Higher-$T_c$ superconducting phase in Sr$_2$RuO$_4$ induced by uniaxial pressure

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We have investigated uniaxial pressure effect on superconductivity of pure Sr$_2$RuO$_4$, whose intrinsic superconducting transition temperature $T_c$ is 1.5 K. It was revealed that a very low uniaxial pressure along the $c$ axis, only 0.2 GPa, induces superconductivity with the onset $T_c$ above 3 K. The present results indicate that pure Sr$_2$RuO$_4$ has two superconducting phases with $T_c = 1.5$ K and with varying $T_c$ up to 3.2 K. The latter phase exhibits unusual features and is attributable to anisotropic crystal distortions beyond the elastic limit.

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The application of uniaxial pressure (UP) can be a powerful tool to control superconductivity (SC) as well as the electronic structure through anisotropic distortions in the crystal lattice. The layered perovskite ruthenate Sr$_2$RuO$_4$, for which convincing evidence has been accumulated in favor of spin-triplet SC, has an undistorted tetragonal structure. It has been experimentally and theoretically revealed that the electronic states of Sr$_2$RuO$_4$ and its related materials are expected to drastically change with an anisotropic distortion. Thus, Sr$_2$RuO$_4$ is one of the materials expected to have a prominent UP effect on its SC.

The intrinsic superconducting transition temperature $T_c$ of Sr$_2$RuO$_4$ was revealed to be 1.5 K for crystals with the best quality. Hydrostatic pressure$^{11,15}$, as well as a small amount of impurities or defects,$^{16,17}$, is known to suppress $T_c$. In contrast, the enhancement of $T_c$ was reported in the Sr$_2$RuO$_4$-Ru eutectic system (the onset $T_c \sim 3-3.5$ K$^{28,29}$ and a submicron Sr$_2$RuO$_4$ single crystal (the onset $T_c \sim 1.8$ K$^{30}$). At present, the mechanisms of the enhancement of $T_c$ remain unresolved. In the eutectic system, lamellae of Ru metal ($T_c = 0.49$ K) with approximate dimensions of $10 \times 10 \times 1 \mu$m$^3$ are embedded with a stripe pattern. It has been established that the 3-K SC with a tiny volume fraction occurs in the Sr$_2$RuO$_4$ region in the vicinity of the Sr$_2$RuO$_4$-Ru interface$^{22-24}$. One possible scenario is that anisotropic distortions in Sr$_2$RuO$_4$, e.g., induced by the presence of Ru, enhance its $T_c$ significantly.$^{19}$

Although UP experiments on Sr$_2$RuO$_4$ have been reported, the change in $T_c$ with UP along the interlayer $c$ and in-plane $a$ axes, $P_{c//}$ and $P_{a//}$, in the elastic limit was predicted from the ultrasonic experiments combined with the Ehrenfest relations$^{24}$,

$$\frac{1}{T_c}(dT_c/dP_{c//}) = (0.7 \pm 0.2) \text{ GPa}^{-1} \quad \text{and} \quad \frac{1}{T_c}(dT_c/dP_{a//}) = -(0.85 \pm 0.05) \text{ GPa}^{-1}.$$

Qualitatively the same UP effects were theoretically predicted based on the change in the density of states at the Fermi level in the band mainly responsible for the SC$^{25}$. On the basis of these predictions, $T_c$ is expected to increase under $P_{c//}$.

Recently, the UP effects on interfacial 3-K SC in the eutectic system have been investigated$^{26,27}$. It was revealed that the volume fraction of the 3-K SC drastically increases by the application of UP in any directions while its onset $T_c$ is almost invariant. These findings urge the UP effect on pure Sr$_2$RuO$_4$ to be investigated as well.

In this letter, we report the effect of $P_{c//}$ on pure Sr$_2$RuO$_4$. We revealed that the onset $T_c$ of pure Sr$_2$RuO$_4$ is immediately enhanced to 3.2 K by $P_{c//}$ of only 0.2 GPa. By comparing the effects of $P_{c//}$ between pure Sr$_2$RuO$_4$ and Sr$_2$RuO$_4$-Ru eutectic crystals, it was newly revealed that the higher-$T_c$ SC in the pure Sr$_2$RuO$_4$ sample was not induced by the development of interfacial 3-K SC originating from a tiny amount of Ru inclusions, but is indeed an intrinsic property of pure Sr$_2$RuO$_4$.

