

# **Variation of the electronic states of $\text{Ca}_2\text{RuO}_4$ and $\text{Sr}_2\text{RuO}_4$ under uniaxial pressures**

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## Abstract

Competition and cooperation among spin, orbital, and lattice degrees of freedom are key concepts to understand intriguing phenomena in condensed matter systems. As one of such fascinating systems, the layered perovskite ruthenates  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  have been attracting wide interest for their variety of electronic states originating from multiple degrees of freedom: for example,  $\text{Ca}_2\text{RuO}_4$  is an antiferromagnetic (AFM) Mott insulator, whereas  $\text{Sr}_2\text{RuO}_4$  is a leading candidate for a spin-triplet superconductor.

For studying a system like  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  which has orbital degree of freedom, uniaxial pressure (UAP) is expected to be effective because it will couple well with orbital which spatially spreads along a certain direction. UAP can realize different crystal structures depending on pressure direction and intentionally control the symmetry of the crystal differently from hydrostatic pressure.

Therefore, we have studied the electronic states of  $\text{Ca}_2\text{RuO}_4$  and  $\text{Sr}_2\text{RuO}_4$  under UAPs with three different pressure directions: two in-plane directions,  $[100]_T$  and  $[110]_T$ , and the out-of-plane direction,  $[001]_T$ , using the tetragonal notation.  $[100]_T$  and  $[110]_T$  direction are parallel and diagonal to the in-plane Ru-O bond of the  $\text{RuO}_6$  octahedra, respectively.

For revealing the in-plane UAP effect on  $\text{Ca}_2\text{RuO}_4$ , we performed magnetization and resistivity measurements. We succeeded in inducing the ferromagnetic metallic (FM-M) phase. The mechanism of this Mott transition is considered to be the same as that under hydrostatic pressure: the out-of-plane flattening distortion of  $\text{RuO}_6$  octahedra is released, and the  $xy$  and  $yz, zx$  bands of Ru  $4d$  electrons approach energetically and overlap. The critical pressures of the FM-M phase for the UAPs (0.4 GPa for  $P_{\parallel[100]_T}$  and 0.2 GPa for  $P_{\parallel[110]_T}$ ) are substantially lower than that for the hydrostatic pressure (0.5 GPa). Interestingly, the critical pressure of the FM-M phase and the pressure dependence of FM component of magnetization were found to be highly anisotropic. These peculiar anisotropic results can be naturally understood as a consequence of the orthorhombic crystal distortions in  $\text{Ca}_2\text{RuO}_4$  and existence of orthorhombic crystalline twin domains in the sample.

Surprisingly, the out-of-plane UAP effect on  $\text{Ca}_2\text{RuO}_4$  was opposite to a simple prediction; from resistivity measurements, we have clarified that the insulating gap is suppressed from 3000 K to 700 K. This result suggests that  $\text{Ca}_2\text{RuO}_4$  approaches a metallic state under the out-of-plane UAP with a mechanism, which is different from that of the Mott transition under in-plane UAP. Since the crystalline field splitting between the  $xy$  and  $yz, zx$  bands should become larger, this gap suppression is expected to be induced by the enhancement of the band width as a result of the release of rotation or/and tilting distortion of  $\text{RuO}_6$  octahedra.

In the study of the out-of-plane UAP effect on the superconductivity (SC) of  $\text{Sr}_2\text{RuO}_4$ , we used  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic crystals in order to compare the UAP-originated 3-K SC with the interfacial 3-K SC in the same sample. We previously revealed that the onset of superconducting transition temperature  $T_c$  of  $\text{Sr}_2\text{RuO}_4$  without Ru inclusions is enhanced from 1.5 K to 3.2 K, which is the same as the onset  $T_c$  of the SC realized near interfaces between  $\text{Sr}_2\text{RuO}_4$  and Ru in the eutectic crystal. In this thesis, we newly proposed the out-of-plane UAP dependence of the spatial distribution of 3-K SC in  $\text{Sr}_2\text{RuO}_4$ -Ru from AC susceptibility and resistivity measurements.

The in-plane UAP effect on  $\text{Sr}_2\text{RuO}_4$  was also revealed to be significantly anisotropic from AC susceptibility measurements; we clarified that  $P_{\parallel[100]\text{T}}$  rather than  $P_{\parallel[110]\text{T}}$  is favorable for inducing 3-K SC.

Our results strongly demonstrate the effectiveness of UAP to control the electronic state of systems which have multiple degrees of freedom.

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# Chapter 1

## Introduction

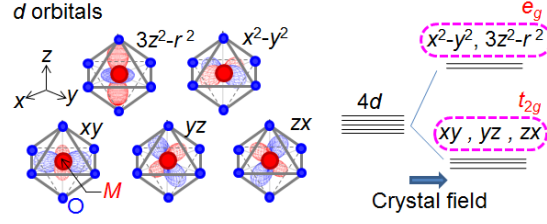
### 1.1 Motivation of the uniaxial pressure study of ruthenates

#### 1.1.1 Background

Competition and cooperation among spin, orbital, and lattice degrees of freedom are key concepts to understand intriguing phenomena in condensed matter systems. As one of such fascinating systems, the layered perovskite ruthenates  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  have been attracting wide interest for their variety of electronic states originating from multiple degrees of freedom: For example,  $\text{Ca}_2\text{RuO}_4$  is an A-centered antiferromagnetic (A-AFM) Mott insulator with the metal-insulator transition temperature  $T_{\text{M-I}} = 357$  K and the A-AFM ordering temperature  $T_{\text{A-AFM}} = 110$  K [1, 2], while  $\text{Sr}_2\text{RuO}_4$  is a leading candidate for a spin-triplet superconductor with the transition temperature  $T_c = 1.5$  K [3, 4].

For revealing the nature of interesting phenomena originating from orbital degree of freedom, ruthenates have ideal complexity and simplicity. The electronic state of ruthenates is determined by the four  $4d$  electrons per one Ru ion. Because Ru is octahedrally surrounded by O ions, in the layered perovskite crystal structure, the energy degeneracy of  $d$  orbitals is partially removed and the two  $e_g$  orbitals ( $x^2 - y^2$  and  $3z^2 - r^2$ ) locate energetically much higher than the rest three  $t_{2g}$  orbitals ( $xy, yz, zx$ ) as shown in Fig. 1.1. Since the Hund's coupling plays only minor roles in  $4d$  electrons, the four electrons in Ru  $4d$  orbitals occupy the three  $t_{2g}$  orbitals: all  $xy$ ,  $yz$ , and  $zx$  orbitals should have one electron but there still is a freedom to which orbital the fourth electron is located. In other words, ruthenates have orbital degree of freedom. However, in case of ruthenates, the situation is not too complex. For comparison, cuprates  $\text{A}_2\text{CuO}_4$  and iron pnictides  $\text{LaFeAsO}_{1-x}\text{F}_x$ , which exhibit high-transition-temperature superconductivity and fascinate many researchers, have no orbital degree of freedom and five orbital possibilities, respectively; While cuprates have one hole per one Cu ion and the hole always occupies  $x^2 - y^2$  orbital, all the  $d$  orbitals of pnictides form their band at the Fermi energy.

It has been recognized that distortions of the  $\text{RuO}_6$  octahedra are responsible for the variety of the electronic states of the ruthenates; the octahedra in  $\text{Sr}_2\text{RuO}_4$  have no distortion, while those in  $\text{Ca}_2\text{RuO}_4$  have three kinds of distortions: flattening, tilting and rotation along/from/around the  $c$



**Figure 1.1:** Orbitals of Ru 4d electrons in  $\text{RuO}_6$  octahedra

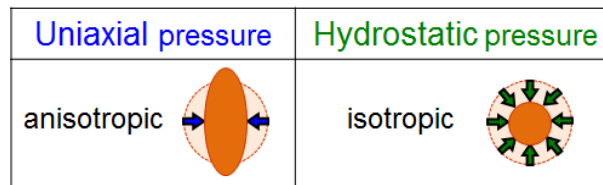
axis [5]. These distortions in  $\text{Ca}_2\text{RuO}_4$  are gradually removed by hydrostatic pressure ( $P_{\text{hydro}}$ ) and the electronic state changes accordingly: At 0.2 GPa, the magnetic structure of the AFM phase changes from the A-AFM to the B-centered AFM (B-AFM) structure, accompanied by a partial release of the flattening [6, 7]. At 0.5 GPa, the flattening distortion is completely released and ferromagnetic metallic (FM-M) phase below the Curie temperature  $T_{\text{FM}} = 12\text{-}28$  K appears [8, 6, 7]. At 10 GPa, the tilting distortion is released and superconductivity emerges [9]. Similar changes in the crystal structure and electronic state are observed also by substitution of Sr for Ca [10, 11, 12, 13]. Similarly, FM-M behavior is observed in  $\text{Ca}_2\text{RuO}_4$  thin films, where in-plane epitaxial stress leads to a structural change [14, 15]. Recently-discovered electric-field-induced Mott transition in  $\text{Ca}_2\text{RuO}_4$  is also accompanied by a change of the lattice distortion [16, 17]. Theoretical studies on relations between the lattice distortions and electronic states are also actively performed [18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28].

Moreover,  $T_c$  of  $\text{Sr}_2\text{RuO}_4$  is also sensitive to lattice distortion: the enhancement of  $T_c$  up to 3 K is observed in  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic crystals, where superconductivity with higher  $T_c$  occurs in the  $\text{Sr}_2\text{RuO}_4$  part around  $\text{Sr}_2\text{RuO}_4$ -Ru interfaces as a consequence of the strong lattice distortion due to lattice mismatch [29, 30, 31]. We revealed that similar enhancement of  $T_c$  occurs in non-eutectic  $\text{Sr}_2\text{RuO}_4$  under uniaxial pressure (UAP) [32]. In contrast,  $T_c$  of  $\text{Sr}_2\text{RuO}_4$  is suppressed by  $P_{\text{hydro}}$  [33, 34]. In addition, double superconducting (SC) transitions are theoretically expected in  $\text{Sr}_2\text{RuO}_4$  under in-plane UAP, because the SC order parameter of  $\text{Sr}_2\text{RuO}_4$  is considered to consist of multiple components and the energy degeneracy of the components is expected to be removed by in-plane uniaxial pressure [35, 36].

### 1.1.2 Motivation

From these previous studies, it is expected that we can induce a wide variety of electronic states in  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  by controlling the lattice distortion. As an effective method to control the lattice distortion, we focus on the following advantages of UAP. UAP can intentionally control the symmetry of the crystal differently from the application of hydrostatic pressure as shown in Fig. 1.2 and realize different crystal structures depending on pressure direction. These advantages mean that under UAP the variation of induced crystal structure is wider and systematic studies can be performed. Especially, for studying a system which has orbital degree of freedom, UAP is expected to be effective because it will couples well with orbital which spatially spreads along a certain direction.

However, UAP has also disadvantages: to achieve pressure homogeneity is rather difficult and



**Figure 1.2:** Comparison between uniaxial pressure and hydrostatic pressure

samples break easily. Thus, the technique of UAP experiments was not established yet, especially for oxides.

In my Ph. D study, we have first established the technique of UAP experiments, and then clarified UAP effects on  $\text{Ca}_2\text{RuO}_4$  and  $\text{Sr}_2\text{RuO}_4$ .



## Chapter 2

# Fundamental properties of $\text{Ca}_2\text{RuO}_4$ and $\text{Sr}_2\text{RuO}_4$

## 2.1 Mott insulator $\text{Ca}_2\text{RuO}_4$

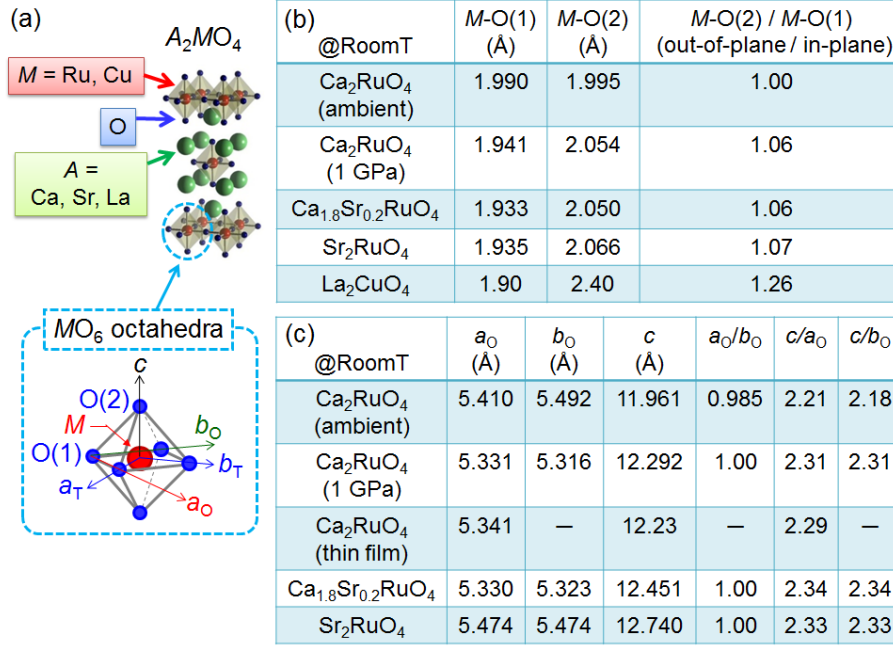
### 2.1.1 Coupling between the electronic state and the lattice distortion

The fundamental crystal structure of  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  is of layered perovskite as shown in Fig. 2.1 (a). In  $\text{Ca}_2\text{RuO}_4$ , the  $\text{RuO}_6$  octahedra have three kinds of lattice distortions: flattening, tilting and rotation along/from/about the  $c$  axis as shown in Fig. 2.2. In contrast,  $\text{RuO}_6$  octahedra of  $\text{Sr}_2\text{RuO}_4$  have no distortions. It is known that subtle lattice distortion strongly couples with the electronic state in this  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  system. The ground state of  $\text{Ca}_2\text{RuO}_4$  is an antiferromagnetic insulator (AFM-I), whereas that of  $\text{Sr}_2\text{RuO}_4$  is a spin-triplet superconductor.

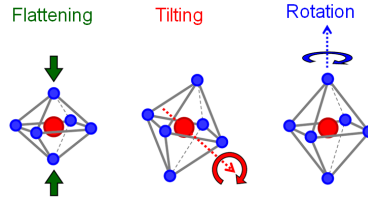
### 2.1.2 Sr substitution

In detail, three lattice distortions in  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  is released as follows with increasing  $x$ , which reflects the proportion of Sr. The flattening distortion is released at  $x = 0.2$  (Fig. 2.3) as a first-order phase transition. The ratio of Ru-O bond lengths (out-of-plane/in-plane) is 1.07 in  $\text{Sr}_2\text{RuO}_4$  without the flattening, while it is 1.00 in  $\text{Ca}_2\text{RuO}_4$  with the flattening, as shown in Fig. 2.1 (b) [5, 37]. Comparing with the ratio of Cu-O lengths of 1.26 in  $\text{La}_2\text{CuO}_4$  [38], the flattening distortion of  $\text{RuO}_6$  octahedra in  $\text{Ca}_2\text{RuO}_4$  is significant. The tilting angle is gradually suppressed from  $12^\circ$  at  $x = 0$  to  $0^\circ$  at  $x = 0.5$  as shown in Fig. 2.4 [12]. While the tilting distortion exists, crystal symmetry is reduced from tetragonal to orthorhombic. The rotation angle remains constant ( $12^\circ$ ) up to  $x = 0.5$ , then gradually decreases, and becomes  $0^\circ$  at  $x = 1.5$ .

The ground state also changes drastically in  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  by elemental substitution as shown in Fig. 2.5 [11]. Since Ca and Sr ions are isovalent in the crystal and the crystal structure is changed by Ca-Sr substitution, this variety of the ground states should originate from the difference in the crystal structure. It has been found that FM and AFM fluctuation are enhanced with increasing the rotation and tilting angle of  $\text{RuO}_6$  octahedra, respectively. Also, the Mott transition and AFM order occur when the flattening distortion is induced. These results indicate that the



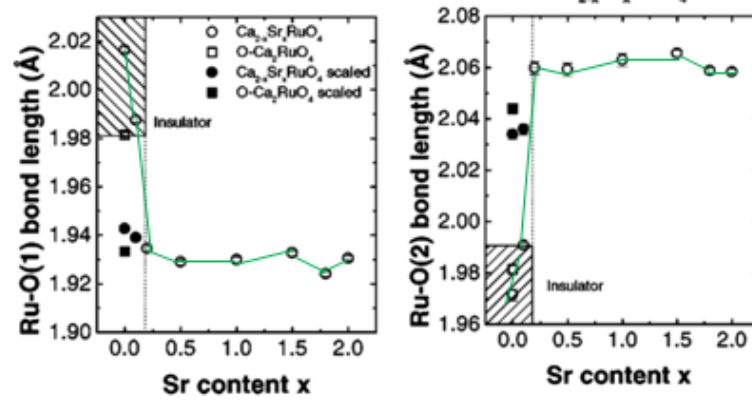
**Figure 2.1:** (a) Crystal structure of  $A_2MO_4$ . ( $A$ : Alkaline earth metal,  $M$ : Transition metal) Subscripts "T" and "O" indicate "Tetragonal" and "Orthorhombic" notation, respectively. (b) In-plane and out-of-plane  $M$ -O bond lengths of  $A_2MO_4$  under several conditions at room temperature. (c) Lattice constants in the orthorhombic notation of  $A_2MO_4$  under several conditions at room temperature. The panels (b) and (c) are made based on Ref. [5, 6, 12, 37, 38, 39].



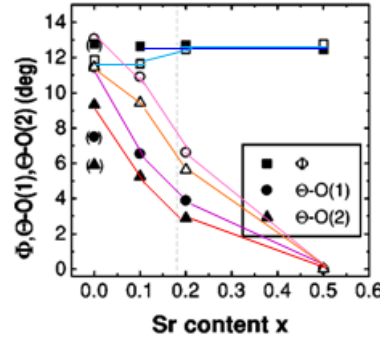
**Figure 2.2:** Lattice distortions of  $\text{RuO}_6$  octahedra

ground state of  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  indeed couples well with the lattice distortions of the  $\text{RuO}_6$  octahedra. Theoretically, first principles calculation was performed with taking the magnitude of the lattice distortions as parameters as shown in Fig. 2.6 [19, 22]. This study revealed that the rotation and tilting induce ferromagnetism and antiferromagnetism, respectively, and the flattening forces them to order. Moreover, it is theoretically clarified that the band width is suppressed by any of these three distortions [40, 41, 42, 19, 22]. The possibility of orbital-selective Mott transition in this system is also an intriguing issue [21, 43].





**Figure 2.3:** Sr-substitution dependence of Ru-O lengths in  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  [12].



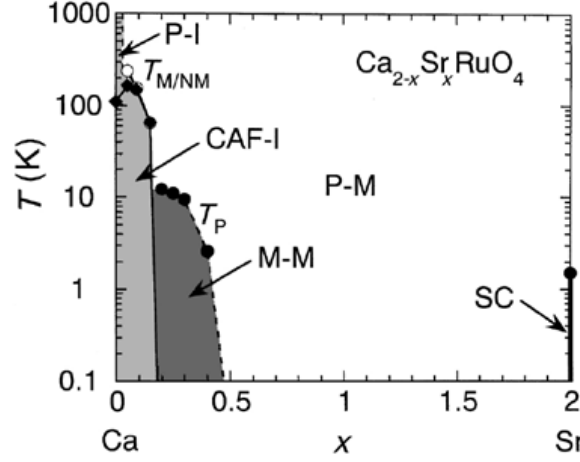
**Figure 2.4:** Sr-substitution dependence of the rotation angle  $\Phi$  and the tilting angle  $\theta$  of  $\text{RuO}_6$  octahedra in  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  [12].

### 2.1.3 Hydrostatic pressure

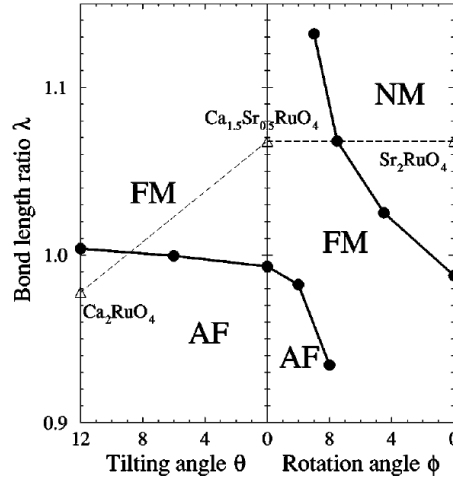
Hydrostatic pressure also induces the change of the electronic state of  $\text{Ca}_2\text{RuO}_4$  which is similar to Sr substitution as shown in Fig. 2.7 [6, 9]. At 0.5 GPa, the flattening distortion is released as a first-order phase transition as shown in Fig. 2.8 (a) [6], and the electronic state becomes metal as shown in Fig. 2.8 (b) [8].

Hydrostatic pressure studies have also revealed that a transition to another AFM state, B-centered AFM (B-AFM) state, occurs at  $T_{\text{B-AFM}} = 150$  K between 0.2 and 0.8 GPa as shown in Fig. 2.7(a) [6, 7]. The B-AFM phase is realized also in  $\text{Ca}_2\text{RuO}_4$  synthesized with the process of oxygen annealing [5]. In both cases, the flattening distortion of  $\text{RuO}_6$  octahedra is partially released in the B-AFM phase.

The essential difference between the A- and B-AFM phases is in the band occupation [24]: The A-AFM phase is realized when the energy level of the Ru  $xy$  orbital is substantially lower than those of the  $yz$ ,  $zx$  orbitals. Here we define  $x$ ,  $y$  and  $z$  in the tetragonal notation. Thus, two of the four  $d$ -electrons derived from Ru fully occupy the  $xy$  band and the others are in the half-filled  $yz/zx$  bands. In other words, the A-AFM phase is realized in a  $xy$ -ferro orbital ordered state. The B-AFM phase starts to emerge when the energy difference between the  $xy$  and  $yz/zx$  orbitals



**Figure 2.5:** Sr-substitution dependence of the ground state of  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  [11]. SC, P-M, M-M, CAF-I and P-I denote superconducting, paramagnetic metallic, metamagnetic metallic, canted antiferromagnetic insulating and paramagnetic insulating, respectively.

