

Enhancement of Superconductivity of Sr_2RuO_4 to 3 K by Embedded Metallic Microdomains

Y. Maeno,^{1,2} T. Ando,¹ Y. Mori,¹ E. Ohmichi,¹ S. Ikeda,^{1,*} S. NishiZaki,¹ and S. Nakatsuji¹

¹*Department of Physics, Kyoto University, Kyoto 606-8502, Japan*

²*CREST, Japan Science and Technology Corporation, Japan*

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We have found that the quasi-two-dimensional superconductor Sr_2RuO_4 with the intrinsic transition temperature $T_c = 1.5$ K exhibits a remarkable enhancement in T_c up to 3 K, if lamellar microdomains of ruthenium metal are embedded. Measurements of the anisotropy in the upper critical fields indicate that the 3-K superconductivity is sustained essentially in the layered structure of Sr_2RuO_4 . We suggest that the enhanced interlayer coherence provided via metallic Ru plays a key role in the doubling of T_c . [S0031-9007(98)07463-8]

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Layered superconductor Sr_2RuO_4 [1] shares the same crystal structure as high- T_c superconductors of copper oxides. The superconductivity of Sr_2RuO_4 is a subject of active current investigations [2], particularly because the spin-triplet pairing has been suggested both theoretically [3,4] and experimentally [5–8], in contrast with the spin-singlet pairing of conventional superconductors as well as of the high- T_c copper oxides. The unconventional nature of the superconductivity is exemplified by the extreme sensitivity of the transition temperature T_c to disorder introduced by nonmagnetic impurities [9]. It was also deduced from that experiment that the impurity-free intrinsic T_c should be about 1.5 K. In fact, after improving the quality of the single crystals, we have now achieved a very sharp superconducting transition at 1.5 K. Curiously, there had been an indication of another diamagnetic transition at substantially higher temperatures [5].

In the present study, we have for the first time established that this intriguing transition is in fact due to superconductivity; moreover, we have clarified the material origin of the higher- T_c phase. Here we report a remarkable enhancement of T_c by a factor of about 2 in a two-phase composite structure made of a single-crystalline matrix of Sr_2RuO_4 in which microdomains of ruthenium metal are embedded. We will also present the anisotropic field-temperature phase diagram of this new superconducting phase. On the basis of the observed enhancement in the interlayer coherence lengths, we suggest that such a dramatic increase in T_c quite possibly originates from the quasi-two-dimensional character of Sr_2RuO_4 .

Single crystals of Sr_2RuO_4 were grown by a floating-zone technique with Ru self-flux using a commercial image furnace equipped with double-elliptical mirrors [10]. Intriguingly, depending systematically upon the composition of the ceramic feed rod and the speed of the crystal growth, the superconducting transitions are either very sharp at 1.0–1.5 K (“the 1.5-K phase”) or rather broad extending up to about 3 K (“the 3-K phase”). The 3-K phase is consistently obtained for higher Ru content of the feed rod and/or faster growth rate, both of which increase the Ru concentration in the melting

zone. For a typical 3-K crystal, the ratio of Sr to Ru in the feed rod was 2 to 1.2 and the crystal growth was performed at the rate of 23 mm/h under a gas mixture of 10% oxygen in 90% argon with the total pressure of 0.2 MPa. We have so far reproduced the occurrence of the 3-K superconductivity in more than ten different growth batches.