Single crystals used in this study were grown by a floating zone method with Ru self-flux$^{28}$. Because RuO$_2$ evaporates from the surface of melt during the growth, excess Ru tends to be left in the center of the melt. Therefore, most of single crystalline rods with the best $T_c$ (no defect at the Ru site) contain Sr$_2$RuO$_4$-Ru eutectic solidification in its core region and pure Sr$_2$RuO$_4$ only around the thin surface part$^{31}$. This feature, as well as the tendency to cleave easily, makes it difficult to obtain a large crystal which only contains Sr$_2$RuO$_4$. In particular, it is extremely difficult to prepare a pure sample suitable for the application of $P_{c//}$. For the application of $P_{c//}$, we succeeded in preparing one large sample of practically pure Sr$_2$RuO$_4$ with almost no Ru inclusions (Sample 1) from a crystalline rod with relatively lower $T_c$ (small amount of defects at the Ru site). The dimensions of Sample 1 are $1.5 \times 1.4 \text{ mm}^2$ in the $ab$ plane and 0.22 mm along the $c$ axis. In order to reduce the amount of lattice defects and oxygen deficiencies as well as the number of Ru inclusions, Sample 1 was annealed in oxygen at 1 atm and $1050 \text{ °C}$ for a week. Then, Sample 1 exhibits a very sharp transition at 1.34 K, as determined from the ac susceptibility.

In addition to Sample 1, two Sr$_2$RuO$_4$ samples containing a small amount of Ru inclusions and five Sr$_2$RuO$_4$-Ru eutectic samples have been used to investigate the $P_{c//}$ effect. Representing those samples, magnetic susceptibility results for a Sr$_2$RuO$_4$ sample with a small amount of Ru inclusions (Sample 2), and a Sr$_2$RuO$_4$-Ru eutectic sample (Sample 3) are compared with the results for Sample 1 in this letter. The approximate dimensions of Samples 2 and 3 were $1.5 \times 1.5 \text{ mm}^2$ in the $ab$ plane and 0.3 mm along the $c$ axis. The amount of Ru inclusions was identified from the polarized-light optical microscope images of the $ab$ surfaces, as exemplified in Figs. 1(a)-1(c). The number density of Ru inclusions on the $ab$ surfaces for Sample 1 is less than $3 \text{ mm}^{-2}$ and about $40 \text{ mm}^{-2}$ after and before annealing, respectively, while the number densities are about $200 \text{ mm}^{-2}$ for Sample 2 and about $400 \text{ mm}^{-2}$.
for Sample 3.

UP was applied parallel to the shortest dimension along the c axis using a piston-cylinder type pressure cell made of Cu-Be alloy with a cylindrical outer body made of hard plastic (polybenzimidazole). The room-temperature pressure value was confirmed to be in a reasonable agreement with low-temperature pressure value determined by superconducting transitions of tin and lead\(^{20}\). The side surfaces of the samples were covered with thin epoxy (Emerson-Cuming, Stycast 1266) to prevent a breakdown of the sample, as described in Ref\(^{20}\). The magnetization was measured down to 1.8 K with an applied dc magnetic field \(\mu_0H_{dc}\) of 2 mT using a SQUID magnetometer (Quantum Design, model MPMS). The background magnetization of the pressure cell was subtracted. The ac susceptibility \(\chi_{ac} = \chi' - i\chi''\) was measured down to 0.3 K by a mutual-inductance technique using a lock-in amplifier (LIA) with a \(^{3}\)He cryostat (Oxford Instruments, model Heliox VL). All \(\chi_{ac}\) data presented here were taken at 293 Hz. The values of \(\chi_{ac}\) were obtained from the relation \(\chi_{ac} = iC_1V_{LIA}/H_{ac} + C_2\), where \(V_{LIA} = V_x + iV_y\) is the read-out voltage of LIA and \(H_{ac}\) is the magnitude of the applied ac magnetic field. The values of \(C_1\) and \(C_2\) were chosen so that \(\chi'\) at 4 K = 0 and \(\chi'\) at 0.3 K = −1 at 0 GPa for each sample; thus \(|\chi'|\) corresponds to the ac shielding fraction. For the \(\chi_{ac}\) curves under \(P_{fc}\), \(C_1\) and \(C_2\) determined at 0 GPa were used.