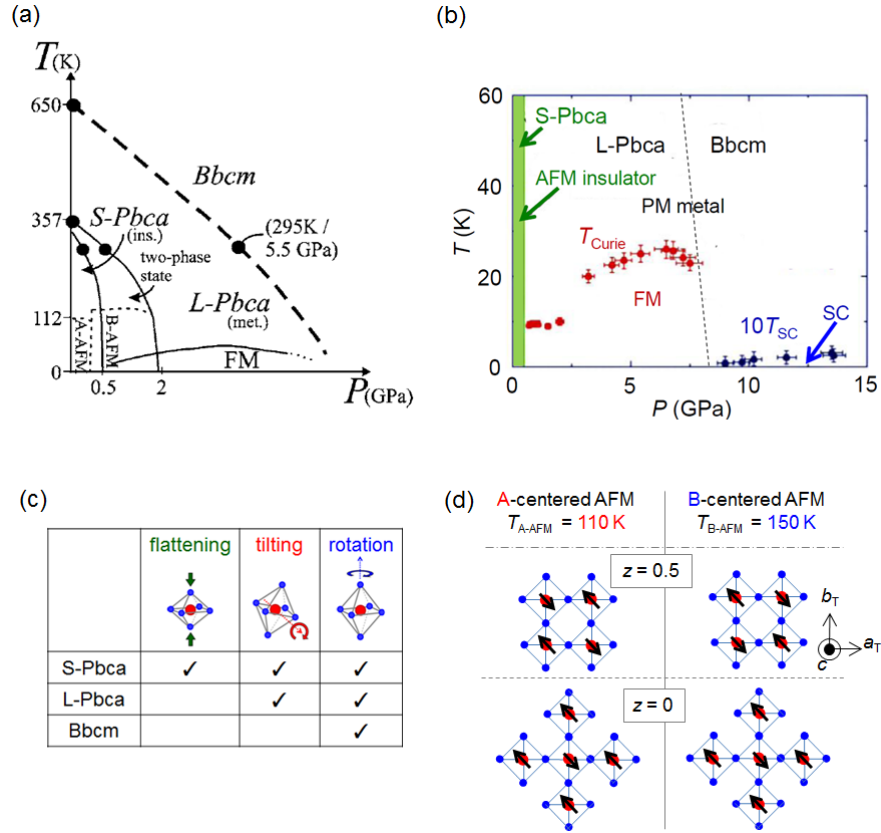


**Figure 2.6:** Magnetic phase diagram of  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  based on first principle calculation [19].

decreases by partial release of the flattening: electrons in the  $xy$  band are transferred to the  $yz/zx$  band, leading to an antiferro orbital order with the B-AFM order. When the flattening distortion is completely released,  $xy$ ,  $yz$  and  $zx$  orbitals are energetically degenerate and occupations of each orbital become  $4/3$ , and then metallic phase is realized.

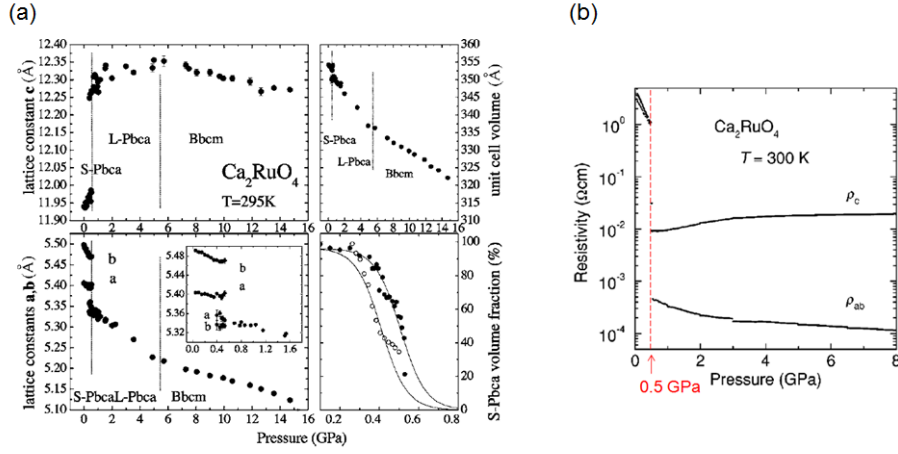
Under hydrostatic pressure, FM order [8, 7, 44, 45] and SC transition [9] are observed in addition to the Mott transition, as shown in Fig. 2.7 (a). The FM-M phase realizes between 0.5 and 8 GPa, and the maximum of the Curie temperature  $T_{\text{FM}}$  is 28 K at 7 GPa. Although the FM long-range order is realized under hydrostatic pressure, only development of FM fluctuation is observed by chemical substitution.

The SC phase emerges above 9 GPa and the SC transition temperature  $T_c$  is 0.4 K at 10 GPa.

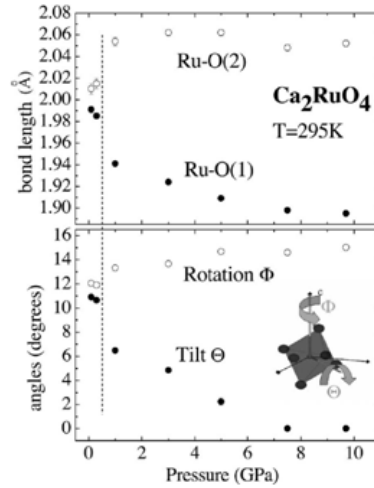


**Figure 2.7:** (a, b) Pressure-temperature phase diagram of  $\text{Ca}_2\text{RuO}_4$  [6, 9]. The panel (a) captures higher temperature region, while the panel (b) features higher pressure region. (c) Correspondence between the name of crystal structure in the group-theory notation and the lattice distortion in the case of  $\text{Ca}_2\text{RuO}_4$ . This figure is made based on the results of Ref. [6]. (d) Spin configuration of  $\text{Ca}_2\text{RuO}_4$  at the AFM orders. This figure is drawn based on Ref. [5].

Because the SC phase is located next to the FM phase and a chemical-substituted material  $\text{Sr}_2\text{RuO}_4$  exhibits spin-triplet superconductivity, the hydrostatic-pressure-induced SC of  $\text{Ca}_2\text{RuO}_4$  is also expected to be of spin-triplet. Thus,  $\text{Ca}_2\text{RuO}_4$  will be a new object for studying spin-triplet superconductivity. However, the high critical pressure of 9 GPa makes it difficult to reveal detailed properties of the superconductivity of  $\text{Ca}_2\text{RuO}_4$ . Therefore, it is significantly important to search for possible superconductivity under UAP, which may induce superconductivity with a lower pressure than the hydrostatic pressure. Relation between crystal structure and ground state is not completely clarified for emergence of superconductivity in  $\text{Ca}_2\text{RuO}_4$ , differently from the case of Mott transition of  $\text{Ca}_2\text{RuO}_4$ . However, as far as considering known experimental results, it seems that the FM order disappears and the superconductivity emerges at around the pressure where the release of tilting distortion occurs, as shown in Figs. 2.7 (b) and 2.9). Therefore, we can predict that some external force to release both the flattening and tilting distortion of  $\text{RuO}_6$  octahedra is preferable for inducing superconductivity in  $\text{Ca}_2\text{RuO}_4$ .



**Figure 2.8:** (a) Hydrostatic pressure dependence of lattice parameter of  $\text{Ca}_2\text{RuO}_4$  [6]. (b) Hydrostatic pressure dependence of electric resistivity of  $\text{Ca}_2\text{RuO}_4$  [8].



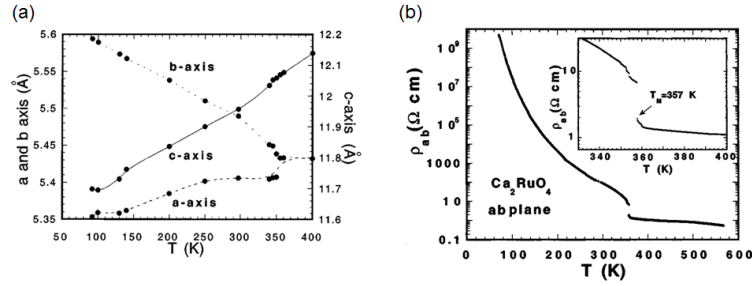
**Figure 2.9:** Hydrostatic pressure dependence of lattice distortion of  $\text{Ca}_2\text{RuO}_4$  [6].

## 2.1.4 Temperature

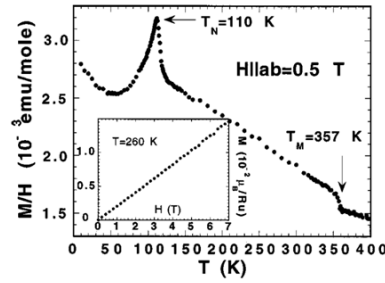
With increasing temperature, flattening and tilting distortions are released at 357 K and 650 K, respectively, as shown in Figs. 2.7 (a) and 2.10 (a) [6, 2]. Above 357 K, where flattening distortion is released, metallic state is realized as shown in Fig. 2.10 (b) [2]. With decreasing temperature,  $\text{Ca}_2\text{RuO}_4$  exhibits antiferromagnetic order below 110 K as shown in Fig. 2.11 [2].

## 2.1.5 Electric field

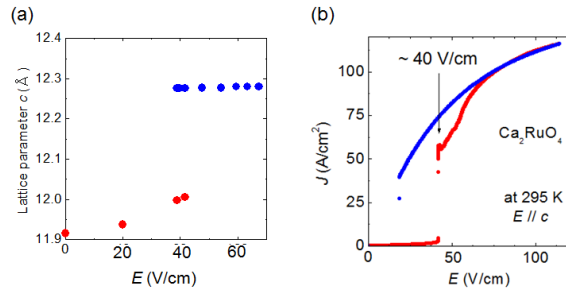
Electric field above 40 V/cm [16] also makes  $\text{Ca}_2\text{RuO}_4$  metallic by releasing the flattening distortion of  $\text{RuO}_6$  octahedra, as shown in Fig. 2.12 [16].



**Figure 2.10:** (a) Temperature dependence of the lattice parameter of  $\text{Ca}_2\text{RuO}_4$  [2]. (b) Temperature dependence of the electric resistivity of  $\text{Ca}_2\text{RuO}_4$  [2].



**Figure 2.11:** Temperature dependence of magnetization of  $\text{Ca}_2\text{RuO}_4$  [2].



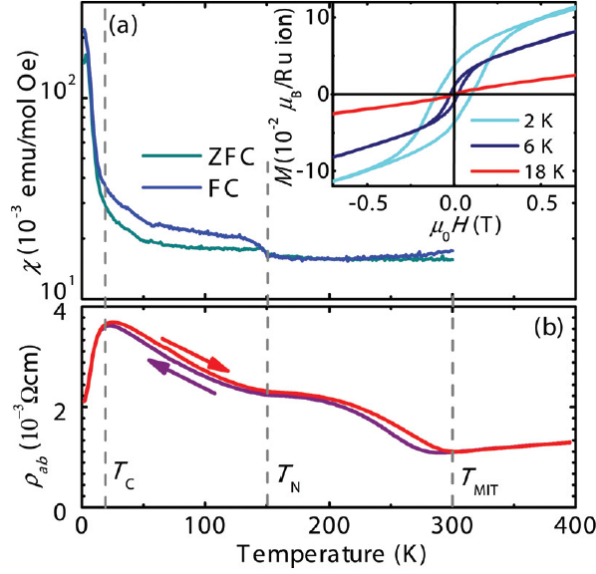
**Figure 2.12:** (a) Electric field dependence of lattice parameter of  $\text{Ca}_2\text{RuO}_4$  [16]. (b) Electric field dependence of electric resistivity of  $\text{Ca}_2\text{RuO}_4$  [16].

### 2.1.6 Thin film

FM-M behavior is also observed in  $\text{Ca}_2\text{RuO}_4$  thin films as shown in Fig. 2.13, where in-plane epitaxial stress leads to a structural change (Fig. 2.1 (c)) [14, 15, 39].

## 2.2 Spin-triplet superconductor $\text{Sr}_2\text{RuO}_4$

In almost all superconductors including high-transition-temperature cuprates, electronic Cooper pairs are of spin-singlet. In contrast, atomic Cooper pairs of superfluid  $^3\text{He}$  are of spin-triplet.



**Figure 2.13:** Ferromagnetic metallic behavior in  $\text{Ca}_2\text{RuO}_4$  thin film [15].

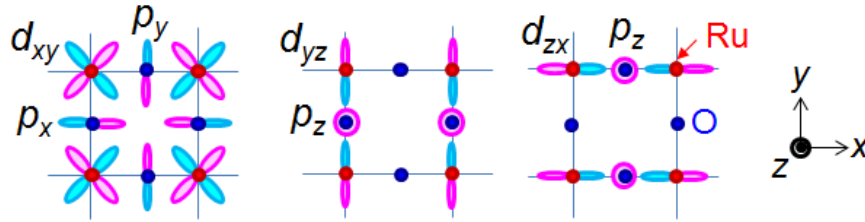
Then whether spin-triplet superconductivity exists or not has been an intriguing question in the research field of superconductivity and many researchers studied to find the answer of this question. At present, the following materials are leading candidates for spin-triplet superconductors:  $\text{Sr}_2\text{RuO}_4$ ,  $\text{UPt}_3$ ,  $\text{UBe}_{13}$ ,  $\text{UNi}_2\text{Al}_3$ ,  $\text{PrOs}_4\text{Sb}_{12}$ , and ferromagnetic superconductors such as  $\text{UGe}_2$ ,  $\text{URhGe}$ ,  $\text{UCoGe}$ . Moreover, in superconductors whose crystal structures do not have the inversion symmetry, the possibility of the mixing state of spin-triplet and singlet Cooper pairs is theoretically proposed. Examples of non-centro-symmetric superconductors are  $\text{CePt}_3\text{Si}$ ,  $\text{CeIrSi}_3$ ,  $\text{CeRhSi}_3$ ,  $\text{Li}_2(\text{Pt,Pd})_3\text{B}$ , and  $\text{UIr}$ .

Among these candidates for spin-triplet superconductors,  $\text{Sr}_2\text{RuO}_4$  has many evidences of spin-triplet superconductivity [46, 47, 48]. Moreover, the electronic structure of  $\text{Sr}_2\text{RuO}_4$  is simple and all the Fermi surfaces are known [3]. Therefore,  $\text{Sr}_2\text{RuO}_4$  is an ideal material for studying spin-triplet superconductivity.

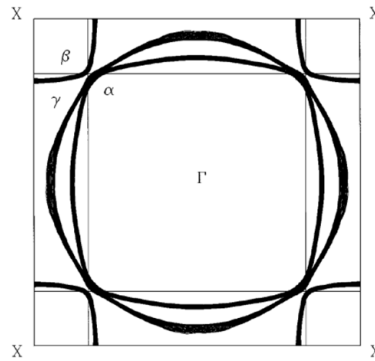
### 2.2.1 Fundamental properties of $\text{Sr}_2\text{RuO}_4$

$\text{Sr}_2\text{RuO}_4$  has a layered perovskite crystal structure similar to the structure of high-transition-temperature cuprate superconductors  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ . The electric conductivity is governed by the  $\text{RuO}_2$  layers. In the perovskite-based crystal structure, a transition-metal ion is octahedrally surrounded by oxygen ions. Then the degeneracy of the five  $d$  orbitals of the transition metal is partially removed due to the crystal-field effect, and the  $d$  levels split into two degenerate  $e_g$  orbitals ( $x^2 - y^2$  and  $3z^2 - r^2$ ) and three degenerate  $t_{2g}$  orbitals ( $xy, yz, zx$ ). In case of the  $4d$  orbitals, the energy splitting between the  $t_{2g}$  orbitals and the  $e_g$  orbitals is more important than Hund's coupling. Therefore, in Ru-based perovskites, four  $4d$  electrons per one Ru ion choose low spin state and occupy the  $t_{2g}$  orbitals. In  $\text{Sr}_2\text{RuO}_4$ , the  $t_{2g}$  orbitals of Ru hybridize with the

$p$  orbitals of O on  $\text{RuO}_2$  layers and form bands. The band originating from the  $xy$  orbital is two dimensional and the band originating from the  $yz$  and  $zx$  orbital is one dimensional (Fig. 2.14). On the  $k_x k_y$  plane, the two-dimensional band forms a circular Fermi surface, while each one-dimensional band forms a straight Fermi surface. However, the actual Fermi surfaces originating from the  $yz$  and  $zx$  bands are rounded squares because of small hybridization of the  $yz$  and  $zx$  bands. As a result, three cylindrical Fermi surfaces are expected as shown in Fig. 2.15. Actually, such Fermi surfaces are observed in dHvA experiments (Fig. 2.16) [3]. The  $\alpha$  surface is a hole Fermi surface originating from the  $yz$ - $zx$  hybridization band, the  $\beta$  surface is an electronic Fermi surface originating from the  $yz$ - $zx$  hybridization band, and the  $\gamma$  surface is an electronic Fermi surface originating from the  $xy$  band. The cylindrical shapes of these Fermi surfaces indicate that the electronic state of  $\text{Sr}_2\text{RuO}_4$  is quasi two dimensional and support the expectation that the conduction occurs mainly in the  $\text{RuO}_2$  plane. The effective electronic masses of the  $\alpha$ ,  $\beta$ , and  $\gamma$  surfaces are 3.4, 7.5, and 14.6 times as large as the mass of the free electron. These electronic masses suggest that electron-electron interaction is moderately strong in  $\text{Sr}_2\text{RuO}_4$ ; non-Fermi liquid behavior has not been observed and the normal state can be quantitatively described well as Fermi liquid.

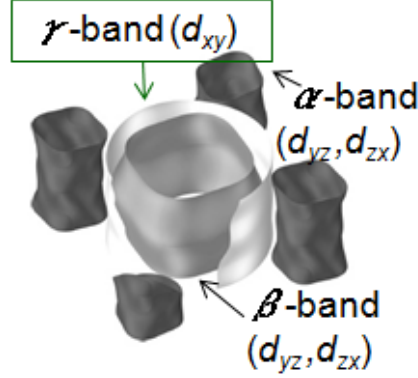


**Figure 2.14:** Hybridization between  $4d$  orbital of Ru and  $2p$  orbital of O.

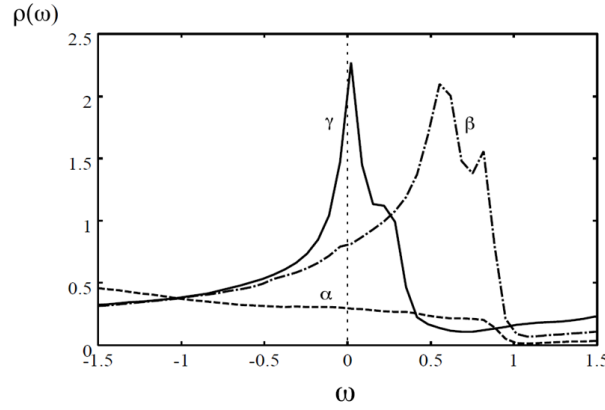


**Figure 2.15:** Fermi surfaces of  $\text{Sr}_2\text{RuO}_4$  determined by band calculation [49].

$\text{Sr}_2\text{RuO}_4$  exhibits superconductivity below 1.5 K and the electronic Cooper pairs are believed to be of spin-triplet chiral  $p$  wave ( $S=1$ ,  $L=1$ ). The superconductivity is mainly driven by the  $\gamma$  surface. Just after the superconductivity was discovered,  $\text{Sr}_2\text{RuO}_4$  attracted much interest as a reference material of high-transition-temperature cuprate superconductors. Later, how-



**Figure 2.16:** Fermi surfaces of  $\text{Sr}_2\text{RuO}_4$  determined by dHvA experiment [3].

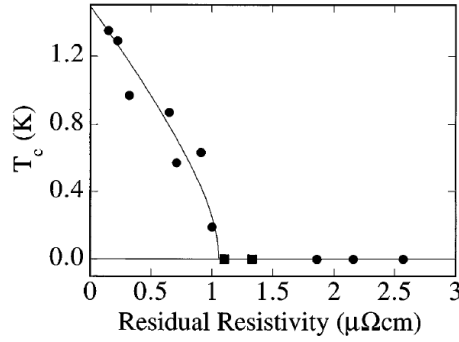


**Figure 2.17:** Density of states of the three bands in  $\text{Sr}_2\text{RuO}_4$  [50].

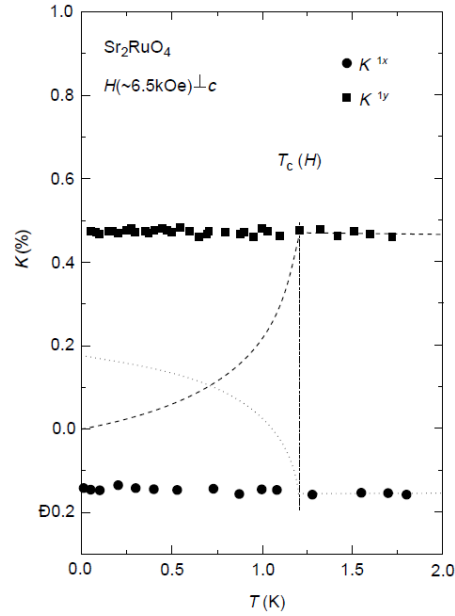
ever, the possibility of spin-triplet superconductivity of  $\text{Sr}_2\text{RuO}_4$  was pointed out [51], because  $\text{SrRuO}_3$  and  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  exhibits ferromagnetism [52] among Ruddlesden-Popper type ruthenates  $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ , to which  $\text{Sr}_2\text{RuO}_4$  belongs, and the Fermi liquid parameters of  $\text{Sr}_2\text{RuO}_4$  are similar to those of  $^3\text{He}$ . Then several studies were performed for verifying the hypothesis. First, non  $s$ -wave superconductivity of  $\text{Sr}_2\text{RuO}_4$  was clarified from the absence of coherence peak in nuclear magnetic relaxation rate  $1/T_1$  [53] and from the significant suppression of  $T_c$  by nonmagnetic impurity (Fig. 2.18) [54] or by lattice defect [55]. Moreover, constant Knight Shift below  $T_c$  in nuclear magnetic resonance (NMR) measurements under field in the  $ab$  plane (Fig. 2.19) revealed that the superconductivity is a spin-triplet state ( $S=1, S_z=0$ ) in which spins are perpendicular to the  $c$  axis [46, 47]. The same result was obtained in the polarized neutron scattering experiment [48].

Orbital part of the SC order parameter of  $\text{Sr}_2\text{RuO}_4$  is considered to be a chiral state, in which time reversal symmetry is broken. The experimental results of muon spin relaxation ( $\mu\text{SR}$ ) [56] and Kerr rotation [57] indicate that local internal magnetic field emerges below  $T_c$  and time reversal symmetry is spontaneously broken (Fig. 2.20). Based on this result and the fact that the spin part of the superconductivity of  $\text{Sr}_2\text{RuO}_4$  is  $S_z=0$  and does not have internal magnetic field, it is





**Figure 2.18:** Suppression of  $T_c$  by nonmagnetic impurity in  $\text{Sr}_2\text{RuO}_4$  [54].



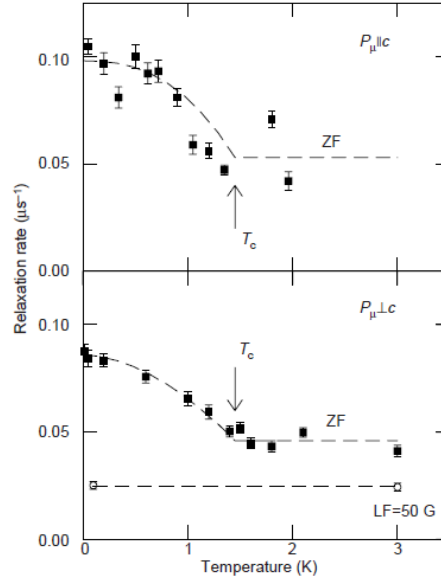
**Figure 2.19:** Knight Shift of  $\text{Sr}_2\text{RuO}_4$  [46].

concluded that the observed internal magnetic field originates from the orbital part and the orbital part of the superconductivity of  $\text{Sr}_2\text{RuO}_4$  is  $L_z \pm 1$ .