A crystalline rod from these batches, typically 5 mm in diameter, consists of a clean surface sheath of Sr_2RuO_4 with a thickness of about 0.5 mm and the core region of the two-phase composite structure of Sr_2RuO_4 and Ru metal. Displayed in Fig. 1 are the optical microscopy pictures of the polished surfaces of a sample of the 3-K phase, taken from the central region. The pictures show lamellar precipitation of Ru metal embedded in the primary phase of Sr_2RuO_4 , typical of a eutectic solidification [11]. In this process, the solidification near the surface occurs from the liquid with the Ru concentration less than that of the eutectic point; only pure Sr_2RuO_4 should solidify as the primary crystal, leaving Ru-rich liquid inside. Active evaporation of Ru from the molten surface also helps to sustain the radial concentration gradient. When the liquid inside reaches the eutectic concentration, the eutectic solidification of Sr_2RuO_4 and Ru starts and persists to the center. In this two-phase composite region, the volume fraction of the Ru metal should be uniquely determined by the composition of the eutectic point. The thickness of a Ru platelet is about 1 μm , the length and depth of each segment are both of the order of 1 to 10 μm , and the separation between the stripes is of the order of 10 μm . Such an ordered pattern of stripes, known to form in the direction of the crystal growth in a lamellar eutectic, persists more than 5 mm along the stripes for the crystal shown in Fig. 1. The direction along the stripes with respect to the crystalline axes of Sr_2RuO_4 , however, is not unique and often varies within a single-domain Sr_2RuO_4 . In fact, the pictures of Figs. 1(a) and 1(b) represent (100) and (010) planes, respectively, of the identical crystalline block.

A similar eutectic structure with needlelike insulating Cu_2O has been reported in the high- T_c superconductor

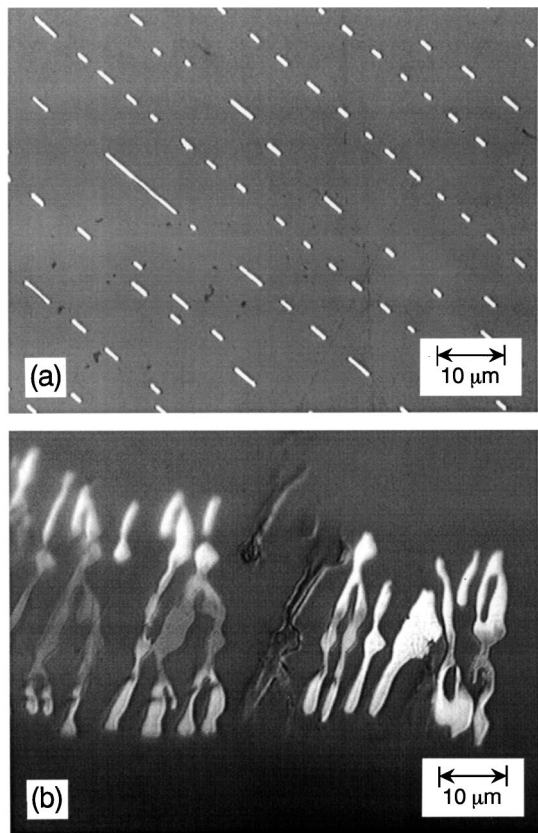


FIG. 1. Optical microscopy pictures of polished surfaces of a Sr_2RuO_4 crystal, showing a lamellar pattern typical of eutectic solidification. The bright regions are Ru metal and the dark regions are Sr_2RuO_4 . The pictures represent the cross sections (a) perpendicular and (b) parallel to the planes of the Ru lamellae. The interlayer c direction of Sr_2RuO_4 is parallel to the scale bars in these pictures.

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [12]. In that system, however, no enhancement in T_c was observed. For the Sr_2RuO_4 system we have confirmed by x-ray diffraction that the lamellae are made of Ru metal, not RuO_2 .

Within the resolution of 0.1% for the powder x-ray diffraction, the lattice parameters of Sr_2RuO_4 are the same for regions both with and without the stripes. Furthermore, the electron-probe microanalysis (EPMA) revealed that the primary phase of the stripe region has the same stoichiometry as the undecorated Sr_2RuO_4 within the precision of 0.3% per element for Sr and Ru [13]. Thus, there is no evidence that the Sr_2RuO_4 contained in the two-phase composite region is different from the pure Sr_2RuO_4 in any way. Although not detectable by the x-ray diffraction of the crushed crystals, a very small amount of SrRuO_3 (a ferromagnetic metal with the Curie temperature of 160 K) is present mainly on the cleavage surface of Sr_2RuO_4 . Since SrRuO_3 is found in both the 1.5-K and 3-K superconductors and it is estimated from the magnetization measurements that the level of the inclusion is too low (less than 400 ppm) to account for the observed superconductivity, we conclude that SrRuO_3 does not contribute to the enhancement in T_c .