Figure 2(a) represents the temperature dependence of the superconducting dc susceptibility \(\Delta \chi_{dc} = \Delta m/\mu_0H_{dc}\) for each sample at 0 GPa, where \(\Delta m\) is the observed magnetization change associated with the superconducting transition divided by the sample volume. Here, the ideal value for the full Meissner state without the demagnetization correction corresponds to \(\Delta \chi_{dc} = -1\); thus \(|\Delta \chi_{dc}|\) is equal to the dc shielding fraction. At 0 GPa, there is no sign of a dc shielding signal for Sample 1 above 1.8 K, confirming that it does not contain any eutectic part. A weak shielding signal with the onset \(T_c\) slightly above 3 K was observed in Samples 2 and 3, consistent with the recent study\(^{20}\). At 0 GPa, the dc shielding fraction at 1.8 K is clearly larger in Sample 3, containing more Ru inclusions.

Surprisingly, even at relatively low \(P_{fc}\) of 0.2 GPa, SC with the onset \(T_c\) of 3.2 K, at which \(\Delta \chi_{dc}\) deviates from zero (see Fig. 2(c)), is induced in Sample 1. As shown in Fig. 2(b), the shielding fraction in the field-cooling (FC) process is nearly half of that in the zero-field-cooling (ZFC) process at \(P_{fc} = 0.3\) GPa. The relatively large FC shielding fraction indicates that the screening area does not contain normal-state regions largely. Figure 2(d) demonstrates the variation of the dc shielding fraction at 1.8 K, \(|\Delta \chi_{dc}(1.8\text{ K})|\), under \(P_{fc}\) for each sample. Unexpectedly, as the amount of Ru inclusions becomes larger, the enhancement of the shielding fraction by \(P_{fc}\) becomes smaller; the order of increasing shielding fractions among different samples is reversed between Figs. 2(a) and 2(b). Below 0.3 GPa, the slope of \(|\Delta \chi_{dc}(1.8\text{ K})|\) versus \(P_{fc}\) for Sample 1 is much greater than those for Samples 2 and 3. These results strongly indicate that the presence of Ru inclusions does not play a positive role in the rapid enhancement of the screening area.

We have also measured the temperature dependence of \(\chi_{ac}\) using the identical samples under \(P_{fc}\) with \(\mu_0H_{dc}\) of 2 \(\mu\)T. These \(\chi_{ac}\) measurements cover low temperatures down to 0.3 K and enable us to observe the full Meissner state. As presented in Fig. 2(a), Sample 1 exhibits a very sharp transition and no dissipation \(\chi''\) above 1.5 K at 0 GPa. This sharp transition again supports that Sample 1 can be treated as a pure Sr$_2$RuO$_4$. By contrast, as shown in Figs. 2(b) and 2(c), broad transitions, typical of the eutectic system\(^{20}\), were observed above 1.5 K for Samples 2 and 3 at 0 GPa.

**FIG. 1:** Polarized-light optical microscope images of the ab planes of (a) Samples 1, (b) 2, and (c) 3. The dark and bright parts correspond to Sr$_2$RuO$_4$ and Ru, respectively.