A strong candidate of the  $d$  vector describing the SC state of  $\text{Sr}_2\text{RuO}_4$ , in which the spin and orbital part is  $S_z=0$  and  $L_z \pm 1$ , is

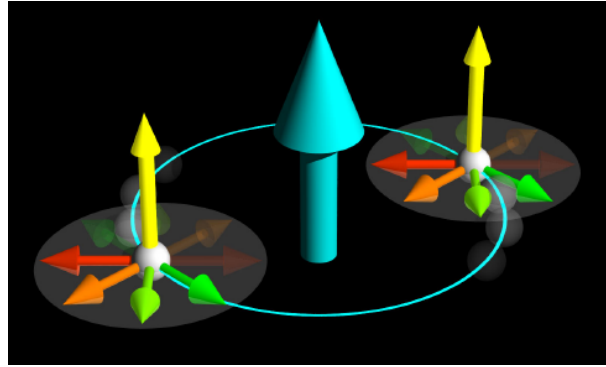
$$d = \Delta \hat{z}(k_x + ik_y) .$$

This  $d$  vector is isotropic in the  $k_x k_y$  plane reflecting the symmetry of the crystal structure and the states described by  $k_x$  and  $k_y$  are degenerate in the orbital part. It is theoretically predicted that the degeneracy of the states of  $k_x$  and  $k_y$  is resolved and double SC transition occurs when in-plane isotropy is broken by UAP or magnetic field [35, 36]. As described in Fig. 2.23, the phase whose SC order parameter consists of one component ( $k_x$ ) is expected in a high-temperature region ( $T_2 < T < T_1$ ), while the phase whose SC order parameter has two components ( $\lambda_x(T)k_x + i\lambda_y(T)k_y$ )



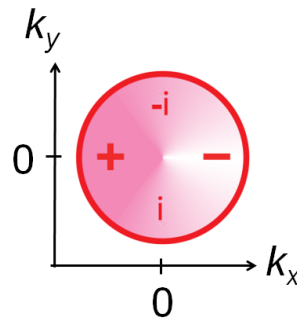
**Figure 2.20:**  $\mu\text{SR}$  experiment of  $\text{Sr}_2\text{RuO}_4$  [56].

realizes in the lower temperature region ( $0 < T < T_2$ ). If such a situation is really induced, imaginary part of AC magnetic susceptibility or specific heat is expected to exhibit two anomalies corresponding to the SC transitions at  $T_1$  and  $T_2$ .

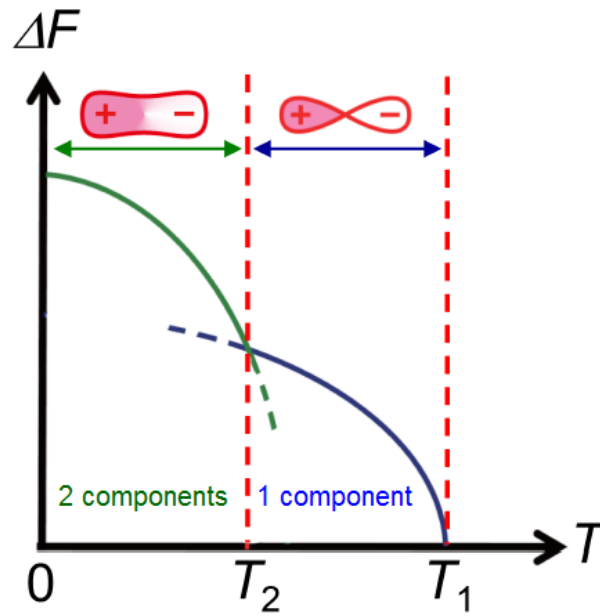


**Figure 2.21:** Strongest candidate for the  $d$  vector of  $\text{Sr}_2\text{RuO}_4$ .

Under magnetic field, SC double transition has already been reported in specific heat [58, 59] and AC magnetic susceptibility [60] (Fig. 2.24). However, these double transitions exist only in low-temperature and high-magnetic-field region, although double transition is theoretically expected to start just below  $T_c$ . Therefore, these double transitions observed in magnetic field can not be explained only by the assumption that SC order parameter in zero field is multi-component, and the origin of the phenomena is still unclear. Therefore, to clarify whether SC double transition occurs under UAP is essential for determining the SC order parameter of  $\text{Sr}_2\text{RuO}_4$ . In other words, if double transition is observed under in-plane UAP, it would be a crucial proof that the SC order

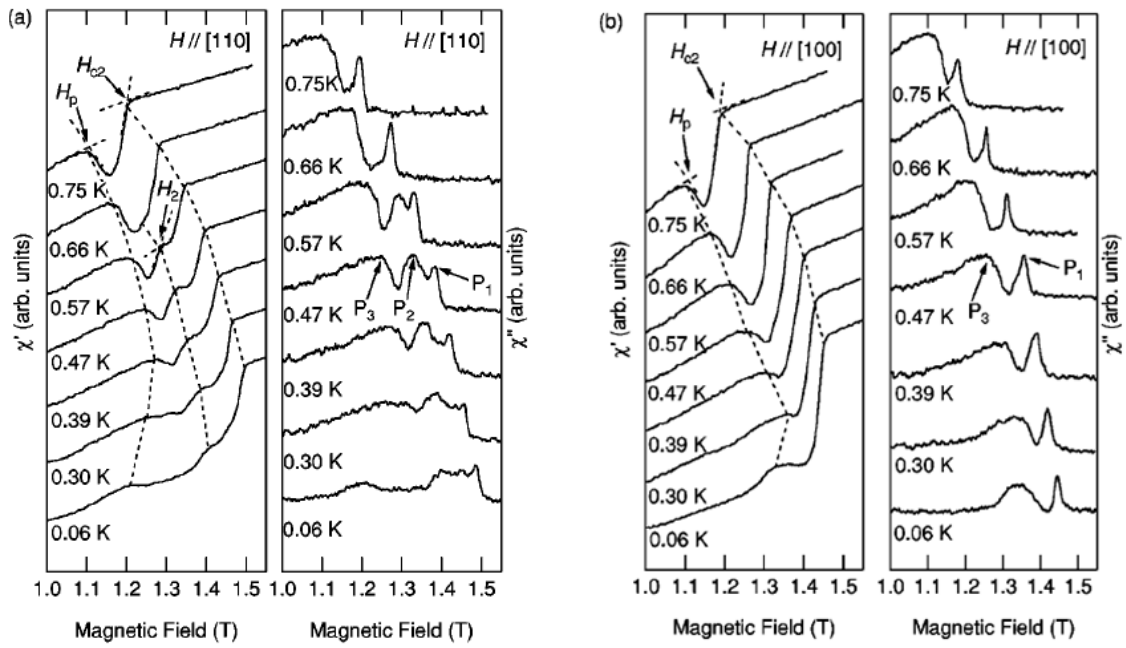


**Figure 2.22:** Orbital part of the SC order parameter of  $\text{Sr}_2\text{RuO}_4$ .



**Figure 2.23:** Expected SC double transition in  $\text{Sr}_2\text{RuO}_4$ .

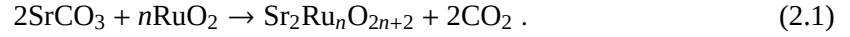
parameter of  $\text{Sr}_2\text{RuO}_4$  is multi-component.



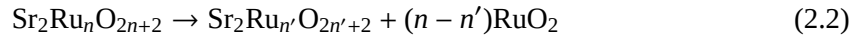
**Figure 2.24:** Double transition of AC magnetic susceptibility of  $\text{Sr}_2\text{RuO}_4$  [60].

### 2.2.2 $\text{Sr}_2\text{RuO}_4$ -Ru eutectic crystal

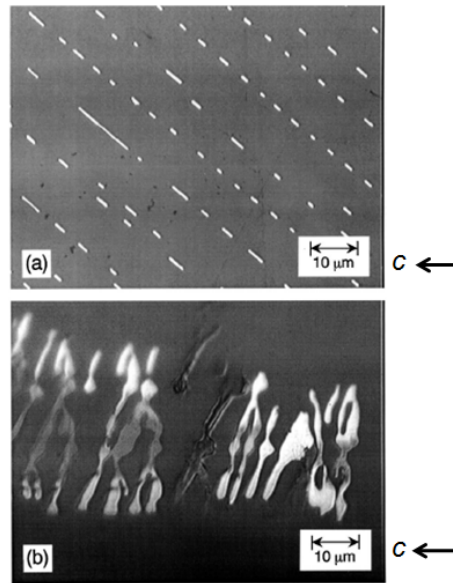
The  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic crystal discovered during the process to improve the quality of the single crystal of  $\text{Sr}_2\text{RuO}_4$  is also interesting. In order to synthesize  $\text{Sr}_2\text{RuO}_4$  [61], firstly, mixture of  $\text{SrCO}_3$  and  $\text{RuO}_2$  is calcined and polycrystal of  $\text{Sr}_2\text{Ru}_n\text{O}_{2n+2}$  is obtained:



Then a single crystal is grown by the floating zone method. What should be noted is that Ru evaporates as  $\text{RuO}_2$  in this process:

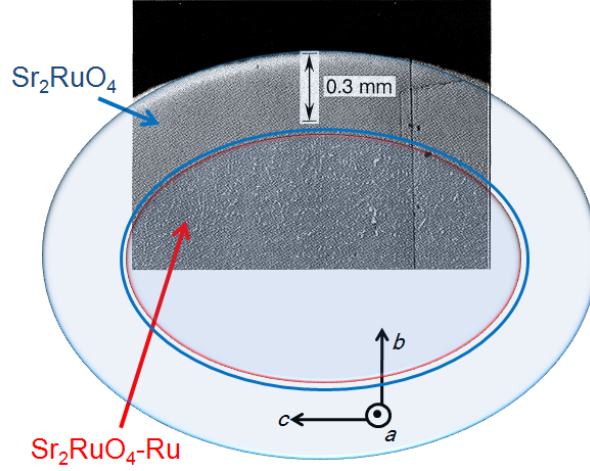


Therefore, in order to get  $\text{Sr}_2\text{RuO}_4$  single crystal without Ru deficiency, the initial  $n$  should be larger than 1 and the synthesis is usually performed with  $n = 1.15$ . If the proportion of  $\text{RuO}_2$  increases more and  $n$  becomes 1.2, Ru metal originating from the excess Ru is embedded in  $\text{Sr}_2\text{RuO}_4$  single crystal. As shown in Fig. 2.25, Ru pieces appears quasi periodically. The typical dimensions of the Ru pieces are  $1 \mu\text{m} \times 10 \mu\text{m} \times 30 \mu\text{m}$  and the typical distance between Ru pieces is  $10 \mu\text{m}$ . The black and white part in Fig. 2.25 are  $\text{Sr}_2\text{RuO}_4$  and Ru pieces, respectively. Figure 2.26 represents the cross section of cylindrical single crystal, and the inner and outer part tends to become  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic and pure  $\text{Sr}_2\text{RuO}_4$ , respectively. Since Ru evaporation is suppressed,  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic is obtained inside.



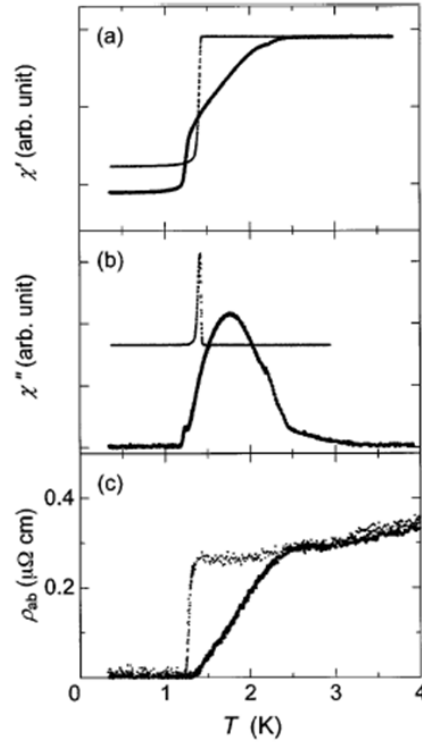
**Figure 2.25:** Picture of  $\text{Sr}_2\text{RuO}_4$  under a polarizing microscope [29].

$\text{Sr}_2\text{RuO}_4$ -Ru eutectic is curious because of the enhancement of  $T_c$ . Although  $T_c$  of  $\text{Sr}_2\text{RuO}_4$  and Ru is 1.5 K and 0.49 K, respectively, the onset  $T_c$  of  $\text{Sr}_2\text{RuO}_4$ -Ru is enhanced up to 3 K. This eutectic is thus called as the “3-K phase” after the onset SC temperature. Although the mechanism of the  $T_c$  enhancement in the eutectic crystal is not fully clarified, several properties of the eutectic are revealed as follows:

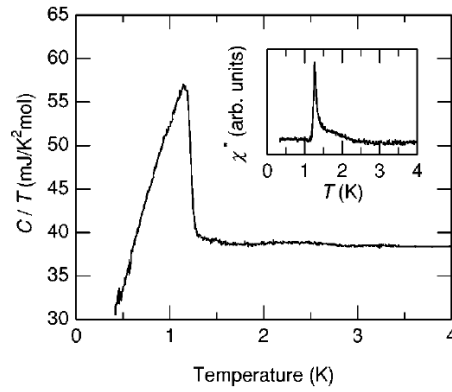


**Figure 2.26:** Picture of  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic under a polarizing microscope [30].

1. AC magnetic susceptibility and electric resistivity of  $\text{Sr}_2\text{RuO}_4$ -Ru (Fig. 2.27) exhibit broad SC transition from 3 K to 1.5 K [29]. Moreover, the SC transition of pure Ru at 0.49 K is also observed in AC susceptibility measurements. These results suggest that in  $\text{Sr}_2\text{RuO}_4$ -Ru some part becomes SC at 3 K, SC region expands on cooling, the whole part of  $\text{Sr}_2\text{RuO}_4$  exhibits superconductivity at 1.5 K, and the whole system becomes SC at 0.49 K.
2. Absence of anomaly around 3 K in specific heat (Fig. 2.28) suggests that superconductivity at 3 K is non-bulk [62]. This result indicates that interface between  $\text{Sr}_2\text{RuO}_4$  and Ru becomes SC at 3 K and the SC region expands on cooling because of the proximity effect.
3. The 3-K superconductivity in  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic exhibits anisotropy which is similar to the anisotropy of the superconductivity in  $\text{Sr}_2\text{RuO}_4$ : both superconductivity is strong against the field in the  $ab$  plane but weak against the field along the  $c$  axis (Fig. 2.29) [30]. The zero bias conductance peak (ZBCP), which occurs only in non  $s$ -wave superconductors, is observed above 1.5 K in the eutectic. This result indicates that the superconductivity above 1.5 K in the eutectic is  $p$ -wave, being similar to the superconductivity in  $\text{Sr}_2\text{RuO}_4$  (Fig. 2.30) [63, 64]. Moreover, it has recently been revealed that proximity effect of the 3-K phase superconductivity does not penetrate into the Ru metal region [65]. These results suggest that the 3-K superconductivity in the eutectic occurs only in the  $\text{Sr}_2\text{RuO}_4$  side of the interface.
4. Sigrist *et al.* proposed phenomenological theory concerned with temperature dependence of SC order parameter in the eutectic based on the description that the  $\text{Sr}_2\text{RuO}_4$  region around interfaces between  $\text{Sr}_2\text{RuO}_4$  and Ru exhibits  $p$ -wave superconductivity at 3 K [66]. Around the interface, spatial symmetry is reduced because of the existence of a Ru inclusion. Thus, the degeneracy of  $k_x$  and  $k_y$  states is resolved, and the SC state whose wave function elongates along the interface (it corresponds to  $k_x$  in Fig. 2.31) has higher  $T_c$ . Therefore, the superconductivity with one-component orbital order parameter emerges at



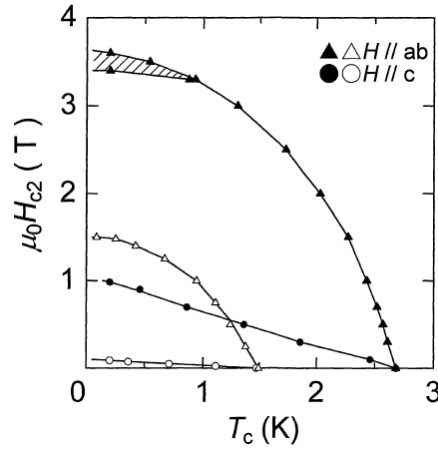
**Figure 2.27:** AC magnetic susceptibility and electric resistivity of  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  [29].



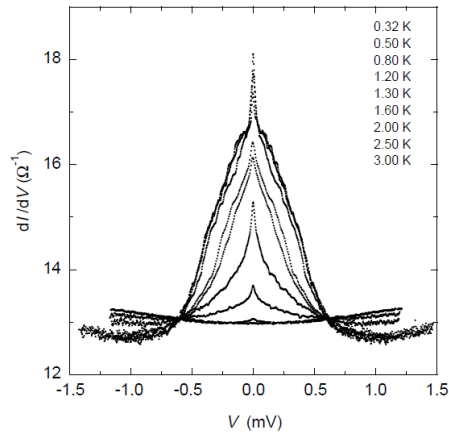
**Figure 2.28:** Specific heat of  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  [62].

3 K. With decreasing temperature, the two-component superconductivity (it corresponds to  $k_y$  in Fig. 2.31) is realized.

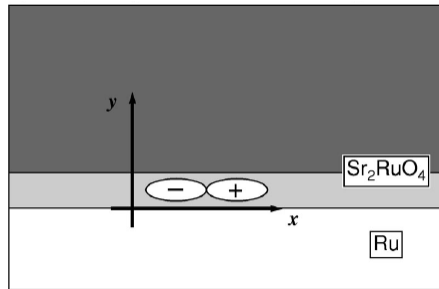
5. The theory mentioned above describes also the phenomenon in  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  that the SC onset temperature is different from the temperature at which ZBCP appears (Fig. 2.32). The ZBCP appears as a consequence of formation of Andreev bound states, which is realized



**Figure 2.29:** Anisotropy of the upper critical magnetic field of  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic [30].



**Figure 2.30:** Zero bias conductance peak of  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic [63].

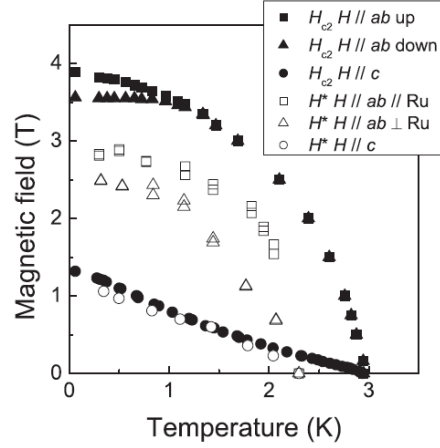


**Figure 2.31:** SC order parameter of  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic at 3 K [62].

when the phase difference between the pair potential for incident electronic quasi-particles and that for reflective hole quasi-particles is  $\pi$ . Thus order parameter component elongating

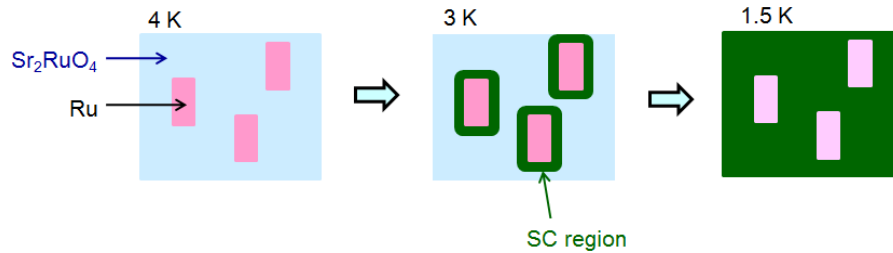


perpendicular to the interface ( $k_y$  in Fig. 2.31) is required for ZBCP. Therefore, ZBCP appears at temperature lower than the onset  $T_c$ .



**Figure 2.32:** Comparison between upper critical magnetic field and the magnetic field of ZBCP appearance in  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic [64].

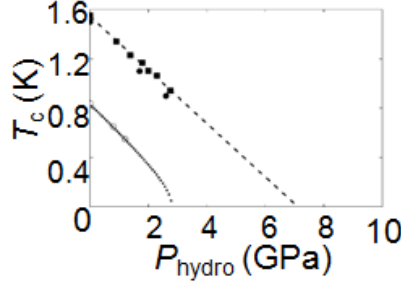
Summarizing the above, the strong candidate for describing the superconductivity in  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic is that the  $\text{Sr}_2\text{RuO}_4$  region around the interface between  $\text{Sr}_2\text{RuO}_4$  and Ru exhibits superconductivity at 3 K and the SC region expands only into  $\text{Sr}_2\text{RuO}_4$  side by proximity effect (Fig. 2.33). Because there must be an anisotropic lattice distortion at the interface due to a lattice mismatch between  $\text{Sr}_2\text{RuO}_4$  and Ru, one possible origin of the  $T_c$  enhancement is anisotropic lattice distortion. Therefore, investigation of the UAP effect on  $T_c$  should provide a crucial hint to solve the mechanism of the  $T_c$  enhancement in  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic.



**Figure 2.33:** Interfacial superconductivity in  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic

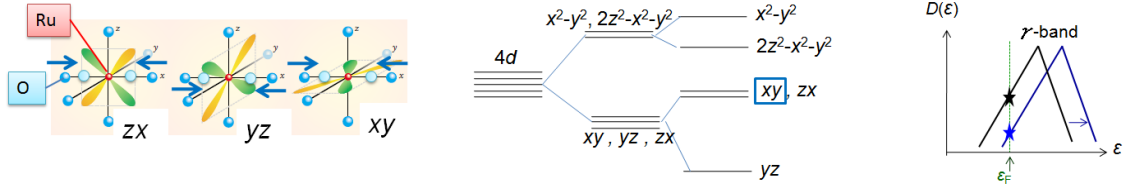
### 2.2.3 Pressure effect on $\text{Sr}_2\text{RuO}_4$

It had already been revealed experimentally that  $T_c$  of  $\text{Sr}_2\text{RuO}_4$  is suppressed by hydrostatic pressure and the pressure dependence of  $T_c$  is  $dT_c/dP_{\text{hydro}} = -0.2 \text{ K/GPa}$  (Fig. 2.34) [33, 34].



**Figure 2.34:** Hydrostatic pressure dependence of the SC transition temperature of  $\text{Sr}_2\text{RuO}_4$  [34].

Before our UAP studies on  $\text{Sr}_2\text{RuO}_4$  UAP effects on  $T_c$  were predicted based on band calculation [50] and elastic approximation [67]. In both cases,  $T_c$  was expected to decrease for  $P_{\parallel a}$  and increase for  $P_{\parallel c}$ . The prediction from the band calculation is based on changes of the density of states (DOS) by UAP. The  $\gamma$  band, which is considered to be responsible for the superconductivity, should shift by UAP relative to the other bands due to the crystalline field effect. Then the DOS at Fermi level  $D(\epsilon_F)$  of the  $\gamma$  band changes accordingly and  $T_c \sim \exp(-1/\lambda D)$  should be also affected. As shown in Fig. 2.35, under UAP along the  $a$  axis, the energy of the  $xy$  orbital, which is the origin of the  $\gamma$  band, is enhanced. In other words, the  $\gamma$  band shifts to high energy side. Then  $D(\epsilon_F)$  of the  $\gamma$  band is suppressed and  $T_c$  is expected to decrease. In contrast, under UAP along



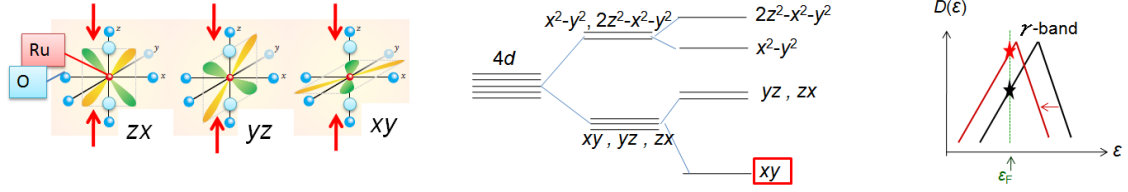
**Figure 2.35:** Prediction of the  $a$ -axis UAP effect on  $\text{Sr}_2\text{RuO}_4$

the  $c$  axis, since  $D(\epsilon_F)$  of the  $\gamma$  band is enhanced as shown in Fig. 2.36,  $T_c$  is expected to increase.