Figures 2(a) and 2(b) compare the diamagnetic transitions of the 1.5-K and 3-K phases. The curves with smaller symbols are for a crystal free from the stripe regions, showing a sharp superconducting transition with the onset at 1.45 K. The T_c of this 1.5-K phase is known to depend little on different oxygen treatment [14]; it is not possible to increase T_c beyond 1.5 K by simply adjusting the stoichiometry of Sr_2RuO_4 . In contrast, the crystal from which pictures of Fig. 1 were taken exhibits a broad diamagnetic transition starting as high as 3 K (curves with larger symbols). It should be noted that, unlike the 1.5-K phase, we have never observed a sharp transition for the 3-K superconductivity. In particular, a large dissipative component χ'' of the complex susceptibility always persists in a wide temperature range. Nevertheless, the large diamagnetic shielding in χ' guarantees that at least a large surface fraction of the sample participates in the enhanced superconductivity. The diamagnetic transition is confirmed also by dc susceptibility measurements using a SQUID magnetometer. After careful examinations on many crystals, we have established a firm correlation between the presence of

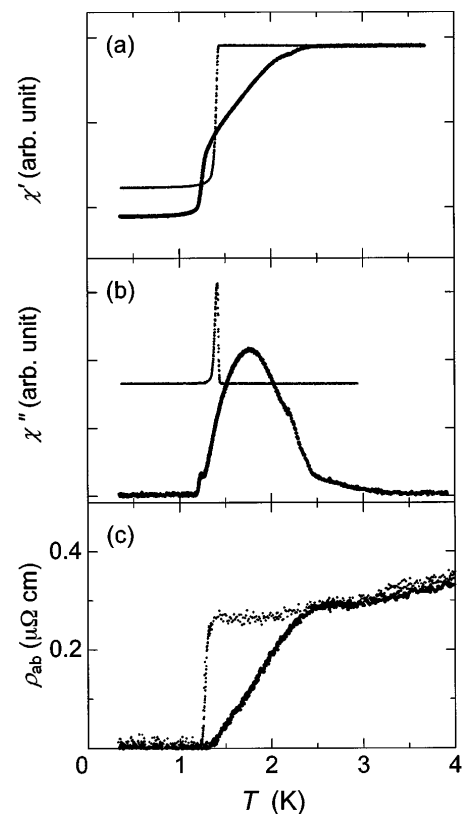


FIG. 2. (a) The in-phase and (b) out-of-phase components of the ac susceptibility, as well as (c) the in-plane resistivity ρ_{ab} . The curves with smaller symbols are for crystals of Sr_2RuO_4 without Ru lamellae, showing sharp superconducting transitions at 1.4–1.5 K. The curves with larger symbols are for crystals containing the eutectic structure of Sr_2RuO_4 and Ru, indicating broad transitions of the 3-K superconductivity. For the susceptibility measurements, the ac field of 0.1 mT at 1000 Hz was applied parallel to the RuO_2 layer.

the Ru lamellae embedded in Sr_2RuO_4 and the occurrence of the 3-K superconductivity.

The resistive transitions in the in-plane resistivity ρ_{ab} are represented in Fig. 2(c). The two curves are for samples taken from the identical crystalline rod. The sample cut from the sheath region without the stripes (smaller symbols) exhibits a sharp transition with the onset at 1.4 K. In contrast, the sample cut from the stripe region exhibits the onset T_c at 2.5 K. Nevertheless, zero resistivity was not obtained down to 1.3 K. In both cases, the normal-state resistivities remain nearly identical up to room temperature and the residual resistivities correspond to the mean free path $\ell = 0.4 \mu\text{m}$.