**FIG. 2:** (Color Online) Temperature dependence of the dc susceptibility \(\Delta \chi_{dc}\) of Samples 1 (circles), 2 (triangles), and 3 (squares) measured with 2 mT at (a) \(P_{fc} = 0\) and (b) 0.3 GPa. The applied dc field has been corrected for the remanent field in the sample space. Open and closed symbols indicate data taken in the FC and ZFC processes, respectively (Samples 1 and 3 only). Note the vertical scale changes between (a) and (b). (c) Enlarged view near the onset for Sample 1 at different \(P_{fc}\). (d) Dependence of the dc shielding fraction on \(P_{fc}\) at 1.8 K. The arrows indicate critical pressure \(P_{c*}\).
By the application of $P_{lc}$, a broad signal of ac shielding with the onset $T_c$ of up to 3.2 K grows in all samples; the enhancement of the ac shielding fraction was clearly observed above 1.5 K even for pure Sr$_2$RuO$_4$. These results are both qualitatively and quantitatively consistent with the results of the dc magnetization measurements in Fig. 2. By contrast, at low temperatures, the ac shielding signal is reduced in magnitude and becomes broader with increasing $P_{lc}$. It should also be noted that the primary 1.5-K SC part in Samples 1 and 2 is sustained with little change of its $T_c$ under $P_{lc}$. These features imply that a region with widely distributed $T_c$ becomes somewhat smaller after removing uniaxial pressure (e.g. Fig. 4(a) of Ref. 2), and that of SC in the eutectic system is qualitatively the same. As shown in Figs. 4(a) and 4(b), the ac shielding fraction in pure Sr$_2$RuO$_4$ was not affected by $H_{ac}$ at any $P_{lc}$ investigated. In contrast, the ac shielding fraction in Sample 3 was sensitively suppressed by $H_{ac}$ of as small as 10 μT-rms below $P_{lc} = 0.4$ GPa (Figs. 4(c) and 4(d)). This “weak” SC in the eutectic system is attributed to the formation of a Josephson network interfacial 3-K SC occurring near the Sr$_2$RuO$_4$-Ru interface penetrates into the normal-state Sr$_2$RuO$_4$ region due to the proximity effect and forms Josephson-type weak links among the Ru lamellae. In this case, because of the small critical current in the Josephson network area, the ac field penetration is expected to become significantly deeper with increasing $H_{ac}$. Therefore the spatial distribution of superconducting regions is different between the two systems.

Interestingly, as shown in Fig. 4(e), the $H_{ac}$ dependence almost disappears in Sample 3 above $P_{lc}$. This disappearance, in conjunction with the observation in Figs. 2(d) and 3(c), can be consistently understood if the nature of the higher-$T_c$ SC induced by UP in pure Sr$_2$RuO$_4$ and that of SC in the eutectic crystal above $P_{lc}$ is qualitatively the same.

From the present study, it is most likely that UP-induced higher-$T_c$ SC is an intrinsic property of Sr$_2$RuO$_4$, because the enhancement of the higher-$T_c$ SC by $P_{lc}$ is more striking in samples with smaller amount of Ru inclusions. Let us here discuss possible mechanisms of the occurrence of
the higher-$T_c$ SC. While hydrostatic pressure destroys SC of Sr$_2$RuO$_4$, UP induces SC with $T_c$ above 3 K. These facts indicate that anisotropic distortions caused by UP in the crystal structure play essential roles in enhancing $T_c$. Nevertheless, the present results are essentially different from the UP effect predicted from the ultrasonic experiments, $dT_c/dP_{\parallel} \sim 1 \text{ K/GPa}$. The observed onset $T_c$ increases up to 3.2 K even at $P_{\parallel}$ of as small as 0.2 GPa but does not exceed 3.2 K at higher $P_{\parallel}$ (see Fig. 2(c)). This disagreement with the hydrostatic pressure effect and the elastic-limit expectation suggests that a qualitative change predicted from the ultrasonic experiments, different from the elastic limit deduced from the Ehrenfest relation for Sr$_2$RuO$_4$. We revealed that the dc shielding fraction associated with the UP-induced higher-$T_c$ SC and the amount of Ru inclusions are anticorrelated. This fact clearly indicates that the higher-$T_c$ SC is not associated with the presence of Ru inclusions.

To summarize, we present the first report on the UP effect on Sr$_2$RuO$_4$. We found an remarkable increase of the onset $T_c$ from 1.5 K to 3.2 K induced by $P_{\parallel}$ below 0.2 GPa. This strong enhancement of $T_c$ cannot be explained by the effect of $P_{\parallel}$ in the elastic limit deduced from the Ehrenfest relation for Sr$_2$RuO$_4$. We revealed that the dc shielding fraction associated with the UP-induced higher-$T_c$ SC and the amount of Ru inclusions are anticorrelated. This fact clearly indicates that the higher-$T_c$ SC is not associated with the presence of Ru inclusions.

There remain some important issues to be clarified. Although the spatial distribution of superconducting regions is revealed to be different between the UP-induced higher-$T_c$ SC and the eutectic 3-K SC, the values of their $T_c$’s are surprisingly similar. It should be clarified whether or not the origin of the enhanced $T_c$ is similar between UP-induced SC and the eutectic SC. Another important issue is to resolve the discrepancy between the results of previous hydrostatic-pressure study and of the present UP experiments. Additional experiments under in-plane UP and the crystal-structure analysis under UP may provide important clues, although it is technically difficult at present to perform such experiments.

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