metamagnetic behavior, i.e. a ferromagnet-like

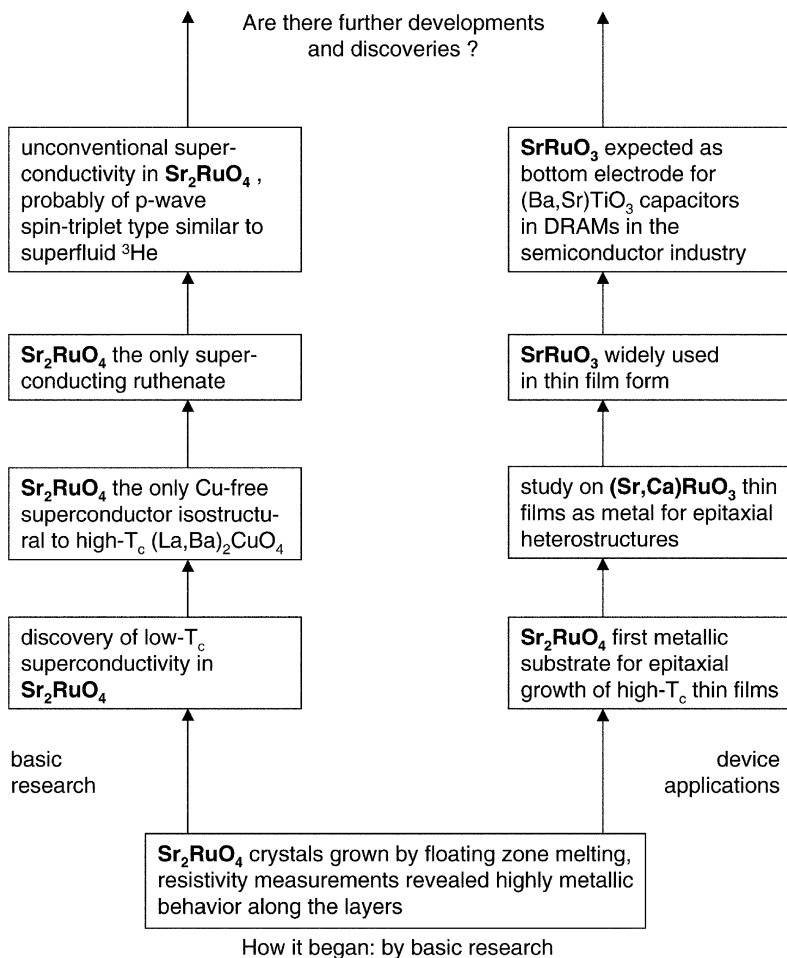


Fig. 24. Summary. It sketches the amazing evolution which originated from the Sr_2RuO_4 crystals grown by floating zone melting.

magnetization arises in a certain range of an applied magnetic field [55]. Furthermore, amazing features in the resistivity of $\text{Sr}_3\text{Ru}_2\text{O}_7$ were recently observed at low temperatures in applied magnetic fields [56]. These features are related to critical fluctuations, quantum phase transitions and quantum critical points in systems with correlated electrons [56].

7. Summary

The summary is presented in Fig. 24. It displays the surprising variety of interesting phenomena and results arising from Sr_2RuO_4 crystals grown by floating zone melting. It also demonstrates the importance of basic research, which not only results in progress within its own framework, but may lead in an unpredictable way to applications.

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