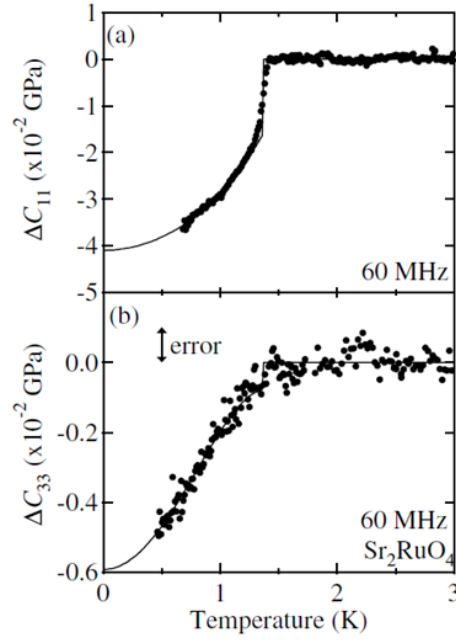
The prediction from an elastic approximation, is made based on the Ehrenfest relation and the results of the ultrasonic experiments. First,  $\frac{dT_c}{d\epsilon_i}$  is obtained by putting the values of  $\Delta C_{ii}(T_c)$  estimated from the result of ultrasonic experiment (Fig. 2.37) [67] to the Ehrenfest equation

$$\left(\frac{dT_c}{d\epsilon_i}\right)^2 = -\frac{V_{\text{mol}} T_c \Delta C_{ii}(T_c)}{\Delta c_p(T_c)} \quad (i = 1, 3) \quad (2.3)$$

( $\epsilon$ : longitudinal strain,  $V_{\text{mol}}$ : volume per 1 mol,  $C_{ii}$ : longitudinal modulus,  $c_p$ : specific heat,  $i=1$  and 3 correspond to the  $a$  and  $c$  axis, respectively.).



**Figure 2.36:** Prediction of the c-axis UAP effect on  $\text{Sr}_2\text{RuO}_4$



**Figure 2.37:** Elastic modulus of  $\text{Sr}_2\text{RuO}_4$  estimated by ultrasonic experiment [67].

Then, by solving the following equations about  $i=1$  and 3,

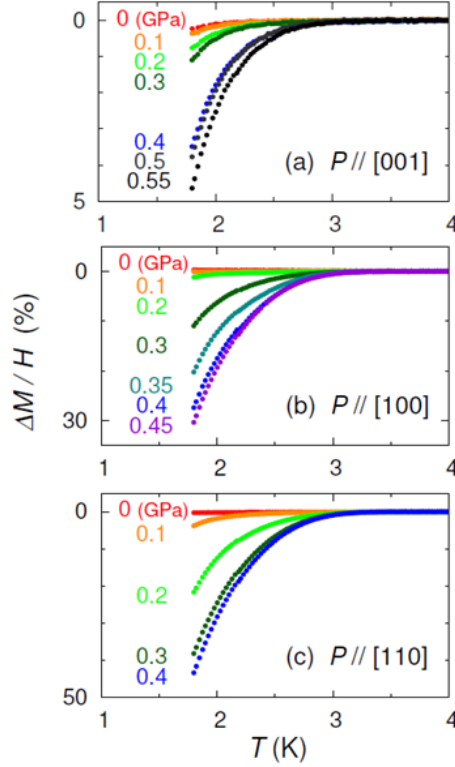
$$\frac{dT_c}{d\epsilon_i} = - \sum_j C_{ij} \frac{dT_c}{dP_j} \quad (i = 1, 3, \quad j = 1, 2, 3), \quad (2.4)$$

$dT_c/dP_1 (= dT_c/dP_a)$  and  $dT_c/dP_3 (= dT_c/dP_c)$  are obtained. Since  $\frac{dT_c}{d\epsilon_i}$  have two possible answers (plus and minus), there are four possibilities for the combination of  $dT_c/dP_1$  and  $dT_c/dP_3$  as the answer of Eq. 2.4. If hydrostatic pressure effect is considered to be a linear combination of the UAP effects along the  $a$ ,  $b$  and  $c$  axis,

$$\frac{dT_c}{dP_{\text{hydro}}} = 2 \frac{dT_c}{dP_a} + \frac{dT_c}{dP_c} \quad (2.5)$$

at least one of  $dT_c/dP_a$  or  $dT_c/dP_c$  should be minus because  $dT_c/dP_{\text{hydro}}$  is minus. To satisfy this condition,  $dT_c/dP_a$  and  $dT_c/dP_c$  are chosen to be  $-1.3$  K/GPa and  $+1$  K/GPa, respectively.

The experimental study of UAP effect on the superconductivity of  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic was reported in 2009 [68, 69]. The temperature dependence of the DC magnetization above 1.8 K (Fig. 2.38) revealed that magnetic shielding fraction below onset  $T_c$  is enhanced with increasing pressure under any of the UAPs along the  $c$  axis, the  $a$  axis and the  $[110]$  direction although onset  $T_c$  is not changed by the pressures. Moreover, the rate of the enhancement of shielding fraction is larger under in-plane UAP than the  $c$ -axis UAP.



**Figure 2.38:** Temperature dependence of the DC magnetization of  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic under UAPs [68].

In 2010, we reported the out-of-plane UAP effect on  $\text{Sr}_2\text{RuO}_4$  [32]. We clarified that  $T_c$  of “pure”  $\text{Sr}_2\text{RuO}_4$  is enhanced up to 3.2 K under pressure along the  $c$  axis ( $P_{\parallel c}$ ). Here, “pure” means that the sample contains almost no Ru inclusions. The result strongly supports our scenario that the anisotropic lattice distortion plays an important role in the  $T_c$  enhancement. Moreover, in  $\text{Sr}_2\text{RuO}_4$ -Ru under  $P_{\parallel c}$ , we found a crossover at  $P_{\parallel c}^* \sim 0.4$  GPa from behavior attributable to interfacial SC to behavior similar to that in pure  $\text{Sr}_2\text{RuO}_4$  under  $P_{\parallel c}$  [32].

## Chapter 3

# Development of uniaxial-pressure experimental technique

First of all, we constructed the system for UAP experiments.

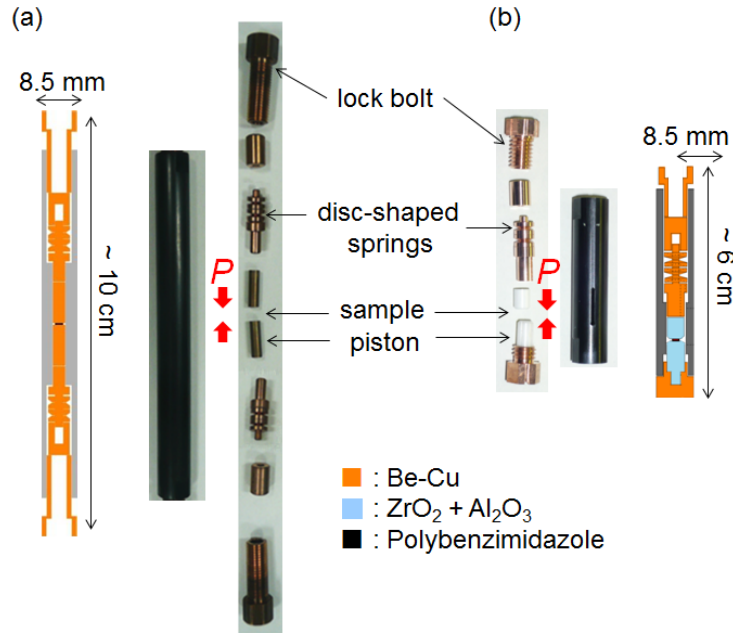
### 3.1 Pressure apparatus

#### 3.1.1 Pressure cell

To apply uniaxial pressure, we used piston-cylinder type pressure cells illustrated in Fig. 3.1. We used two designs of the pressure cell (the longer and shorter ones) depending on the purpose. As the common features of these pressure cells, a sample is pressed directly by the pistons without any pressure medium and the disc-shaped springs keep pressure by the tightened lock bolts. Based on our designs, the pressure cells were made by R&D Support.

The longer pressure cell (Fig. 3.1(a)) is designed mainly for magnetization measurement. Thus, the geometry is symmetric. All the inner parts are made of Be-Cu (hard alloy), whereas the outer body is made of polybenzimidazole (hard plastic) to reduce background contributions. Because the outer body is made of an electric insulator, this cell can be used also for two-wire resistivity measurement as described in detail in Chap. 3.2.1. The diameter of the pistons is 3 mm.

The shorter cell (Fig. 3.1(b)) was designed by myself for resistivity and AC susceptibility measurements. The most parts are made of Be-Cu. Depending on purposes, we chose Be-Cu or mixture of  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$  (insulator) for pistons, and polybenzimidazole or Be-Cu for the outer body. Although the diameter of the pistons is 4 mm, the sample diameter should be less than 3 mm because of the taper of the pistons. The improved points compared with the longer cell are the windows which enable accesses to the sample space from outside of the cell, the thin rod which penetrates the piston backup through windows and prevent the parts below the piston backup from rotating to break a sample, and the shorter length which enables the attachment to many refrigerators. Thanks to the windows, resistivity measurement, mini-coil susceptibility measurement, pressure calibration using a strain gauge, and direct thermal link between a sample and the bath are achieved as described in detail in Chap. 3.1.3, 3.2.



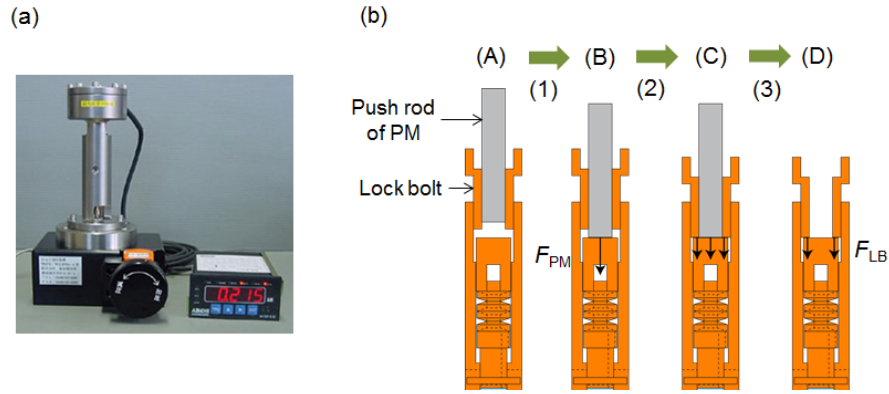
**Figure 3.1:** Photos and schematic figures of the uniaxial pressure cells used in this study. (a) Cell for magnetization and 2-wire resistivity measurement. Left figure is a schematic image of the cross section of the cell. Middle and right figure is the photo of the outer body and the inner parts, respectively. In the right photo, from top to bottom, a lock bolt, spring backup, disc-shaped springs, a piston backup, piston, piston, piston backup, disc-shaped springs, a spring backup, and lock bolt are represented. A sample is located between the pistons and pressed directly by the pistons as the pressure direction is shown by red arrows. (b) Cell for resistivity and AC susceptibility measurement. Left and middle figure is the photo of the inner parts and the outer body, respectively. Right figure is a schematic image of the cross section of the cell. In the left photo, from top to bottom, a lock bolt, spring backup, disc-shaped springs, a piston backup, piston, piston, and lock bolt are represented.

### 3.1.2 Pressurization

Pressure was applied to a sample at room temperature using the pressurize machine (PM) shown in Fig. 3.2(a). We have two PMs: the first PM (WG-KY01-4) was designed and made by Kyowa Seisakusho and used for the longer pressure cell, whereas I modified the design of the second PM for the use of the shorter pressure cell and asked HMD for its fabrication. As the common features of these PMs, they have two push rods inside: the bottom rod can be moved up and down by rotating the dial and change the force applied by PM ( $F_{PM}$ ), whereas the top rod is fixed on the lid and connected to a load cell which gauges the value of  $F_{PM}$ .

As also illustrated in Fig. 3.2(b) the process of the pressurization is as follows: (1) Set a pressure cell in a PM and increase  $F_{PM}$  to an intended value by rotating the dial, (2) tighten the lock bolt of the cell, and (3) release  $F_{PM}$  completely by rotating the dial and take the cell out. At the end of the process (1) (in other words, at the state (B) of Fig. 3.2(b)), the force applied to a sample ( $F_S$ ) is as same as  $F_{PM}$ , because the lock bolt of the pressure cell is loose and the force

applied by the lock bolt ( $F_{LB}$ ) is zero. In the process (2), although the distance between push rods of the PM does not change,  $F_{PM}$  is reduced because some force is covered by the lock bolt. At the end of the process (2) (in other words, at the state (C)),  $F_S$  becomes the sum of  $F_{PM}$  and  $F_{LB}$  and above the intended value. At the end of the process (3) (in other words, at the state (D)),  $F_S$  is as same as  $F_{LB}$ . In order to confirm that  $F_S$  is as same as the intended value, we performed the force calibrations as mentioned in Chap. 3.1.3.



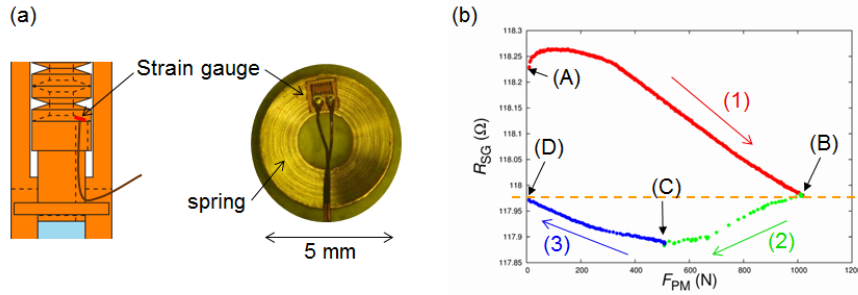
**Figure 3.2:** (a) Photo of the pressurize machine. (b) Schematic figure of the pressurization process. The states (A), (B), (C) and (D) and the processes (1), (2) and (3) correspond to the notation in the text and Fig. 3.3(b).  $F_{PM}$  and  $F_{LB}$  are the force applied by the pressurize machine and the lock bolt of the pressure cell, respectively.

### 3.1.3 Pressure estimation

Since samples are made to have cuboid shape, we estimated pressure value by dividing force by the sample area perpendicular to the force. The force value in the longer pressure cell was calibrated using superconducting transition of Pb and Sn as mentioned in Ref. [70]. The force value in the shorter cell was monitored using a strain gauge (KFRS-02-120-C1-13, Kyowa Dengyo), which was attached on a disc-shaped spring as shown in Fig. 3.3(a). The wires of the strain gauge are taken out through the hole of the piston backup and the window of the outer body.

The strain gauge on the spring changes its resistance  $R_{SG}$  depending on  $F_S$ , and  $F_{PM}$  can be read by the load cell. At the state (B) in Figs. 3.2(b) and 3.3(b),  $F_S$  is as same as  $F_{PM}$ , which is known to be an intended value. Therefore, in order to make  $F_S$  the intended value at the end of the pressurization process (in other words, at the state (D)), the lock bolt of the pressure cell should be tightened so that  $R_{SG}$  exhibit the same value between the state (B) and (D), as shown in Fig. 3.3(b).

$R_{SG}$  was measured using the four-wire resistivity measurement mode of a Multimeter 2000 (Keithley).



**Figure 3.3:** (a) Schematic figure and photo of the setting of the strain gauge for monitoring the force applied to a sample. (b) Changes during the pressurization process of the resistance of the strain gauge  $R_{SG}$  and the force applied by the pressurize machine  $F_{PM}$ . The states (A), (B), (C) and (D) and the processes (1), (2) and (3) correspond to the notation in the text and Fig. 3.2(b).

### 3.1.4 Sample preparation

Single crystals of  $\text{Sr}_2\text{RuO}_4$  and  $\text{Ca}_2\text{RuO}_4$  were grown by a floating-zone method [61, 1].  $\text{Sr}_2\text{RuO}_4$  crystals were synthesized in our Prof. Y. Maeno's Lab. and  $\text{Ca}_2\text{RuO}_4$  crystals were provided by Prof. F. Nakamura. The directions of crystal axes were determined by the Laue method using a Back Reflection Laue Camera RASCO-BL 2 (Rigaku). Following the Laue information, samples were cut out by a Refine Saw RCA-005 (Refine Tec. Ltd.) to have a cuboid shape whose top and bottom surfaces are perpendicular to the direction along which pressure will be applied. Typical dimensions of samples for out-of-plane UAP are 0.5 mm along the pressure direction, and  $2.0 \times 2.0 \text{ mm}^2$  in the plane perpendicular to the pressure direction. In the case of samples for in-plane UAP, the plane perpendicular to the pressure direction has smaller area, because  $\text{Ca}_2\text{RuO}_4$  and  $\text{Sr}_2\text{RuO}_4$  cleave easily along the  $ab$  plane. Therefore, typical dimensions of samples for in-plane UAP are 0.5 mm along the pressure direction, and  $2.0 \times 0.5 \text{ mm}^2$  in the plane perpendicular to the pressure direction. Laue pictures were taken again after the cutting to check the misalignment (usually less than 10 degrees), and the top and bottom surfaces of the sample were polished with a tilt for modifying the alignment. The polishing has another purpose to make the two surfaces parallel to each other for improving pressure homogeneity. Polishing was performed with a Polishing Machine MA-200 (Musashino Denshi) with diamond slurries MP-9000(W), MP-1000(W) and MP-250(W) (Musashino Denshi). The side surfaces of a sample were covered with epoxy (Stycast 1266, Emerson-Cuming) to prevent the sample from breaking. In order to allow the epoxy to spread freely under pressure, enough space was kept between the epoxy and the inner wall of the pressure cell. Thanks to the space in addition to the result of a previous study which suggests that compressive force applied to oxides by surrounding Stycast 1266 is ignorable [71], uniaxial *pressure* not uniaxial *strain* is expected.



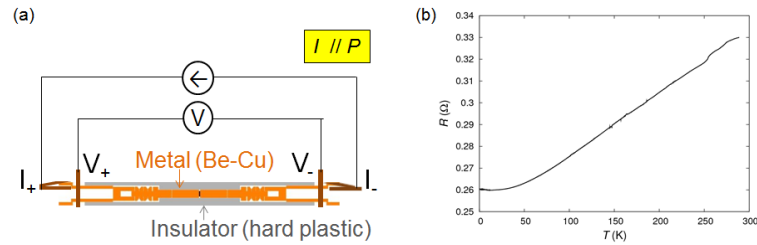
## 3.2 Measurements

### 3.2.1 Resistivity

Depending on a purpose, we performed two kinds of electric resistivity measurements: two-wire and four-wire methods. Although the resistance  $R$  measured by the two-wire method includes some extrinsic contributions, this two-wire method is easier than the four-wire method and still useful to detect the intrinsic change of the sample resistivity if the change is large.

#### Two-wire resistivity

For two-wire resistivity measurements, the longer pressure cell was used. By making use of the fact that the outer body is made of insulating plastic, we utilized the pistons made of Be-Cu metal as electrodes (Fig. 3.4(a)). In this method, electric current is applied parallel to the UAP direction. It should be noted that the measured resistance includes not only the sample resistance but also extrinsic resistance such as contact resistance between the sample and the piston or between the inner parts of the pressure cell and resistance of the inner parts themselves. However, this method has an advantage that measurement is easier than the four-wire method described in Chap. 3.2.1. In order to check the magnitude and the temperature dependence of the extrinsic resistance, we performed two-wire resistivity measurement using Au as a dummy sample (Fig. 3.4(b)). As a result, we have confirmed that the extrinsic resistance exhibits metallic behavior and is so small ( $\sim 0.3 \Omega$ ) that the metal-insulator transition is expected to be detected in this two-wire method. It should be noted that contact resistance cannot be measured in this two-wire method.

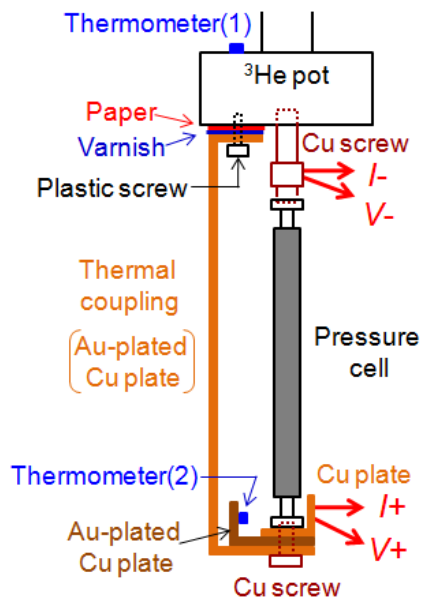


**Figure 3.4:** (a) Schematic figure of the setting of two-wire resistivity measurement. (b) Temperature dependence of the background resistance in this two-wire method. Au is used as a dummy sample.

At room temperature, resistance was measured while sweeping pressure with a DC current, whose direction was reverted in order to cancel the thermoelectric voltage. A DC current source 7651 (Yokogawa) and a Multimeter 2000 (Keithley) are utilized.

For measuring temperature dependence of resistance, we adopted an AC method using a Lock-in-amplifier SR830 (Stanford Research Systems) and  $^3\text{He}$  cryostat Heliox VL (Oxford Instruments). In order to keep the amplitude of the electric current constant under the change of sample resistance, a resistance whose value is  $10^3$  times more than sample resistance is inserted in the circuit. The setting of the low temperature measurement is described in (Fig. 3.5).  $\text{RuO}_2$  thermometers were attached at the top of the  $^3\text{He}$  pot of the  $^3\text{He}$  cryostat and the bottom of the

pressure cell. We confirmed that the difference between these temperatures is less than 10 mK in the lowest temperature range ( $\sim 0.3$  K). Since the top of the pressure cell which is the minus side of the electric circuit was electrically connected to the  $^3\text{He}$  pot, the thermal link made of Au-plated Cu plate between the  $^3\text{He}$  pot and the bottom of the cell which is the plus side of the circuit was electrically disconnected from the  $^3\text{He}$  pot.