An important observation for the 3-K phase is the anisotropy in the upper critical fields. Figure 3 represents the variation of the out-of-plane resistivity ρ_c with the direction of the magnetic field. Since this curve was obtained for the field $\mu_0 H = 3 \text{ T}$ and temperature $T = 1.5 \text{ K}$, the 1.5-K superconductivity, intrinsic to the undecorated Sr_2RuO_4 , would be completely suppressed (see Fig. 4 below). The sharp dips in ρ_c for the field direction precisely parallel to the RuO_2 plane reflect a strong anisotropy of the 3-K superconductivity. Combining this with the observation of the large diamagnetic signals, we conclude that the 3-K phase is characteristic of a layered superconductivity sustained essentially in the primary phase Sr_2RuO_4 , rather than in the Ru metal itself or in an unidentified impurity phase.

We have further determined the temperature dependence of the upper critical fields $\mu_0 H_{c2}$ of another typical 3-K sample as shown in Fig. 4. (The crystal of the 3-K phase used for Fig. 3 has a slightly higher T_c than the one used for Fig. 4.) For comparison, curves for the 1.5-K phase are also shown. Here, H_{c2} is defined as the midpoint of the resistive transition. From the smooth extrapolation

of the curves to $T = 0 \text{ K}$ [$\mu_0 H_{c2\parallel c}(0) = \Phi_0 / \{2\pi \xi_{ab}(0)^2\}$ and $\mu_0 H_{c2\parallel ab}(0) = \Phi_0 / \{2\pi \xi_{ab}(0) \xi_c(0)\}$, where Φ_0 is the flux quantum], we obtain the coherence length $\xi_{ab}(0) = 18 \text{ nm}$ and $\xi_c(0) = 5.0 \text{ nm}$ for the 3-K phase, compared with $\xi_{ab}(0) = 66 \text{ nm}$ and $\xi_c(0) = 3.3 \text{ nm}$ for the 1.5-K phase [15]. It should be noted that the interlayer coherence length ξ_c , expected to scale as T_c^{-1} provided that the anisotropy and the Fermi velocity remain unchanged, is actually longer for the 3-K phase despite higher T_c . This results in the substantial reduction in the anisotropy of superconductivity: $\xi_{ab}(0)/\xi_c(0) = 3.6$ for the 3-K phase, as compared with 20 for the 1.5-K phase.

We have experimentally established that T_c of Sr_2RuO_4 is enhanced by a factor of about 2 in the presence of lamellar microdomains of metallic Ru, formed by eutectic solidification. The enhanced superconductivity of Sr_2RuO_4 most probably originates in the interface region of the Ru lamellae because this is where a major modification of the electronic structure is expected. Let us now discuss the spatial development of superconductivity of such a system on cooling. As the temperature is lowered below 3 K, the gap function in the surface sheaths of the Ru lamellae will penetrate into the bulk of both Sr_2RuO_4 and Ru. The normal coherence length is given by $\xi_n = (\hbar v_F l / 6\pi k_B T)^{1/2} \{1 + 2/\ln(T/T_{cn})\}$ [16] with $T_{cn}(\text{Sr}_2\text{RuO}_4) = 1.5 \text{ K}$ and $T_{cn}(\text{Ru}) = 0.49 \text{ K}$. With the Fermi velocity v_F given from Ref. [17], we obtain $\xi_n(\text{Sr}_2\text{RuO}_4) = 0.7 \mu\text{m}$ at 2 K. As ξ_n diverges logarithmically towards 1.5 K, the percolation of the interconnecting current paths due to the proximity effect proceeds on further cooling until the entire Sr_2RuO_4 becomes superconducting. The observation of the large dissipation in the complex susceptibility indeed supports this picture that the superconducting sheaths around Ru

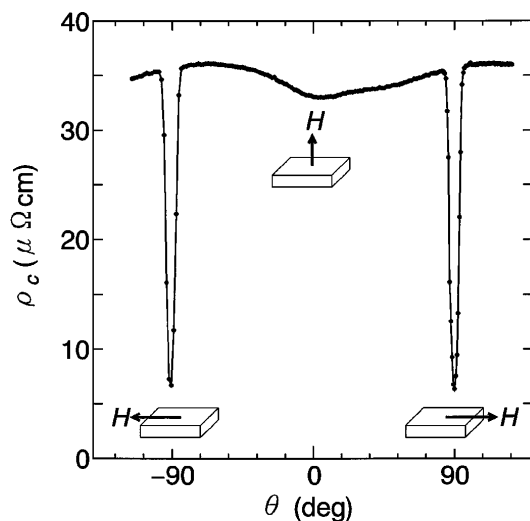


FIG. 3. The variation of the out-of-plane resistivity ρ_c of a 3-K crystal with the direction of the magnetic field H for $\mu_0 H = 3 \text{ T}$ and $T = 1.5 \text{ K}$. The angle between the field direction and the c axis of Sr_2RuO_4 is denoted as θ .