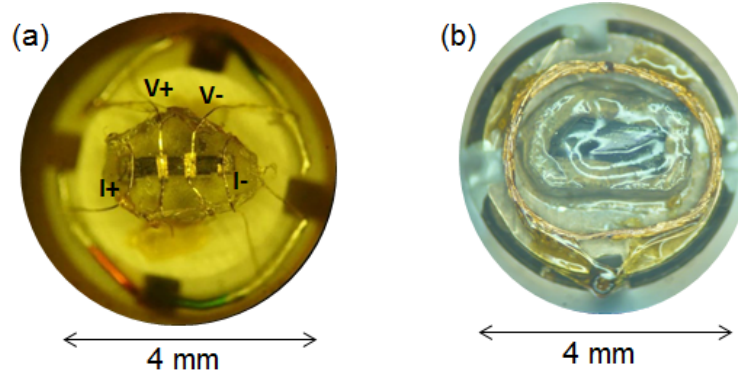


**Figure 3.5:** Schematic figure of the setting of two-wire resistivity measurement at low temperature.

#### Four-wire resistivity

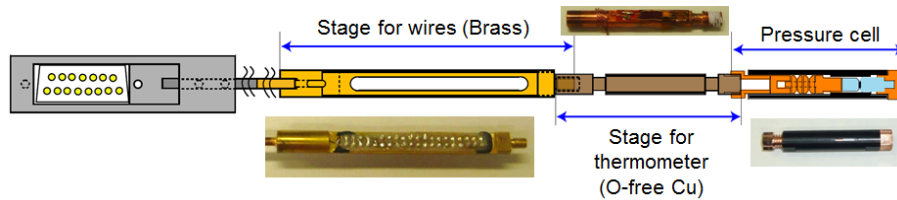
For four-wire resistivity measurement, the shorter pressure cell was used. In this method, since the sample and electrodes directly touch the pistons, pistons made of mixture of  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$  were chosen for electrical insulation, whereas Be-Cu is selected for the material of the other parts. We adopted this four-wire method in the study of in-plane UAP effect on  $\text{Ca}_2\text{RuO}_4$ . The side surface of  $\text{Ca}_2\text{RuO}_4$  sample was covered with epoxy to prevent cleaving, wires were put on the top surface of the sample (Fig. 3.6(a)). In order to improve pressure homogeneity, the wires should be as thin along the pressure direction as possible. Therefore, Au wires of diameter of  $25\ \mu\text{m}$  pressed to have thickness of  $7\ \mu\text{m}$  were just put without any conducting paste. In order to achieve good electric contact, Au was sputtered on the areas on which wires were put. Heat and electric field should be avoided during sputtering of Au on  $\text{Ca}_2\text{RuO}_4$  because  $\text{Ca}_2\text{RuO}_4$  crystals break down at the structural transition induced by heat ( $84\ ^\circ\text{C}$ ) or by electric field. For this purpose, a sample was put on a Cu plate as a heat sink and 5-min sputtering was performed 5 times with inserting 5-min intervals for cooling. The thickness of the sputtered Au is about 120 nm. In this four-wire resistivity measurement, current is applied perpendicular to the UAP direction.

Both in the pressure sweep at room temperature and in the temperature sweep at a fixed



**Figure 3.6:** (a) Photo of the setting of four-wire resistivity measurement. The black part is a  $\text{Ca}_2\text{RuO}_4$  sample and the surrounding transparent part is epoxy. The white part is the bottom piston of the pressure cell. Four Au wires put on the sample for resistivity measurement are connected to thicker and stronger Cu wires of diameter of  $100\ \mu\text{m}$  at the taper area of the piston, and the Cu wires are taken out through the hollows of the piston and the holes of the bottom lock bolt. (b) Photo of the setting of AC susceptibility measurement by the mini-coil method. The sample and the coil are put on a Be-Cu piston. The coil wires of  $20\ \mu\text{m}$  diameter are taken out through one of the hollows of the piston and the holes of the bottom lock bolt. 3 Cu wires of  $200\ \mu\text{m}$  diameter are attached to the piston on the rest hollows with Ag paste and taken out through the rest holes of the bottom lock bolt.

pressure, DC method was adopted and current direction was reverted in order to cancel the thermoelectric voltage. We used a Source Meter 2401 (Keithley) for low-temperature measurement, whereas a DC current source 7651 (Yokogawa) and a Multimeter 2000 (Keithley) was used for room-temperature measurement. We constructed a probe by ourselves (Fig. 3.7) for resistivity measurements using a SQUID magnetometer system (MPMS, Quantum Design) for temperature control and field application. A Cernox thermometer was attached above the pressure cell and temperature was monitored using a Temperature Monitor 218 (Lakeshore). For the magnetoresistance measurement, magnetic field was applied parallel to the pressure direction. The accuracy of the field alignment was better than 5 degrees.



**Figure 3.7:** Schematic figure and photo of the probe for four-wire resistivity measurement using a SQUID magnetometer system (MPMS, Quantum Design).

### 3.2.2 AC susceptibility

We performed two kinds of AC susceptibility  $\chi_{AC}$  measurement: the big-coil and mini-coil methods. I established the mini-coil method in order to get greater signal by improving the filling factor.

As the common feature of these methods, the temperature dependence of the AC susceptibility  $\chi_{AC}(T) = \chi'(T) - i\chi''(T)$  was measured with a mutual inductance method using a Lock-in-amplifier SR830 (Stanford Research Systems) and  $^3\text{He}$  cryostat Heliox VL (Oxford Instruments).  $\chi_{AC}$  is related to the read-out voltage of the LIA ( $V_{LIA} = V_x + iV_y$ ) as  $\chi_{AC} = -iC_1 V_{LIA} / f H_{AC}^0 + C_2$ . Here,  $H_{AC}^0$  and  $f$  are the amplitude and frequency of the applied AC magnetic field, and  $C_1$  and  $C_2$  are complex coefficients. Since we performed AC susceptibility measurement in order to clarify the UAP effect on SC properties of  $\text{Sr}_2\text{RuO}_4$  whose  $T_c$  is about 1.5 K under ambient condition, the values of  $C_1$  and  $C_2$  were chosen so that  $\chi'(4 \text{ K}) = 0$  and  $\chi'(0.3 \text{ K}) = -1$  under ambient pressure and zero DC magnetic field for each sample; thus  $|\chi'|$  corresponds to the AC shielding fraction. For the  $\chi_{AC}$  curves under finite pressure or finite DC field,  $C_1$  and  $C_2$  determined under 0 GPa and 0 T were used.  $\chi''$  corresponds to energy dissipation. Both the AC magnetic field  $H_{AC}$  and the DC magnetic field  $H_{DC}$  were applied parallel to the pressure direction. The accuracy of the field alignment was better than 5 degrees.

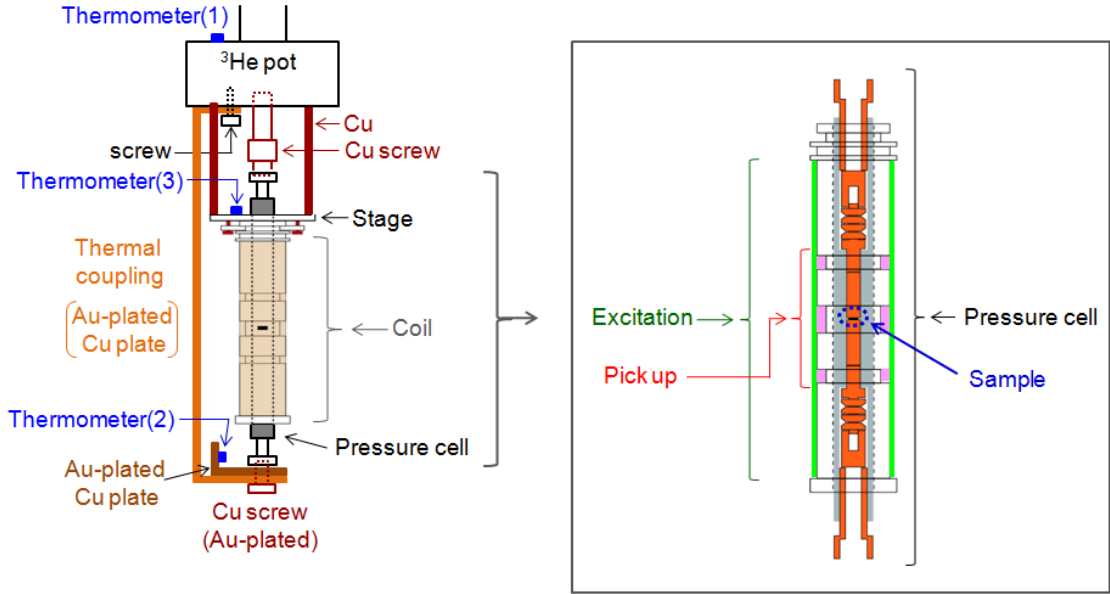
#### Big-coil method

Figure 3.8 represents the setting of the big-coil method. In the big-coil method, the longer pressure cell was used and both the pick-up and excitation coils were set outside the cell. The pick-up coil has cancellation part in which wires are wound in the inverse way.  $\text{RuO}_2$  thermometers were put at the top of  $^3\text{He}$  pot, the top of the coil, and the bottom of the pressure cell, and we confirmed that the difference among these temperatures is less than 5 degrees.

#### Mini-coil method

As described in Chap. 3.1.4, the area perpendicular to the pressure direction is smaller in samples for in-plane UAP than in samples for out-of-plane UAP, because  $\text{Sr}_2\text{RuO}_4$  crystals cleave easily along the  $ab$  plane. As a result, the signal obtained with the big-coil method is smaller for samples for in-plane UAP because of their smaller filling factors. In order to solve the problem, I established the technique to put a pick-up coil inside the UAP cell and improve the filling factor; This is what we call the mini-coil method. For example, when the sample area is  $2.0 \times 0.5 \text{ mm}^2$  and the diameter of the pick-up coil is 2.5 mm, the filling factor is 20%: the filling factor is improved by more than 15 times compared with the big-coil case (1.3%).

The setting of the mini-coil method is described in Fig. 3.6(b). The shorter pressure cell was used in this method: polybenzimidazole is chosen as the material of the outer body in order to avoid eddy current, whereas Be-Cu is selected as the material of the other parts for better thermal link. In this method, the height of the pick-up coil should be shorter than the sample thickness for the coil not to be pressed by the pistons. Therefore, in order to increase the turn number, thin Cu wire of 20  $\mu\text{m}$  diameter is used. The pick-up coil does not have cancellation part because of the limited space. The coil wires as well as Cu wires of 200  $\mu\text{m}$  diameter for the thermal link between the bottom piston and  $^3\text{He}$  pot were taken out through the hollow of the bottom piston



**Figure 3.8:** Schematic figure of the setting of AC susceptibility measurement in the big-coil method. The pick-up coil has three parts: without a sample, the voltage induced in the middle coil is cancelled out by the voltage induced in the top and bottom coils, because the top and bottom coils are wound in the inverse way compared with the middle coil.

and the hole of the bottom lock bolt. Moreover, sheets made of braided Cu wires surrounded the pressure cell and were connected to  $^3\text{He}$  pot for thermal link.

### 3.2.3 Magnetization

Magnetization  $M$  was measured with a SQUID magnetometer (MPMS, Quantum Design). The magnetic field direction is parallel to the pressure direction. The accuracy of the field alignment was better than 5 degrees. To extract the SQUID response originating from the sample, the separately measured background signal was subtracted from the raw signal. For the background measurement, epoxy (Stycast 1266) with dimensions similar to those of the sample was used.



## Chapter 4

# Uniaxial pressure effects on $\text{Ca}_2\text{RuO}_4$

### 4.1 *In-plane* anisotropy of the uniaxial-pressure effect

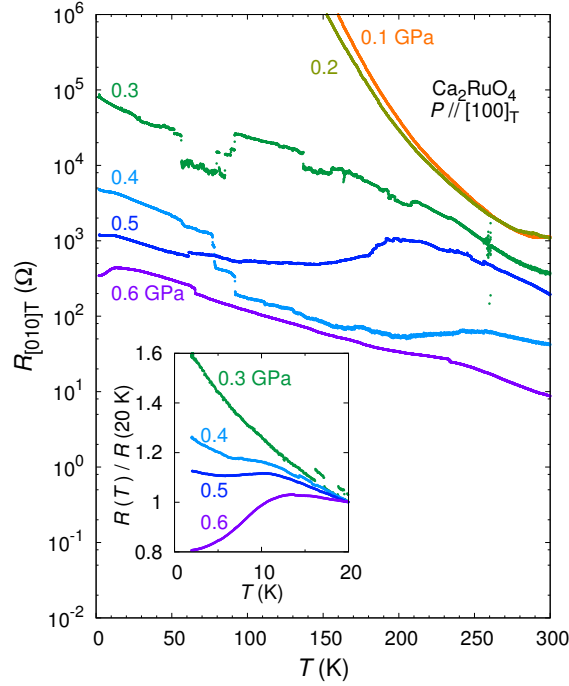
#### 4.1.1 Short summary

We investigated in-plane anisotropy of the UAP effect on  $\text{Ca}_2\text{RuO}_4$  by measuring the resistance and magnetization, with a expectation that metal-insulator transition is induced: with UAP applied along the  $ab$  plane, samples are expected to expand along the  $c$  axis and to exhibit metallic behavior. We applied pressure either parallel to the in-plane Ru-O bond of  $\text{RuO}_6$  octahedra (we denote this as the  $[100]_T$  direction using the tetragonal notation) or diagonal to the Ru-O bond (the  $[110]_T$  direction). From both resistivity and magnetization measurements, we clarified that a FM-M state with  $T_{\text{FM}}$  of 12 K is induced by  $P_{\parallel[100]_T}$  of 0.4 GPa or  $P_{\parallel[110]_T}$  of 0.2 GPa. Thus, we succeeded in inducing the FM-M phase at lower critical pressure than by hydrostatic pressure (0.5 GPa). This result indicates that the flattening distortion of the  $\text{RuO}_6$  octahedra is more easily released by in-plane UAP. In addition to the anisotropy of the critical pressure of the FM-M phase, FM component of the magnetization exhibits anisotropy: although the magnetization increases monotonically with pressure diagonal to the orthorhombic principal axes, the magnetization exhibits peculiar dependence on pressure along the in-plane orthorhombic principal axes. This peculiar dependence can be explained by a qualitative difference between the UAP effects along the orthorhombic  $a$  and  $b$  axes, as well as by the presence of twin domain structures. We have also revealed that the B-AFM phase appears under  $P_{\parallel[100]_T}$  above 0.6 GPa or  $P_{\parallel[110]_T}$  above 1.3 GPa coexisting with the A-AFM phase. These striking anisotropic behavior demonstrates that the UAP is a powerful tool to control electronic states of layered oxides.

#### 4.1.2 Resistivity under UAP

Figure 4.1 displays the temperature dependence of the four-wire resistance of  $\text{Ca}_2\text{RuO}_4$  under  $P_{\parallel[100]_T}$ . Below 0.2 GPa,  $R(T)$  exhibits typical insulating behavior fitted well with the activation-type formula  $R(T) \propto \exp(\Delta/2T)$  with  $\Delta = 4000\text{-}5000$  K, which is similar to that under ambient pressure [1, 72, 8, 73]. At 0.3 GPa, the resistance divergence is strongly reduced, suggesting the emergence of the metallic phase in a certain portion of the sample. Above 0.4 GPa, a peak in  $R(T)$  (inset of Fig. 4.1) and large negative magnetoresistance (Fig. 4.2) are observed at around 12 K,

which are typical behavior of itinerant ferromagnets. Step-like changes of  $R(T)$  are attributable to microcracks in the sample. We comment here that an accurate estimation of resistivity in high pressure is rather difficult due to the coexistence of the metallic and insulating phases, reflecting the first-order nature of the Mott transition, as well as due to microcracks in the sample. For a brief comparison, the resistance value of 1 k $\Omega$  at 0.1 GPa and 300 K (see Fig. 4.1) corresponds to  $\sim 5 \Omega\text{cm}$  according to a simple estimation based on the sample dimensions. This value is consistent with the reported value of the resistivity  $\rho_{ab} = 4 \Omega\text{cm}$  at ambient pressure and 300 K. [8]

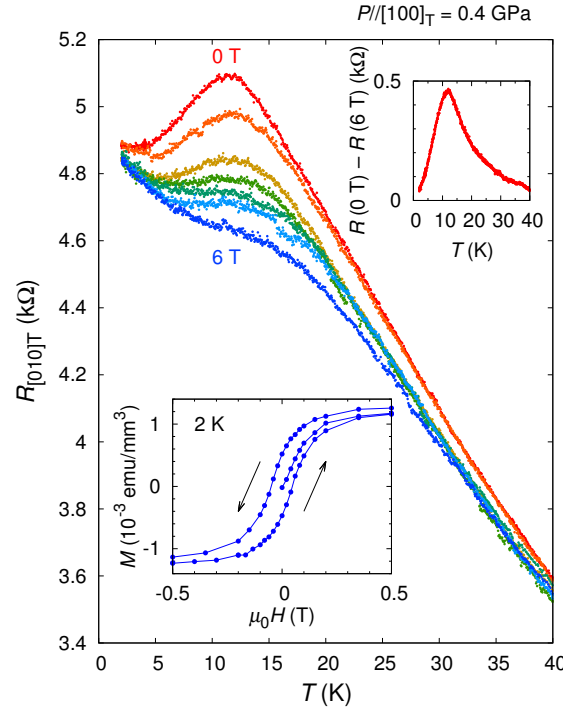


**Figure 4.1:** Temperature dependence of the four-wire resistance  $R_{[010]T}$  of  $\text{Ca}_2\text{RuO}_4$  under  $P_{||[100]T}$  measured in a cooling process. The inset represents the temperature dependence of  $R_{[010]T}$  normalized by that at 20 K. The decrease of resistance below 12 K indicates an emergence of a FM order.

### 4.1.3 Magnetization under UAP

FM order is also observed in the magnetization  $M$  (the bottom inset of Fig. 4.2 and Fig. 4.3). The  $M(H)$  curves exhibit clear hysteresis near  $H = 0$  and saturation of  $M$  at higher fields. Although small hysteresis is observed even above  $T_{\text{FM}}$  because of the re-orientation of the canted AFM domains as previously reported [5], the size of the hysteresis loop steeply increases below about 10 K, indicating the emergence of the FM phase. In Fig. 4.3, the evolution of the FM order for  $P_{||[100]T}$  and  $P_{||[110]T}$  is compared in the  $M(T)$  curves at 10 mT. Interestingly, we found that the FM state appears above 0.4 GPa for  $P_{||[100]T}$  whereas above 0.2 GPa for  $P_{||[110]T}$ . These anisotropic critical pressures of the FM order are consistent with results of the resistivity measurements.



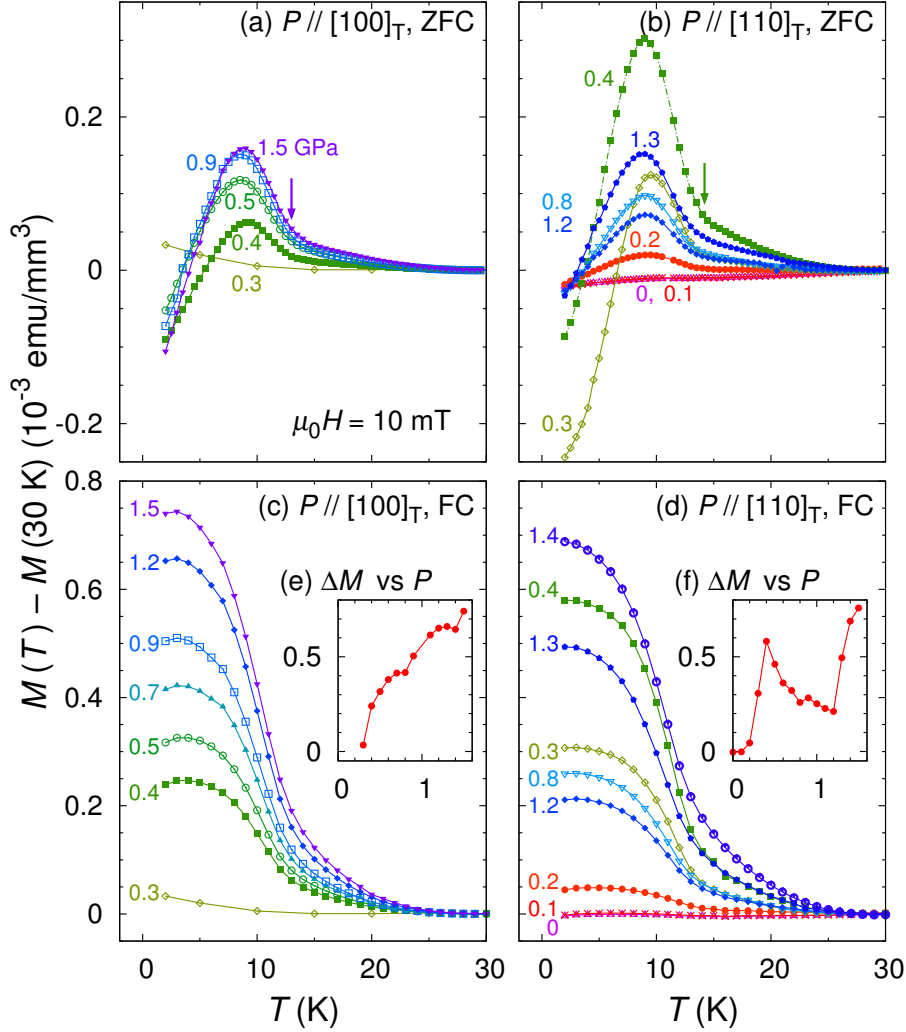


**Figure 4.2:** Temperature dependence of the four-wire resistance  $R_{[010]T}$  of  $\text{Ca}_2\text{RuO}_4$  at  $P_{||[100]T}$  of 0.4 GPa under magnetic field  $H_{||[100]T}$ . The sample is different from that of Fig. 4.1. All the resistivity data were taken with the field-cooling process. We have checked that  $R(T)$  does not differ by cooling processes. The top inset displays the difference of the four-wire resistance between 0 and 6 T. The peak indicates  $T_{\text{FM}} \sim 12$  K. The bottom inset displays the magnetic field  $H_{||[100]T}$  dependence of the magnetization  $M_{||[100]T}$  at 2 K under  $P_{||[100]T}$  of 0.4 GPa. It exhibits a typical hysteresis corresponding to a FM ordering.

We also found that  $M(2 \text{ K}) - M(30 \text{ K})$  in field-cooling (FC) process, which indicates magnetization component due to the FM order, exhibits anisotropic pressure dependence as shown in Fig. 4.3(e) and (f). This quantity increases almost monotonically with  $P_{||[100]T}$ . In contrast, under  $P_{||[110]T}$  it first increases from 0.2 to 0.4 GPa, then decreases from 0.4 to 1.2 GPa, and increases again above 1.2 GPa.

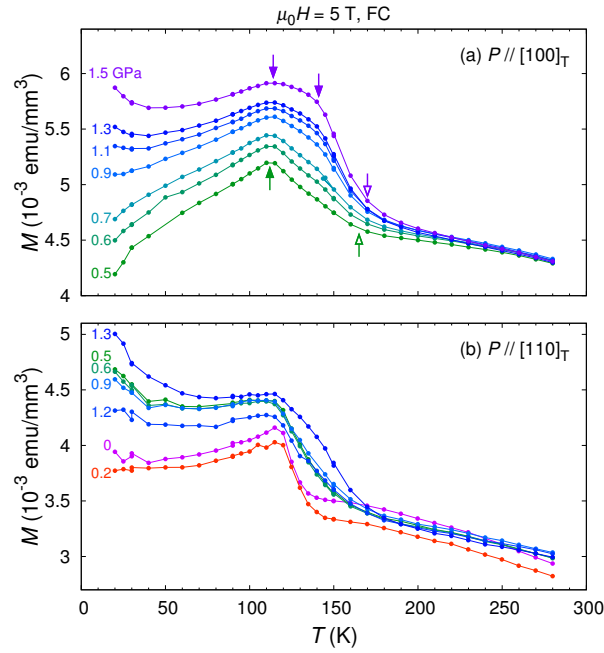
We also detected AFM transitions in the  $M(T)$  curves at 5 T (Fig. 4.4). At ambient pressure,  $M(T)$  exhibits a peak at 115 K as a result of the A-AFM transition [2]. With increasing  $P_{||[100]T}$  or  $P_{||[110]T}$ , the peak structure attributable to the A-AFM transition is retained. In addition, under  $P_{||[100]T}$  above 0.6 GPa or  $P_{||[110]T}$  above 1.3 GPa, a shoulder-like structure appears at around 140 K. Previous  $P_{\text{hydro}}$  studies revealed that a transition to another AFM state, the B-AFM state, occurs at  $T_{\text{AFM}} = 145$  K between 0.2 and 0.8 GPa [6, 7]. With an analogy to the  $P_{\text{hydro}}$  result, the shoulder-like feature observed in our study is also interpreted as the emergence of the B-AFM insulating state. We emphasize that the onset critical pressure of the B-AFM state is highly anisotropic.

We note that the coexistence of the FM-M and AFM insulating phases is attributable to the



**Figure 4.3:** Development of the magnetization  $M$  measured with a field of 10 mT parallel to the pressure for (a)(c)  $P \parallel [100]_T$  and (b)(d)  $P \parallel [110]_T$ . The panels (a) and (b) presents data taken with the warming process after zero field cooling (ZFC), and the panels (c) and (d) presents data with the field cooling (FC). The insets represent the pressure dependence of  $\Delta M = M(2 \text{ K}) - M(30 \text{ K})$  in FC for (e)  $P \parallel [100]_T$  and (f)  $P \parallel [110]_T$ . The units of the vertical and horizontal axes are  $10^{-3} \text{ emu/mm}^3$  and GPa, respectively.

first-order nature of the transition as well as experimentally inevitable inhomogeneity of the lattice distortion under pressure. Similar coexistence is reported in thin film and  $P_{\text{hydro}}$  studies [6, 7, 15].



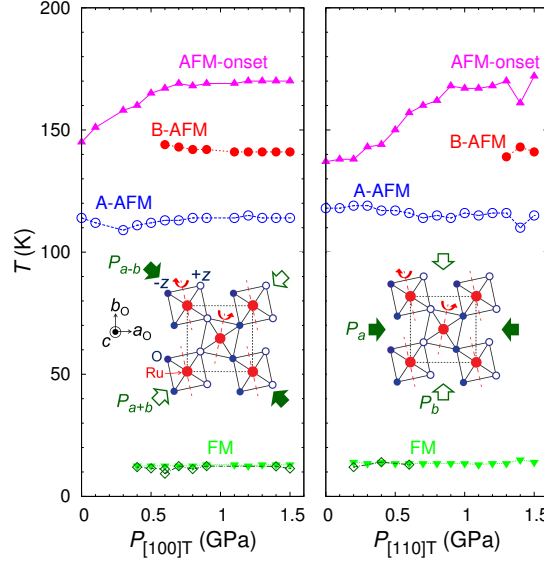
**Figure 4.4:** Temperature dependence of the magnetization  $M$  measured with a field of 5 T parallel to the pressure in field-cooling process for (a)  $P_{\parallel[100]T}$  and (b)  $P_{\parallel[110]T}$ . The closed arrows around 115 K and 140 K indicate the peak and shoulder structures, corresponding to the A-centered and B-centered AFM transitions, respectively. The open arrows present the onset of the AFM orders.

#### 4.1.4 Phase diagram

For analyzing the evolution of magnetic states by in-plane UAPs, we adopt two definitions for  $T_{\text{FM}}$  based on the magnetoresistance or magnetization. (1) For one definition,  $T_{\text{FM}}$  is determined as the temperature where  $\Delta R \equiv R(0 \text{ T}) - R(6 \text{ T})$  exhibits a maximum as shown in the top inset of Fig. 4.2, because  $\Delta R$  is related to the strength of the ferromagnetic fluctuation, which should be maximized at  $T_{\text{FM}}$ . (2) For the other,  $T_{\text{FM}}$  is determined as the temperature where  $M(T)$  at 10 mT in ZFC process exhibits an abrupt increase, as shown by the arrows in Fig. 4.3(a,b).  $T_{\text{FM}}$  of two definitions takes almost the same values for the both pressure directions as shown in Fig. 4.5. The value of  $T_{\text{FM}}$ ,  $\sim 12$  K, is very similar to that under  $P_{\text{hydro}}$  between 0.5 and 2.5 GPa [74, 8, 7]. We emphasize that the critical pressure of the FM-M phase under in-plane UAP is substantially smaller than that under  $P_{\text{hydro}}$ : In particular, the critical pressure under  $P_{\parallel[110]T}$  (0.2 GPa) is less than half of that under  $P_{\text{hydro}}$  (0.5 GPa). This fact demonstrates that the in-plane UAP is indeed effective for changing the electronic state of  $\text{Ca}_2\text{RuO}_4$ .

For the in-plane UAP effects on the AFM phases, we define three characteristic temperatures found in the magnetization at 5 T: the onset temperature of magnetization increase, the temperature of magnetization peak, and the temperature of the shoulder-like structure (Fig. 4.4). They are considered to indicate the onset temperature of an AFM transition  $T_{\text{AFM}}^{\text{onset}}$ , the ordering temperatures of the A- and B-AFM phases  $T_{\text{A-AFM}}$  and  $T_{\text{B-AFM}}$ , respectively. We found that  $T_{\text{A-AFM}}$

and  $T_{\text{B-AFM}}$  do not vary with  $P_{\parallel[100]\text{T}}$  or  $P_{\parallel[110]\text{T}}$  in the present pressure range once they start to be observed. In contrast,  $T_{\text{AFM}}^{\text{onset}}$  exhibits substantial pressure dependence. We infer that  $T_{\text{AFM}}^{\text{onset}}$  is a characteristic temperature of the development of short-range magnetic correlation above the underlying second-order AFM transition temperatures. We attribute the increase of  $T_{\text{AFM}}^{\text{onset}}$  with increasing  $P_{\parallel[100]\text{T}}$  or  $P_{\parallel[110]\text{T}}$  to the appearance of a small fraction of the B-AFM order. The enhancement starts at 0 GPa under  $P_{\parallel[100]\text{T}}$  whereas at 0.2 GPa under  $P_{\parallel[110]\text{T}}$ .



**Figure 4.5:** Pressure dependence of  $T_{\text{FM}}$  and  $T_{\text{AFM}}$  for (a)  $P_{\parallel[100]\text{T}}$  and (b)  $P_{\parallel[110]\text{T}}$ . Diamonds and reversed triangles denote  $T_{\text{FM}}$  determined from magnetoresistance and magnetization, respectively. Triangles, open circles, and closed circles indicate  $T_{\text{AFM}}^{\text{onset}}$ ,  $T_{\text{A-AFM}}$ , and  $T_{\text{B-AFM}}$ , respectively. The insets schematically describes the  $\text{RuO}_2$  plane with the UAP. The broken lines denote the tilting axes. Because of the tilting, half of the O ions described with the open circles are located above the undistorted  $\text{RuO}_2$  plane, while the others with the closed circles below the plane. Dotted lines indicate a unit cell.

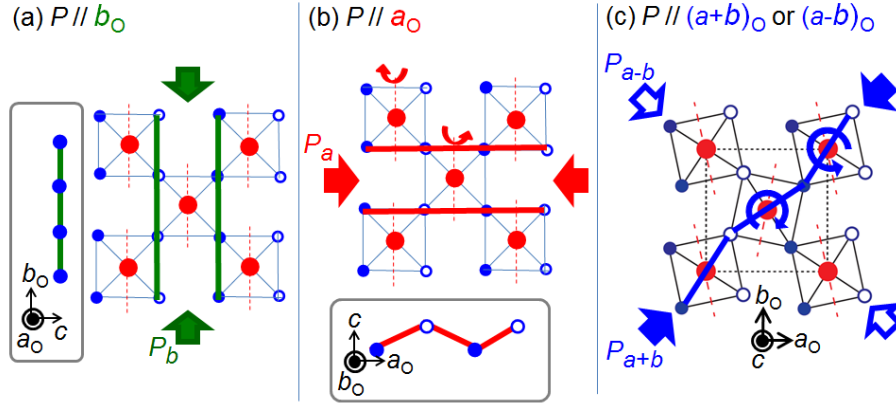
To check the reproducibility, we have measured three samples for  $P_{\parallel[100]\text{T}}$  (one for  $M$  and two for  $R$ ) and other three samples for  $P_{\parallel[110]\text{T}}$  (one for  $M$  and two for  $R$ ). For  $P_{\parallel[100]\text{T}}$ , all samples provide consistent results. For  $P_{\parallel[110]\text{T}}$ , we obtain consistent results except for one sample for  $R$  measurement, attributable to difference in the crystal mosaic structures that we will describe in Chap. 4.1.5.

#### 4.1.5 Discussion

In this subsection, we discuss the origin of the anisotropic pressure response of the electronic state of  $\text{Ca}_2\text{RuO}_4$ . In particular, while the response of the magnetization to  $P_{\parallel[100]\text{T}}$  is rather monotonic and qualitatively similar to that to  $P_{\text{hydro}}$ , that to  $P_{\parallel[110]\text{T}}$  is unusual in two points: (1) The FM magnetization increases twice, first between 0.1 and 0.4 GPa and then above 1.2 GPa (Fig. 4.3(d)). (2) The clear signature of the B-AFM phase is observed at substantially higher

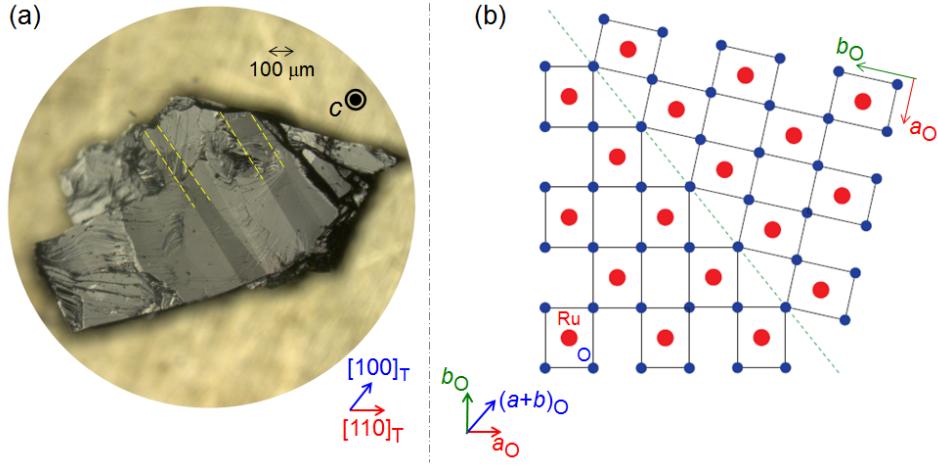
pressure than the FM-M phase (Fig. 4.4(b)). This is rather surprising because under  $P_{\text{hydro}}$  the B-AFM phase emerges at lower pressures than the FM-M phase and these two phases coexist over a wide pressure range [6, 7].

It is known that release of the flattening distortion is a necessary condition for the FM-M phase. Importantly, the flattening is closely related to the orthorhombicity: there is a strong orthorhombicity with  $a/b \sim 0.98$  in the presence of the flattening whereas  $a/b$  is about 1.00 in its absence [5, 6]. Here  $a$  and  $b$  are the orthorhombic in-plane lattice constants. Therefore, it is naturally expected that the FM-M phase is favored by  $P_{\parallel b}$  through the reduction of orthorhombicity. In a microscopic viewpoint, because the  $b$ -axis pressure should not couple to tilting or rotation distortions, the pressure along the  $b$  axis is expected to shorten the in-plane Ru-O length directly and to force the  $\text{RuO}_6$  octahedra to elongate along the  $c$  axis more effectively as described in Fig. 4.6. For the other in-plane pressure directions, the strain is absorbed by the enhancement of the tilting or/and rotation and only slightly affects the Ru-O bond lengths.



**Figure 4.6:** Lattice distortions expected to be induced under (a)  $P_{\parallel b}$ , (b)  $P_{\parallel a}$ , and (c)  $P_{\parallel(a+b)}$  or  $P_{\parallel(a-b)}$ . Orthorhombic notation is used here. The main figures schematically describes the  $\text{RuO}_2$  plane. For simplicity, here we ignore the rotation of  $\text{RuO}_6$  octahedra around the  $c$  axis at the initial zero-pressure state and consider the lattice distortions induced by an in-plane UAP. The broken lines denote the tilting axes. Because of the tilting, half of the O ions described with the open circles are located above the undistorted  $\text{RuO}_2$  plane, while the others with the closed circles below the plane. Dotted lines in the panel (c) indicate a unit cell. (a) Under  $P_{\parallel b}$ , the Ru-O bond length along the  $b$  axis is expected to be shortened, and as a result  $\text{RuO}_6$  octahedra would elongate along the  $c$  axis in order to keep octahedra volume constant. (b) Under  $P_{\parallel a}$ , the tilting distortion would be enhanced first like a folding screen, because it seems easier than to shorten the Ru-O bond length along the  $a$  axis. (c) Under  $P_{\parallel(a+b)}$  or  $P_{\parallel(a-b)}$ , the rotation distortion is expected to be induced first.

For understanding the observed pressure responses, we need to consider the presence of orthorhombic crystalline twin domains exemplified in Fig. 4.7.  $P_{\parallel[100]\text{T}}$  corresponds to either  $P_{\parallel(a+b)}$  or  $P_{\parallel(a-b)}$  depending on domains (the left inset of Fig. 4.5). However, since the effect on the lattice is expected to be equivalent between  $P_{\parallel(a+b)}$  and  $P_{\parallel(a-b)}$ , the UAP effect for  $P_{\parallel[100]\text{T}}$  should be the same for both domains. The observed monotonic pressure dependence of the magnetization for



**Figure 4.7:** (a) Photo of the orthorhombic twin domains of  $\text{Ca}_2\text{RuO}_4$  taken with a polarized optical microscope. Yellow broken lines denote domain boundaries: the darkness of the left side of the line is different from that of the right side because of the difference of reflectivity due to the twin domains. Note that the color of the image is not modified except for the addition of the yellow lines. (b) Schematic figure of the orthorhombic twin domains of  $\text{Ca}_2\text{RuO}_4$ . Red and blue circles represent Ru and O ions, respectively. Arrows denote the orthorhombic  $a$  or  $b$  axes. Broken line represents the domain boundary: the twin boundaries run along the orthorhombic  $(a + b)$  axis.

$P_{\parallel[100]T}$  is attributable to such absence of the domain effect. In contrast, the presence of a domain structure is expected to play a key role under  $P_{\parallel[110]T}$ : Smaller critical pressure of the FM-M phase is expected for the domain under  $P_{\parallel b}$  (the  $b$ -domain) than for the domain under  $P_{\parallel a}$  (the  $a$ -domain) as we have described. Therefore, the non-monotonic pressure dependence of the magnetization can be understood naturally: First, the FM-M phase is induced at  $P_{\parallel[110]T} = 0.2$  GPa within the  $b$ -domain possibly with the absence of the B-AFM phase, giving rise to the initial overall increase of the magnetization. The decrease of magnetization above 0.4 GPa (Fig. 4.3(f)) is likely to occur also in the  $b$  domain. With increasing pressure, the FM-M phase is induced within the  $a$ -domain above 1.2 GPa accompanied by the B-AFM phase, resulting in the second increase of the magnetization below 12 K (Fig. 4.3(f)) and the appearance of a shoulder-like structure at around 145 K (Fig. 4.4(b)). This extraordinary domain selectivity highlights the uniqueness of UAP that cannot be systematically explored with  $P_{\text{hydro}}$ .

We note that the essential electronic difference between the A- and B-AFM phases is in the orbital occupation of four Ru  $4d$  electrons [75, 24]. In both phases each of three electrons occupies the  $xy$ ,  $yz$ , and  $zx$  orbitals respectively, due to Hund's coupling. The A-AFM phase is realized in the ferro-orbital state with the fourth electron occupying the  $xy$  orbital for all Ru sites, whereas the B-AFM phase is realized in an antiferro-orbital state with a partial  $xy$ -band occupation. The observed anisotropy of the critical pressure of the B-AFM phase should be related to this difference. Band calculation of  $\text{Ca}_2\text{RuO}_4$  incorporating lattice distortions under in-plane UAPs is needed for further discussion.

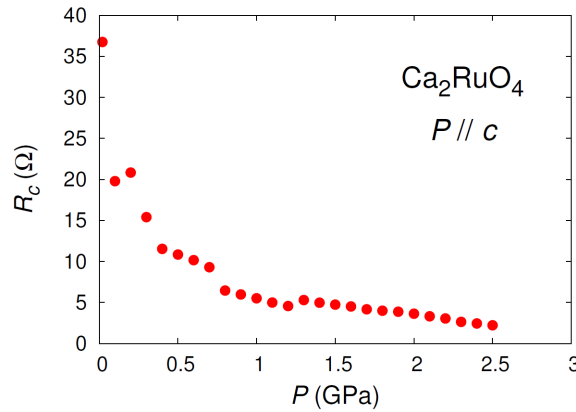
## 4.2 Suppression of the insulating gap under *out-of-plane* uniaxial pressure

### 4.2.1 Short summary

We performed resistance measurement of  $\text{Ca}_2\text{RuO}_4$  under out-of-plane UAP with a expectation that the insulating gap will increase because of the enhanced energy difference between  $xy$  and  $yz$ ,  $zx$  orbitals of Ru  $4d$  electrons. Surprisingly, the experimental result is opposite from the prediction: although the temperature dependence of the out-of-plane resistance remains insulating under  $P_{\parallel c}$  up to 2.5 GPa, the insulating gap  $\Delta$  is suppressed from 3000 K to 700 K. This result strongly suggests the possibility of a new metallic state in  $\text{Ca}_2\text{RuO}_4$ : the metallic state under out-of-plane UAP is probably induced by the enhanced band width caused by the suppression of the rotation or tilting distortion, whereas the metallic state under hydrostatic or in-plane uniaxial pressure is realized by the suppression of the crystal field splitting when the flattening distortion is released.

### 4.2.2 Resistivity under UAP

Figure 4.8 represents the out-of-plane UAP dependence of the two-wire resistance  $R_{\parallel c}$  of  $\text{Ca}_2\text{RuO}_4$  at room temperature. We note that the initial drop of resistance from 0 GPa to 0.2 GPa is mainly attributed to the improvement of the contact resistances between the sample and the piston and between the inner parts of the pressure cell, and thus this is not intrinsic. What is surprising is that the resistance continues to decrease up to 2.5 GPa. This result suggests the possibility that a metallic phase is induced or the insulating gap is suppressed in  $\text{Ca}_2\text{RuO}_4$  under  $P_{\parallel c}$  in contrast to the simple prediction described in Chap. 4.2.1.



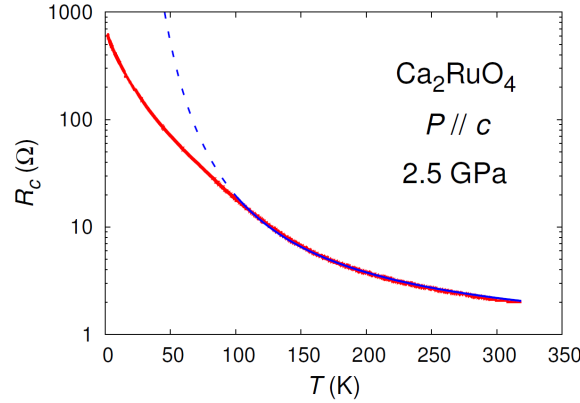
**Figure 4.8:** Out-of-plane UAP dependence of resistance  $R_{\parallel c}$  of  $\text{Ca}_2\text{RuO}_4$  at room temperature. Gradual decrease of the resistance up to 2.5 GPa seems to indicate the suppression of the insulating gap, although the initial drop from 0 GPa to 0.2 GPa would be caused by an extrinsic contribution, which is the improvement of the contact resistances between the sample and the piston and between the inner parts of the pressure cell.

In order to check the reproducibility of this suppression of the resistance by  $P_{\parallel c}$ , we measured two-wire  $R_{\parallel c}$  under  $P_{\parallel c}$  for 11  $\text{Ca}_2\text{RuO}_4$  samples. The resistance decreased with  $P_{\parallel c}$  for 5 samples, although it increased for 2 samples. For the other 4 samples, the resistance was unstable and did not exhibit clear pressure dependence. In order to reveal the out-of-plane UAP effect on the intrinsic resistance, we should consider the pressure dependence of extrinsic resistances; with increasing pressure, the measured value of resistance will be enhanced by cracks, whereas it will be suppressed by the improved electric contact between the sample and the piston and between the inner parts of the pressure cell. Since these two extrinsic contributions have opposite pressure dependence, it is difficult to clarify the out-of-plane UAP effect on  $\text{Ca}_2\text{RuO}_4$  only from the pressure dependence of the two-wire out-of-plane resistance.

Therefore, we measured the temperature dependence of the resistance  $R_{\parallel c}$  of  $\text{Ca}_2\text{RuO}_4$  under  $P_{\parallel c}$  of 2.5 GPa (Fig. 4.9). Metallic temperature dependence of  $R_c$  was not observed in the present pressure range up to 2.5 GPa. However, we have revealed the suppression of the insulating gap: the  $R(T)$  data between 300 K and 100 K are fitted well with the activation-type insulating behavior,

$$R_c = R_0 \exp(\Delta/2k_B T) \quad (4.1)$$

giving  $\Delta \approx 700$  K, which is substantially smaller than the gap obtained from the out-of-plane resistivity of a single crystal  $\text{Ca}_2\text{RuO}_4$  at ambient pressure ( $\Delta \approx 3000$  K [8]). The resistance below 100 K cannot be fitted with the activation-type behavior, eq. (4.1), and exhibits a much weaker divergence. This weakness of the increase of resistance on cooling also supports our conclusion that the electronic state of  $\text{Ca}_2\text{RuO}_4$  tends to be closer to a metallic state by  $P_{\parallel c}$ .



**Figure 4.9:** Temperature dependence of the out-of-plane resistance  $R_{\parallel c}$  under  $P_{\parallel c}$  of 2.5 GPa. Red line represents the experimental result measured with an AC current of 0.01 mA-rms at 7 Hz. Blue solid line indicates an activation-type curve within the fitting region, whereas dashed line outside the fitting region.