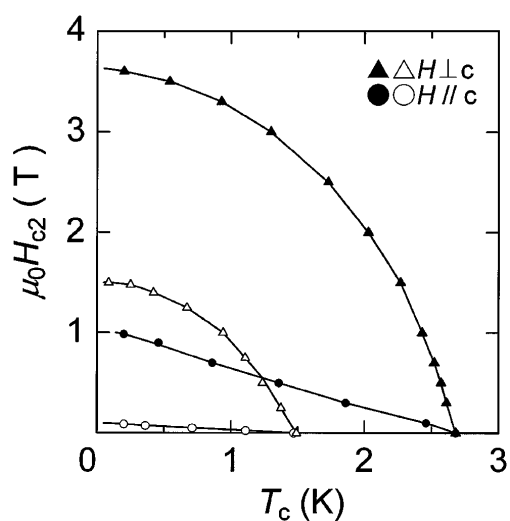


FIG. 4. Temperature dependence of the anisotropic upper critical fields for the 3-K phase (solid symbols), determined from the resistivity midpoint in ρ_c . For comparison, the data for the 1.5-K phase (open symbols) are also presented.

lamellae are only weakly connected by the Josephson coupling. Since $\xi_n(\text{Ru})$ becomes comparable to the thickness of the lamella at 1 K, the proximity effect is expected to be substantial also in the Ru metal. In fact, we have never detected any sign of additional transition attributable to conventional superconductivity of Ru metal.

Enhancement of superconductivity up to 2.7 K in the eutectic formed by Ir ($T_c = 0.10$ K) with a small amount of YIr₂ was reported by Matthias *et al.* [18]. In that system a small lattice mismatch between Ir and YIr₂ leads to the strain-induced lattice softening [19], believed to be responsible for the extraordinary enhancement in T_c . In the present system, however, a preliminary investigation by microscopic Raman scattering indicated that there are no spatial variations in the phonon frequencies [20]. We believe it unlikely that the same lattice-softening mechanism holds for the enhancement in T_c in the Sr₂RuO₄-Ru eutectic.

The marked reduction in the anisotropy of the coherence lengths indicates that the enhanced interlayer coupling is the major difference in the electronic states of the 3-K phase. For the 1.5-K phase, the coupling between the conducting RuO₂ layers within Sr₂RuO₄ is marginally strong so that metallic transport is three dimensional only at low temperatures; dimensional crossover occurs at 130 K to two-dimensional metal with nonmetallic ρ_c at higher temperatures [2,21]. We therefore speculate that the enhanced interlayer coupling in the presence of the Ru lamellae is mainly acting in favor of enhanced superconductivity. It is worth investigating whether similar enhancement of T_c may occur in other quasi-two-dimensional superconductors. Theoretical investigations are also needed to examine how the suppression of superconducting fluctuations in the quasi-two-dimensional superconductor by enhanced interlayer coherence may lead to the increase in T_c .

In addition to the remarkable enhancement in T_c , the present system provides a unique configuration in the study of superconductivity: the natural insertion of a metallic island of μm width enclosed by a single crystalline matrix of the quasi-two-dimensional, unconventional superconductor. This configuration may prove useful in clarifying the pairing symmetry of Sr₂RuO₄ [22–24], as well as the nature of trapped fluxoid and the characteristics of the electron transmission and reflection at the metal-superconductor interface [25,26].

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*Present address: Venture Business Laboratory, Kyoto University, Kyoto 606-8501, Japan.

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