### 4.2.3 Discussion

Naively, it is expected that  $P_{\parallel c}$  enhances the flattening distortion of  $\text{RuO}_6$  octahedra and increases the insulating gap  $\Delta$  of  $\text{Ca}_2\text{RuO}_4$ . Surprisingly, however, the suppression of  $\Delta$  was observed. We

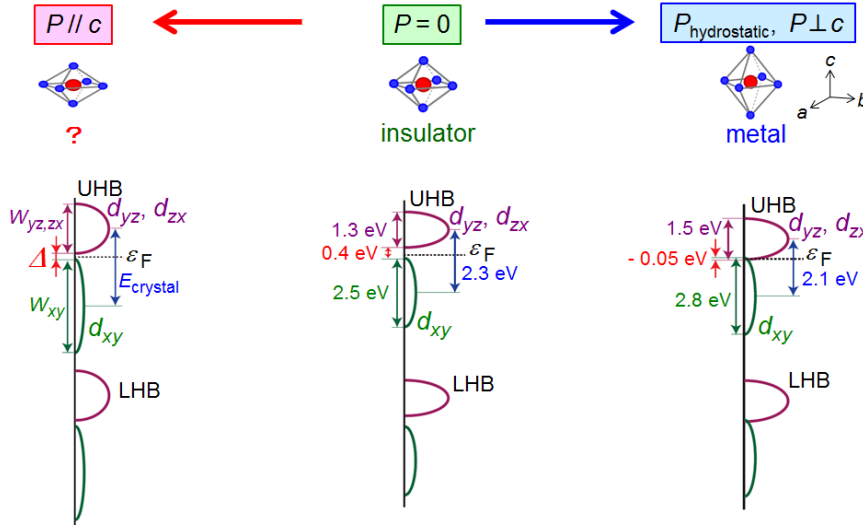


consider that band width plays an important role for this unexpected behavior. As shown in the middle figure of Fig. 4.10, the insulating gap of  $\text{Ca}_2\text{RuO}_4$  locates between the upper Hubbard band (UHB) originating from the  $yz$  and  $zx$  orbitals of Ru  $4d$  electrons and the UHB originating from the  $xy$  orbitals. Therefore, the gap size  $\Delta$  has the following relation:

$$\Delta = E_{\text{crystal}} - W_{xy}/2 - W_{yz,zx}/2 \quad (4.2)$$

Here,  $E_{\text{crystal}}$  is the value of the crystal field splitting between the  $xy$ -UHB and the  $yz, zx$ -UHB.  $W_{xy}$  and  $W_{yz,zx}$  are the band width of the  $xy$ -UHB and  $yz, zx$ -UHB, respectively. Since  $P_{\parallel c}$  is expected to intensify the flattening distortion of  $\text{RuO}_6$  octahedra along the  $c$  axis,  $E_{\text{crystal}}$  will be enhanced by  $P_{\parallel c}$ . Thus, for  $\Delta$  to be suppressed,  $W_{xy}$  or  $W_{yz,zx}$  or both should increase under  $P_{\parallel c}$ . If the rotation distortion of  $\text{RuO}_6$  octahedra is weakened, the Ru-O-Ru bond angle on the  $xy$  plane approaches to 180 degrees, and the hybridization between the Ru  $xy$  orbital and the O  $x$  or  $y$  orbital increases resulting in wider  $W_{xy}$ . Similarly, both  $W_{xy}$  and  $W_{yz,zx}$  will increase when the tilting distortion of  $\text{RuO}_6$  octahedra is suppressed. Therefore, we consider that the rotation or tilting or both distortions are weakened in  $\text{Ca}_2\text{RuO}_4$  under  $P_{\parallel c}$  and the electronic state approaches to a metallic state, which is different from the metallic state which emerges as the result of the suppression of  $E_{\text{crystal}}$  by the elongation of  $\text{RuO}_6$  octahedra along the  $c$  axis.

Let us comment on the possibility that a two-dimensional metallic state is already realized in the sample. Here, two-dimensional metallic state means a state where only the in-plane transport is metallic. Indeed, in the hydrostatic pressure experiments, it was reported that the  $c$ -axis resistivity  $\rho_c$  exhibits a non-metallic temperature dependence even in the metallic phase [8]. Therefore, in order to clarify whether a metallic phase is induced or only the insulating gap is suppressed, the in-plane resistivity of  $\text{Ca}_2\text{RuO}_4$  under  $P_{\parallel c}$  should be measured as a future issue. The four-wire method is appropriate for this measurement, because we would like to measure resistance under a condition in which extrinsic resistances do not decrease with pressure. Anyway, the electronic state of  $\text{Ca}_2\text{RuO}_4$  under  $P_{\parallel c}$  is really fascinating, because it probably approaches to a new metallic state which is different from the metallic state under hydrostatic or in-plane uniaxial pressure. Clarification of the ground state characteristics under  $P_{\parallel c}$  is also important.



**Figure 4.10:** Schematic figure of the electronic states of  $\text{Ca}_2\text{RuO}_4$  under ambient pressure (middle figure), out-of-plane UAP (left figure), and in-plane UAP or hydrostatic pressure (right figure). Here,  $\Delta$  is the insulating gap and  $E_{\text{crystal}}$  is the value of the crystal field splitting between the  $xy$ -UHB and the  $yz, zx$ -UHB.  $W_{xy}$  and  $W_{yz, zx}$  are the band width of the  $xy$ -UHB and  $yz, zx$ -UHB, respectively. Because of the flattening distortion of  $\text{RuO}_6$  octahedra along the  $c$  axis, the energy level of the  $xy$  band is lower than that of the  $yz, zx$  band and the insulating state realizes in  $\text{Ca}_2\text{RuO}_4$  under ambient condition. Under  $P_{\parallel c}$ , since  $\Delta$  decreases despite the intensified flattening distortion, only  $W_{xy}$  or both  $W_{xy}$  and  $W_{yz, zx}$  are considered to be enhanced by the suppression of the rotation or/and tilting distortion. Under hydrostatic or in-plane uniaxial pressure, which release the flattening distortion, the metallic state is induced by the suppression of  $E_{\text{crystal}}$ . For the middle and right figures,  $E_{\text{crystal}}$ ,  $W_{xy}$  and  $W_{yz, zx}$  are estimated from band calculation, optical conductivity, and X-ray spectroscopy [26, 76, 77, 78, 79, 80, 81]; based on the estimation, an insulating gap of 0.4 eV exists at Fermi level  $\epsilon_F$  in the middle figure, whereas the  $xy$ -UHB and the  $yz, zx$ -UHB overlap by 0.05 eV in the right figure.

## Chapter 5

# Uniaxial pressure effects on $\text{Sr}_2\text{RuO}_4$

## 5.1 *In-plane* anisotropy of the uniaxial-pressure effect on $\text{Sr}_2\text{RuO}_4$

### 5.1.1 Short summary

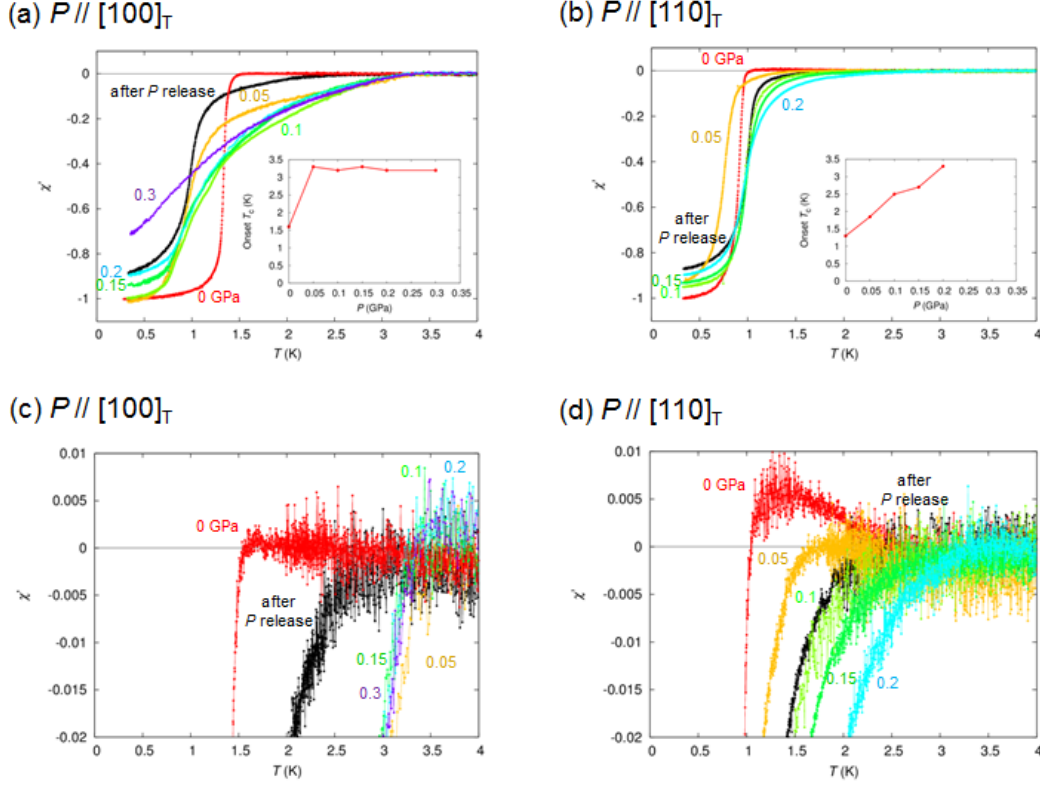
We measured AC susceptibility of  $\text{Sr}_2\text{RuO}_4$  with the mini-coil method under in-plane UAPs along the two distinct directions,  $[100]_{\text{T}}$  or  $[110]_{\text{T}}$ , in order to obtain hints for conclusive evidence of the superconducting order parameter of  $\text{Sr}_2\text{RuO}_4$  whose orbital part is expected to be two-component under ambient condition. Notably, by  $P_{\parallel[100]_{\text{T}}}$ , the onset of superconducting transition temperature  $T_{\text{c}}$  is enhanced up to 3.3 K at only 0.05 GPa and remains 3.3 K up to 0.3 GPa. In contrast, the onset  $T_{\text{c}}$  is gradually enhanced by  $P_{\parallel[110]_{\text{T}}}$ . These contrasting results suggest that  $P_{\parallel[100]_{\text{T}}}$  rather than  $P_{\parallel[110]_{\text{T}}}$  is favorable for inducing 3-K superconductivity (SC). Because it is observed that the shielding fraction around 3 K is suppressed after releasing the pressure, the 3-K SC under in-plane UAP should be mainly induced by elastic lattice distortion. Since crystal symmetry should be reduced by in-plane UAP, the orbital part of the superconducting order parameter of  $\text{Sr}_2\text{RuO}_4$  is expected to be one-component in the 3-K SC realized by in-plane UAP, and to become two-component below a certain temperature. The double transition reflecting the existence of two different superconducting phases, the non-chiral SC at higher temperature and the chiral SC at lower temperature, was not observed in the imaginary part of the AC susceptibility.

### 5.1.2 AC susceptibility under UAP

Figure 5.1 represents the temperature dependence of the real part of the AC susceptibility of  $\text{Sr}_2\text{RuO}_4$ . We revealed that the in-plane UAP dependence of the onset  $T_{\text{c}}$  is highly anisotropic, as shown in the insets of Figs. 5.1 (a) and (b): the onset  $T_{\text{c}}$  is abruptly enhanced up to 3.3 K at only 0.05 GPa and remains 3.3 K for higher  $P_{\parallel[100]_{\text{T}}}$ . In contrast, the onset  $T_{\text{c}}$  is gradually enhanced under  $P_{\parallel[110]_{\text{T}}}$ . Moreover, compared with the  $P_{\parallel[110]_{\text{T}}}$  case, the superconducting transition is remarkably broadened under  $P_{\parallel[100]_{\text{T}}}$ .

Previous studies on the  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic,  $\text{Sr}_2\text{RuO}_4$  under out-of-plane UAP, and  $\text{Sr}_2\text{RuO}_4$  around dislocations suggest that  $\text{Sr}_2\text{RuO}_4$  has the optimal  $T_{\text{c}}$  of 3.3 K and this 3-K SC may have

quality different from the 1.5-K SC under ambient condition [66, 64, 32, 82]. In this study, we have newly clarified that 3-K SC is induced in  $\text{Sr}_2\text{RuO}_4$  also by in-plane UAP and  $P_{\parallel[100]T}$  is more favorable than  $P_{\parallel[110]T}$  for inducing the 3-K SC.

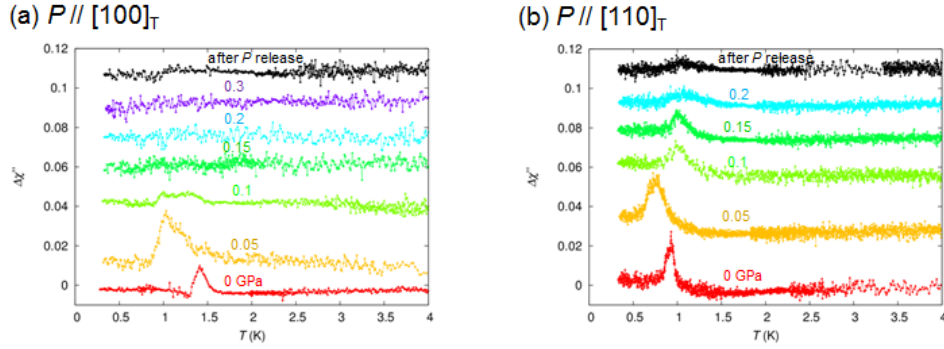


**Figure 5.1:** Temperature dependence of the real part of the AC susceptibility of  $\text{Sr}_2\text{RuO}_4$  under (a)(c)  $P_{\parallel[100]T}$  and (b)(d)  $P_{\parallel[110]T}$  measured with an AC magnetic field of 20 mOe-rms. The panels (c) and (d) are enlarged views around the superconducting onset. Black curves show the data taken about one week after releasing pressure from 0.3 GPa for  $P_{\parallel[100]T}$  and from 0.2 GPa for  $P_{\parallel[110]T}$ . The insets of Fig. (a) and (b) represent the pressure dependence of the onset  $T_c$  under  $P_{\parallel[100]T}$  and  $P_{\parallel[110]T}$ , respectively, clarifying the contrasting behavior between them.

We also measured the AC susceptibility of  $\text{Sr}_2\text{RuO}_4$  at about one week after releasing pressure from 0.3 GPa for  $P_{\parallel[100]T}$  and from 0.2 GPa for  $P_{\parallel[110]T}$ , as shown in Figs. 5.1 and 5.2. In both  $P_{\parallel[100]T}$  and  $P_{\parallel[110]T}$  cases, the onset  $T_c$  is suppressed down to about 2.5 K and the shielding fraction is remarkably suppressed between the original bulk  $T_c$  at ambient pressure and 3.3 K. These results indicate that the 3-K SC under in-plane UAPs is induced mainly by an elastic distortion, although some additional contribution of plastic distortion like a dislocation [82] cannot be completely excluded because the onset  $T_c$  after releasing pressure is still higher than the original value.

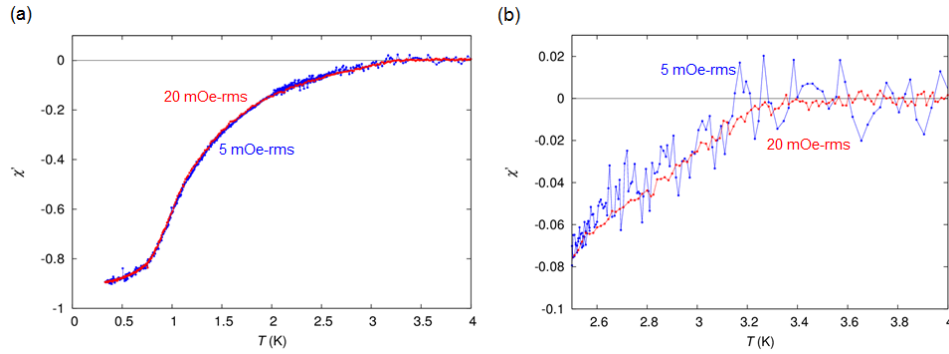
Figure 5.2 represents the temperature dependence of the imaginary part of the AC susceptibility of  $\text{Sr}_2\text{RuO}_4$ . Peak structure originating from energy dissipation is not clearly observed at

around 3 K at least in this resolution. Double transition below 1.5 K at 0.05 and 0.1 GPa probably results from  $T_c$  distribution caused by the inhomogeneity of lattice distortion.



**Figure 5.2:** Temperature dependence of the imaginary part of AC susceptibility of  $\text{Sr}_2\text{RuO}_4$  under (a)  $P_{\parallel[100]T}$  and (b)  $P_{\parallel[110]T}$  measured with a AC magnetic field of 20 mOe-rms.

As shown in Figure 5.3, the 3-K SC induced by  $P_{\parallel[100]T}$  is robust against changes in the amplitude of AC magnetic field. This tendency was the same also in the case of  $P_{\parallel[110]T}$ . These results are similar to that of the 3-K SC induced by out-of-plane UAP, but different from that of the 3-K SC in  $\text{Sr}_2\text{RuO}_4$ -Ru eutectic crystal [68], suggesting that the 3-K SC induced in  $\text{Sr}_2\text{RuO}_4$  by in-plane UAPs is not filamentary.

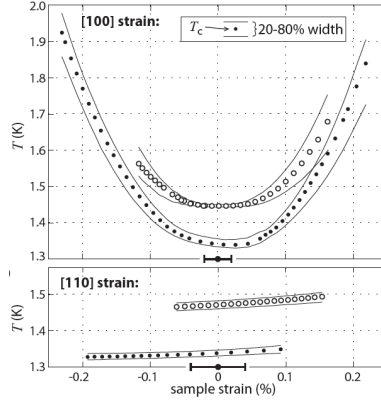


**Figure 5.3:** Difference between 5 and 20 mOe-rms of the temperature dependence of the real part of AC susceptibility of  $\text{Sr}_2\text{RuO}_4$  under  $P_{\parallel[100]T}$  of 0.2 GPa. The panel (b) is an enlarged view around the superconducting onset. Two curves are coincident well with each other, suggesting bulk-like SC.

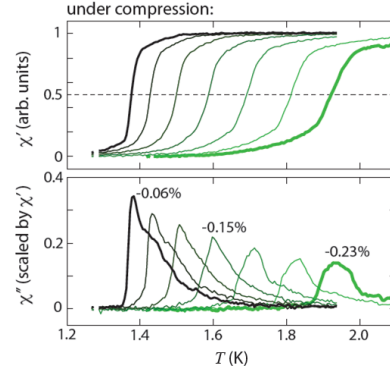
### 5.1.3 Discussion

Similar to the present study, much larger enhancement of  $T_c$  is observed for the *strain* along  $[100]_T$  than  $[110]_T$ , as shown in Fig. 5.4 [83]. The fact that unusual symmetric change in  $T_c$  for both compressive and expansive  $[100]_T$  strains supports the two-component order parameter of

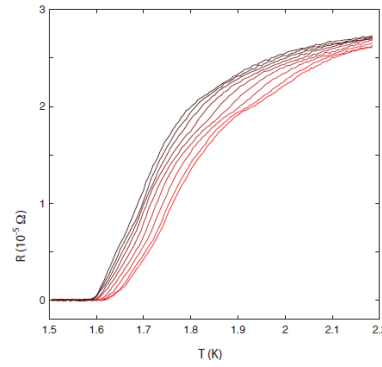
the SC in  $\text{Sr}_2\text{RuO}_4$ . The  $[100]_T$  strain results of Ref. [83] may seem to be quantitatively different from our  $P_{||[100]_T}$  results: as shown in Figs. 5.5 and 5.4,  $T_c$  is gradually enhanced and reaches only 1.9 K at  $-0.23\%$  strain, which corresponds to 0.23 GPa in our experiment according to the simplest estimation. We can naturally explain this different behavior by considering the difference of experimental setup: the pick-up coil of our measurements surrounds the entire sample as shown in Fig. 3.6 (b) and detects the whole magnetic signal originating from the sample, whereas the pick-up coil in the study of Ref. [83] is much smaller than a sample and detects only the magnetization of near the central region which is expected to be coherently distorted. Therefore, the superconducting transition observed in our study is dominated by strongly distorted region with higher  $T_c$ . In fact, as shown in Fig. 5.6, the resistivity measurements in the uniaxial *strain* experiments [84, 85] reveal that the sample under strain contain a part with much higher  $T_c$  than proved by the AC susceptibility. The qualitative difference between  $[110]_T$  strain and pressure effects is a future issue: under  $[110]_T$  compressive strain,  $T_c$  is suppressed, although the change is quite small.



**Figure 5.4:** Uniaxial-strain dependence of superconducting transition temperature of  $\text{Sr}_2\text{RuO}_4$  [83]. Negative and positive strains correspond to compressive and stretching strain, respectively.



**Figure 5.5:** Temperature dependence of AC susceptibility of  $\text{Sr}_2\text{RuO}_4$  under compressive uniaxial *strain* along the  $[100]_T$  direction [83].



**Figure 5.6:** Temperature dependence of resistivity of  $\text{Sr}_2\text{RuO}_4$  under compressive uniaxial *strain* along the  $[100]_T$  direction [84]. The black left curve shows the data of zero strain and the red right curve shows the data of up to 0.06 % strain.

## 5.2 Out-of-plane uniaxial pressure effect on eutectic $\text{Sr}_2\text{RuO}_4\text{-Ru}$

### 5.2.1 Short summary

Superconducting transition temperature  $T_c$  of  $\text{Sr}_2\text{RuO}_4$ , which is 1.5 K under ambient condition, is known to be enhanced up to about 3 K by out-of-plane UAP [32] or by formation of  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  eutectic crystal [29]. The former superconductivity (SC) can be called as  $P_{\parallel c}$ -originated 3-K SC, whereas the latter is called interfacial 3-K SC because previous studies indicate that the 3-K SC occurs around the interfaces between  $\text{Sr}_2\text{RuO}_4$  and Ru. In order to clarify the difference between these 3-K SCs, we measured AC susceptibility and resistance of  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  eutectic crystal under  $P_{\parallel c}$ .  $H$ - $T$  phase diagrams determined from the temperature dependence of the AC susceptibility under various DC magnetic fields exhibit concave-up behavior with decreasing temperature both in  $P_{\parallel c}$ -originated SC and in interfacial SC, suggesting both SCs have granular-like properties. In contrast, resistance behavior highlights the difference between  $P_{\parallel c}$ -originated SC and interfacial SC. Interestingly, sharp drop of resistance at about 1.5 K, which corresponds to the bulk  $T_c$  of  $\text{Sr}_2\text{RuO}_4$  under ambient condition, is induced at 0.1 GPa and disappears again at 0.3 GPa. We consider that this non-monotonic behavior indicates that the spatial distribution of the 3-K SC changes from 0 GPa to 0.3 GPa.

### 5.2.2 AC susceptibility under UAP

Figure 5.7 represents the temperature dependence of the AC susceptibility  $\chi_{AC}$  of  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  under  $P_{\parallel c} = 0$  and  $P_{\parallel c} = 0.5 \text{ GPa} > P^*$ , where  $P^*$  is the characteristic pressure described below.

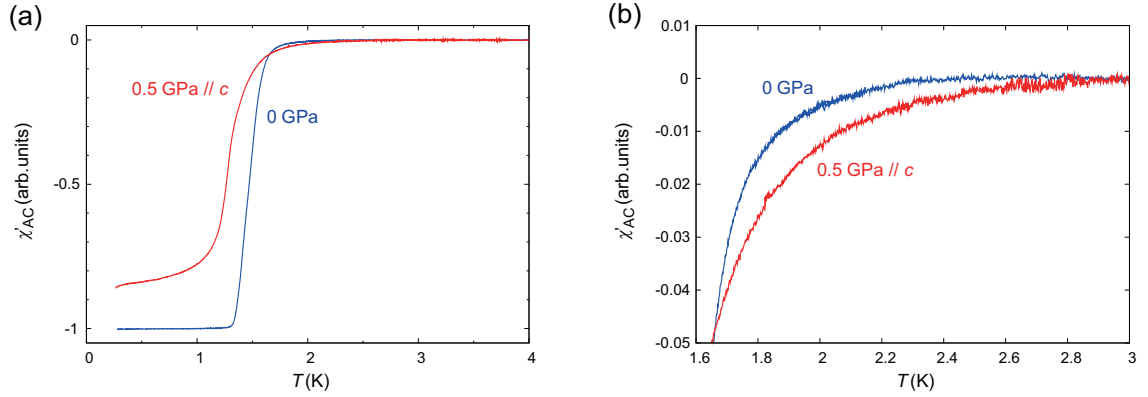
In a previous study [32], we revealed that the shielding fraction of 3-K SC in a  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  eutectic crystal is enhanced by  $P_{\parallel c}$  and properties of 3-K SC change at a critical pressure  $P^* \sim 0.4 \text{ GPa}$  in the following three points: the slope of the pressure dependence of the shielding fraction of 3-K SC becomes 12 times steeper above  $P^*$  (Fig. 5.8), shielding fraction increases below  $T_c$  of Ru (0.49 K) only above  $P^*$  (Fig. 5.9), and  $H_{AC}$ -sensitive behavior of 3-K SC disappears above  $P^*$  (Fig. 5.10).

Thus, we consider that the behavior at 0 GPa originates from the interfacial SC, whereas the behavior at 0.5 GPa reflects properties of the  $P_{\parallel c}$ -originated SC. An enlarged view around the superconducting onset is shown in Fig. 5.7(b). The shielding fraction between 1.7 K and 3.0 K is enhanced, consistent with previous reports [69, 68]. The decrease of the volume fraction at lower temperatures is attributable to partial destruction of SC due to excess or inhomogeneity of distortion as well as to cracks in the sample [32].

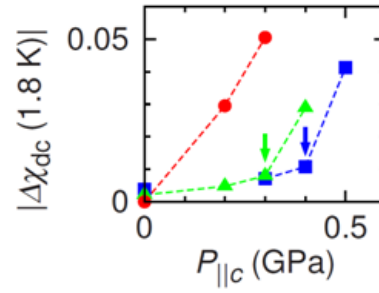
Next, we measured  $\chi_{AC}$  of the same sample at 0.5 GPa under several DC magnetic fields (Fig. 5.11). In the  $P_{\parallel c}$ -enhanced shielding region ( $0 < |\chi'| < 0.05$ ),  $\chi'(T)$  curves exhibit parallel shift to lower temperature with increasing field (Fig. 5.11(b)). This behavior is different from the field response of  $\chi_{AC}$  of the interfacial SC below  $P_{\parallel c}^*$ ; the interfacial SC does not exhibit parallel shift, as exemplified in the region of  $0 < |\chi'| < 0.6$  in Fig. 5.12 [31].

In order to illustrate the difference between the 3-K SC in  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  above  $P_{\parallel c}^*$  ( $P_{\parallel c}$ -originated SC) and that below  $P_{\parallel c}^*$  (interfacial SC), we present in Fig. 5.13 the  $H$ - $T$  phase diagram of these SCs. Figure 5.13 also contains the  $H$ - $T$  phase diagram of the bulk SC of  $\text{Sr}_2\text{RuO}_4$  at





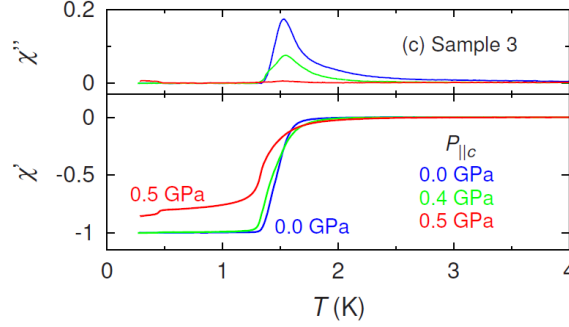
**Figure 5.7:** Zero-field temperature dependence of the real part of the AC susceptibility of  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  under  $P_{\parallel c} = 0$  and  $P_{\parallel c} = 0.5$  GPa: (a) the overall behavior and (b) an enlarged view around the superconducting onset. These data were obtained with  $\mu_0 H_{AC} = 2 \mu\text{T-rms}$  and  $f = 293$  Hz.



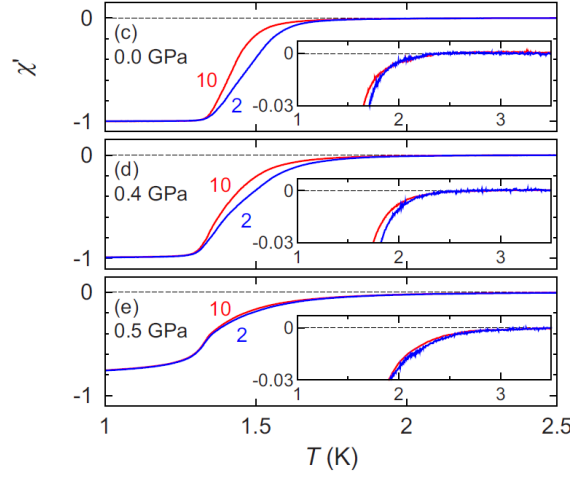
**Figure 5.8:** Out-of-plane UAP dependence of the DC shielding fraction of  $\text{Sr}_2\text{RuO}_4$  and  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  at 1.8 K and 2 mT [32]. Red and blue points represent the results of  $\text{Sr}_2\text{RuO}_4$  and  $\text{Sr}_2\text{RuO}_4\text{-Ru}$ , respectively. Green points represent the results of a  $\text{Sr}_2\text{RuO}_4$  crystal whose number of Ru inclusions is between that of  $\text{Sr}_2\text{RuO}_4$  and  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  eutectic. The arrows indicate critical pressure  $P^*$ .

$P_{\parallel c} = 0$  [86]. All the  $H$ - $T$  phase diagrams are determined by  $\chi_{AC}$ . We define superconducting transition temperature  $T_c$  in the following two ways:  $T_c^{\text{cross}}$  is defined as the temperature of the intersection of the extrapolations of the most rapidly changing part of  $\chi'$  and the normal state  $\chi'$  as shown in Fig. 5.11(b), and  $T_c^{\text{onset}}$  is defined as the temperature at which  $\chi'$  reaches  $-0.005$ . We used the steepest slope in  $0 < |\chi'| < 0.05$  to determine  $T_c^{\text{cross}}$  of  $P_{\parallel c}$ -originated SC, so that  $T_c^{\text{cross}}$  captures the characteristics of the  $P_{\parallel c}$ -originated SC. For the same reason, the steepest slope in  $0 < |\chi'| < 0.6$  is used for  $T_c^{\text{cross}}$  of the interfacial SC.

We have revealed that the  $H$ - $T$  curves of the  $P_{\parallel c}$ -originated SC and the interfacial SC are concave up with decreasing temperature, while the  $H$ - $T$  curves of the bulk SC of  $\text{Sr}_2\text{RuO}_4$  is convex up. We also clarified that the slopes of the  $H$ - $T$  curve of the  $P_{\parallel c}$ -originated SC are smaller than those of the interfacial SC resulting in a crossing at around 0.04 T. Note that these features



**Figure 5.9:** Temperature dependence of the AC susceptibility of  $\text{Sr}_2\text{RuO}_4$ -Ru under different  $P_{\parallel c}$ 's measured with  $\mu_0 H_{AC} = 2 \mu\text{T-rms}$  and 293 Hz [32]. Under 0.5 GPa, a jump is observed at 0.49 K both in the imaginary part  $\chi''$  and the real part  $\chi'$ .



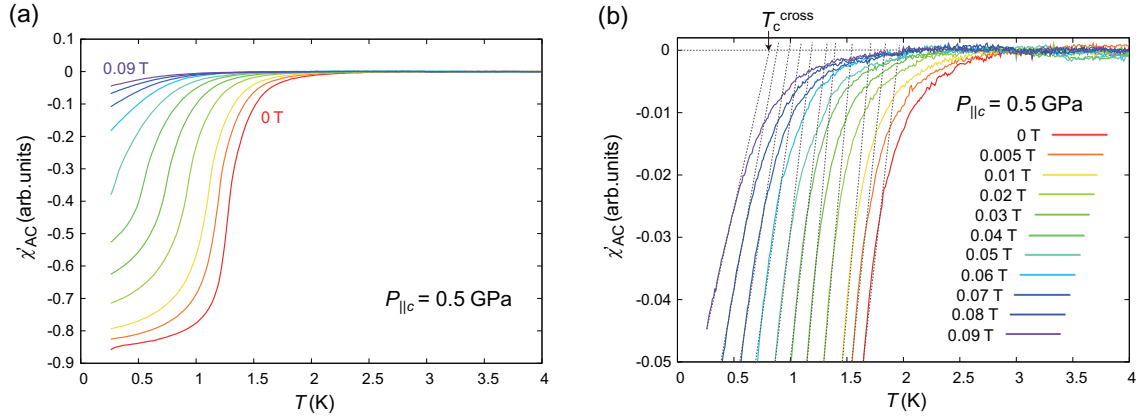
**Figure 5.10:** Temperature dependence of the real part of the AC susceptibility of  $\text{Sr}_2\text{RuO}_4$ -Ru under  $P_{\parallel c}$  for  $\mu_0 H_{AC}$  of 2 and 10  $\mu\text{T-rms}$  (293 Hz) [32]. The insets are enlarged views near the onset. The dashed lines mark  $\chi' = 0$ .

are not affected by the definitions of  $T_c$ .

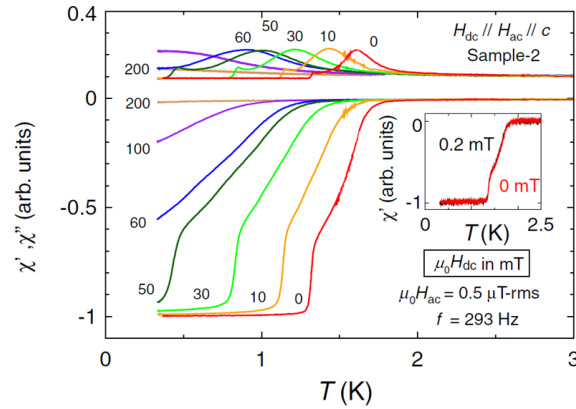
It is known that  $H$ - $T$  curves of granular superconductors exhibit concave-up behavior with decreasing temperature. A calculation of the effective critical field  $H_j$  of an assembly of intergranular Josephson junctions revealed that  $H_j$  exhibits  $1/T$  dependence in the vicinity of  $T_c(H=0)$  [87, 88]. In order to examine this possibility, we fitted the equation

$$\mu_0 H_j(T) = a \left( \frac{1}{T} - \frac{1}{T_c(H=0)} \right) \quad (5.1)$$

to the data in the range  $0.5T_c(H=0) < T < T_c(H=0)$ . The well-fitted results shown in Fig. 5.13 imply that both the  $P_{\parallel c}$ -originated SC and the interfacial SC have granular-like features. The difference in the slope of the  $H$ - $T$  curve is possibly related to certain changes in the spatial dis-



**Figure 5.11:** Temperature dependence of the real part of the AC susceptibility of  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  at  $P_{\parallel c} = 0.5$  GPa under different  $H_{DC}$ 's, measured with  $\mu_0 H_{AC} = 2 \mu\text{T-rms}$  and  $f = 293$  Hz: (a) the entire behavior and (b) an enlarged view of the  $P_{\parallel c}$ -enhanced shielding region.

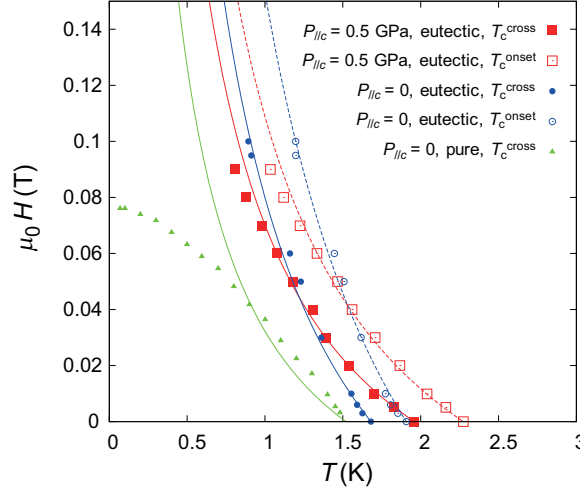


**Figure 5.12:** Temperature dependence of the AC susceptibility of  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  at  $P_{\parallel c} = 0$  GPa under different  $H_{DC}$ 's [31].

tribution of superconducting regions caused by pressure, such as an increase of intergranular distance or a change in the shape of superconducting grains themselves. We note, however, that possibilities of extrinsic origins such as cracks have not been excluded so far.

### 5.2.3 Resistivity under UAP

In order to obtain a hint to clarify the difference of the spatial distribution between  $P_{\parallel c}$ -originated 3-K SC and interfacial 3-K SC, we measured four-wire resistance of  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  under  $P_{\parallel c}$  (Fig. 5.14). At 0 and 0.3 GPa, only a broad transition is observed. In clear contrast, two transitions, a sharp superconducting transition at about 1.5 K and a broad superconducting transition below about 3 K are observed under 0.1 GPa. This peculiar pressure dependence sug-

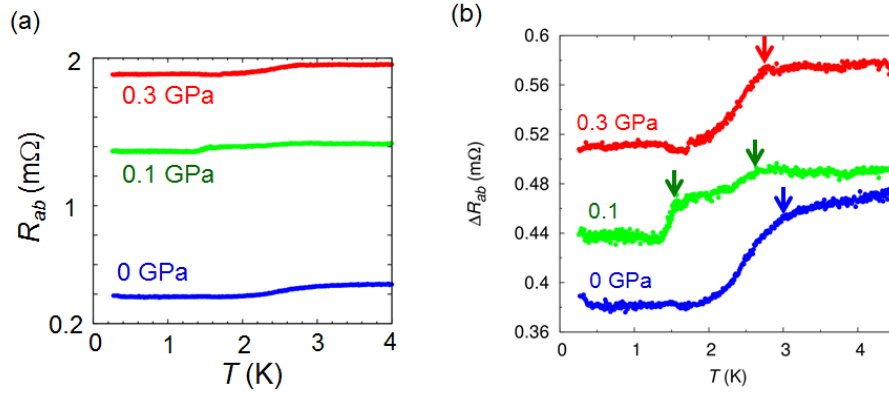


**Figure 5.13:** Comparison of  $H$ - $T$  phase diagrams for  $H_{\parallel c}$  based on two different  $T_c$  definitions:  $T_c^{\text{cross}}$  and  $T_c^{\text{onset}}$  (see text). Solid and dashed lines indicate fitting curves with Eq. (5.1) for a model of an assembly of intergranular Josephson junctions [87]. These curves reproduce the concave-up behavior of the  $P_{\parallel c}$ -originated SC above  $P_{\parallel c}^*$ , as well as that of the interfacial SC below  $P_{\parallel c}^*$ .

gests that the interfacial 3-K SC formed at 0 GPa is destroyed by  $P_{\parallel c}$  whereas the  $P_{\parallel c}$ -originated 3-K SC develops with  $P_{\parallel c}$ . At 0 GPa, a superconducting path is formed above the bulk  $T_c$  of about 1.5 K by the proximity effect of the interfacial 3-K SC. Under 0.1 GPa, the interfacial 3-K SC is substantially suppressed, while  $P_{\parallel c}$ -originated 3-K SC is not yet induced much; as a result, a superconducting path formation is not complete above the bulk  $T_c$  and the resistance suddenly drops at bulk  $T_c$ . At 0.3 GPa, a superconducting path is formed above the bulk  $T_c$  by the proximity effect of the  $P_{\parallel c}$ -originated 3-K SC. Non-zero resistance at the base temperature of 0.3 K, which is enough below the bulk  $T_c$  is attributable to micro cracks in the sample and indicates that the estimation of resistivity from resistance is difficult. Increase of resistance with pressure suggests that the number of cracks increases by pressure.

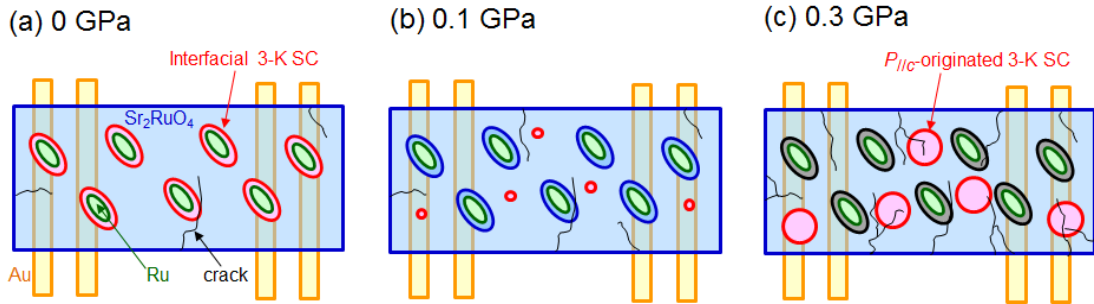
#### 5.2.4 Discussion

From the AC susceptibility and resistance measurements mentioned above, we clarified that the  $P_{\parallel c}$ -originated 3-K SC is granular-like similarly to the interfacial 3-K SC but their spatial distribution and out-of-plane UAP dependence are different. Based on these findings, we propose pressure evolution of the spatial distribution of SC in  $\text{Sr}_2\text{RuO}_4$ -Ru under  $P_{\parallel c}$  as shown in Fig. 5.15. At 0 GPa,  $\text{Sr}_2\text{RuO}_4$  regions around the interfaces between  $\text{Sr}_2\text{RuO}_4$  and Ru exhibit SC at 3 K because of the moderate lattice distortion, these superconducting regions expand on cooling because of the proximity effect, and one complete superconducting path is formed between V+ and V- wires above bulk  $T_c$  of ambient  $\text{Sr}_2\text{RuO}_4$  (1.5 K). Under 0.1 GPa,  $T_c$  of  $\text{Sr}_2\text{RuO}_4$  around the interfaces is suppressed because of the too much lattice distortion, and 3-K SC emerges in other regions in which moderate distortion is induced by  $P_{\parallel c}$ . The distance between the regions of this



**Figure 5.14:** Temperature dependence of in-plane resistance of  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  under out-of-plane UAP. (a) Raw data. (b)  $R(T)$  curves for 0.1 and 0.3 GPa are shifted. Arrows indicate an onset of superconducting transition. Non-zero resistance enough below the bulk  $T_c$  is attributable to the cracks of the sample and indicates that the estimation of resistivity from resistance is difficult.

newly-induced 3-K SC is so long that a complete superconducting path cannot be formed by proximity effect above 1.5 K. At 0.3 Pa, the region of the  $P_{\parallel c}$ -originated 3-K SC expands and more than one complete superconducting path is formed above 1.5 K, although  $T_c$  of interfacial  $\text{Sr}_2\text{RuO}_4$  is suppressed more. This description is consistent with the results of our previous paper [32].



**Figure 5.15:** Schematic figure of spatial distribution of superconductivity in  $\text{Sr}_2\text{RuO}_4\text{-Ru}$  under  $P_{\parallel c}$ . (a), (b), and (c) represents the case of 0, 0.1, and 0.3 GPa, respectively. A blue big rectangle denotes a sample of  $\text{Sr}_2\text{RuO}_4\text{-Ru}$ , green small ellipses denote Ru lamellae, and yellow thin rectangles denote Au wires attached for resistance measurement. Black lines denote micro cracks.  $T_c$  of red, blue, green, and black regions is about 3 K, 1.5 K (bulk  $T_c$  of ambient  $\text{Sr}_2\text{RuO}_4$ ), 0.49 K ( $T_c$  of Ru metal), and 0 K, respectively.



## Chapter 6

# Summary: Uniaxial pressure effects on $\text{Ca}_2\text{RuO}_4$ and $\text{Sr}_2\text{RuO}_4$

In this study, we have studied the electronic states of  $\text{Ca}_2\text{RuO}_4$  and  $\text{Sr}_2\text{RuO}_4$  under UAPs with three different pressure directions: two in-plane directions,  $[100]_T$  and  $[110]_T$ , and the out-of-plane direction,  $[001]_T$ , using the tetragonal notation.  $[100]_T$  and  $[110]_T$  direction are parallel and diagonal to the in-plane Ru-O bond of the  $\text{RuO}_6$  octahedra, respectively.

We succeeded in inducing the ferromagnetic metallic (FM-M) phase into  $\text{Ca}_2\text{RuO}_4$  by in-plane UAPs. The mechanism of this Mott transition is considered to be the same as that under hydrostatic pressure: the out-of-plane flattening distortion of  $\text{RuO}_6$  octahedra is released, and the  $xy$  and  $yz, zx$  bands of Ru  $4d$  electrons approach energetically and overlap. The smaller uniaxial critical pressure of the FM-M phase than hydrostatic one demonstrates the advantage of the in-plane uniaxial pressure for changing the electronic state of  $\text{Ca}_2\text{RuO}_4$ . We revealed highly anisotropic pressure-temperature phase diagrams among the AFM and FM phases. The possible absence of the B-AFM phase around the emergence of the FM-M phase under  $P_{\parallel[110]_T}$  suggests the pressure along the orthorhombic  $b$  axis induces an electronic state different from those under  $P_{\text{hydro}}$ .

We clarified that the insulating gap of  $\text{Ca}_2\text{RuO}_4$  is suppressed from 3000 K to 700 K under out-of-plane UAP. This result is surprising because  $P_{\parallel c}$  should increase the crystalline field splitting. This gap suppression is expected to be induced by the enhancement of the band width as a result of the release of rotation or/and tilting distortion of  $\text{RuO}_6$  octahedra.

The in-plane UAP effect on  $\text{Sr}_2\text{RuO}_4$  was also revealed to be significantly anisotropic; we clarified that  $P_{\parallel[100]_T}$  is more favorable for inducing 3-K superconductivity (SC) than  $P_{\parallel[110]_T}$ . These 3-K SCs under in-plane UAPs are considered to have the superconducting order parameter whose orbital part is one-component and to be induced mainly by elastic distortion.

For out-of-plane UAP effect on  $\text{Sr}_2\text{RuO}_4$ , we newly proposed the pressure dependence of the spatial distribution of 3-K SC in  $\text{Sr}_2\text{RuO}_4$ -Ru based on the behavior of AC susceptibility and resistivity.

To summarize, we have succeeded in inducing several phase transitions in  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  using UAPs. These results strongly demonstrate the effectiveness of UAP to control the electronic state of systems which have multiple degrees of freedom.

As a future investigation, UAP application to thin film will be interesting for  $\text{Ca}_2\text{RuO}_4$ , because thin film  $\text{Ca}_2\text{RuO}_4$  is already metallic under ambient pressure and a prominent effect like the emergence of SC is expected under in-plane UAP. For  $\text{Sr}_2\text{RuO}_4$ , in order to clarify the lattice distortion which induces 3-K SC under in-plane UAPs in detail, neutron measurements will be essential.



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