Suppression of superconductivity in Sr_2RuO_4 caused by defects

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We have investigated depairing effects in Sr_2RuO_4, the unconventional superconductor in the layered perovskite structure. We prepared crystals of Sr_2RuO_4 with very low levels of impurity elements, and systematically controled their superconducting transition temperature T_c ranging from 1.5 to 0.6 K by adjustments of crystal growth conditions. The dependence of T_c on the residual resistivity ρ_0 in these crystals suggests that the defects are strong pair breakers, in addition to impurities. We further characterized the effects of pair breaking in this unconventional superconductor. We found that the in-plane coherence length $\xi_{ab}(0)$ evaluated from $H_{c2}(T)$ is inversely proportional to T_c, and decreases with increasing mean free path l; the latter behavior is opposite to that of conventional superconductors. In addition, we examined the temperature dependence of $H_{c2\parallel c}$ which substantially deviates from the BCS theory and even from a recent theory of a *p*-wave superconductor. [S0163-1829(99)11225-6]

I. INTRODUCTION

The superconductor Sr_2RuO_4 (Ref. 1) shares the same layered perovskite structure as the La-based cuprate superconductors. More and more experiments[2–5] confirm that Sr_2RuO_4 is a non-*s*-wave superconductor and is most probably a *p*-wave superconductor. One of the most powerful pieces of evidence is the nonmagnetic impurity effect reported by Mackenzie *et al.*[2] This finding indicated that the nonmagnetic impurity, Al, strongly suppresses T_c of Sr_2RuO_4, which can be interpreted well by the modified pair-breaking theory of Abrikosov-Gorkov (AG).[6] For unconventional superconductors, the same mechanism of suppression is expected to be valid for the lattice defects. Additionally, previous experiments showed that the crystals with the same impurity level of Al might have quite different T_c and that the residual resistivity ρ_0 is a better controlling parameter of T_c.[2] These two points motivated us to clarify the additional pair-breaking effect due to lattice defects for Sr_2RuO_4.

In this paper, we have investigated the influence of lattice defects also on the upper critical field $H_{c2}(T)$ and characterized how the coherence length ξ varies with T_c. The relation between ξ and the mean-free path l will be discussed. Furthermore, we adopted a recent theory[7] of a *p*-wave superconductor to examine the temperature dependence of H_{c2} along the interlayer c direction ($H_{c2\parallel c}$) for the crystal with the highest T_c, and compared it with the BCS theory prediction.

II. EXPERIMENT

All the crystals used in this study were grown using a floating-zone image furnace. The feed rods, containing 15% excess Ru serving as flux, were melted in the mixture of 10% O_2+90% Ar with a total pressure of 3 bar. The crystals were grown at the feed speed of 4 to 6 cm/h. In the processes of both reaction and sintering of polycrystalline feed rods, we always placed a layer of Sr_2RuO_4 powders between the sample of Sr_2RuO_4 and the aluminum crucible to prevent Al contamination. Previous study indicated that all the crystals grown in this way have almost the same low impurity levels, <50 ppm.[2] Nevertheless, the T_c of the present crystals depends sensitively on growth conditions, especially on the feed speed. Higher feed speed (>5 cm/h) always produced crystals with lower $T_c(<0.8\,\mathrm{K})$, and the optimal feed speed was ~4.5 cm/h for the highest $T_c(\sim 1.5\,\mathrm{K})$. At lower speed, the growth condition was not optimized and T_c decreased. This observation strongly suggested that the higher feed speed produced serious defects in the crystal, thus resulting in lower T_c. To investigate the effect of annealing on lattice defects, we annealed some of the as-grown crystals at different temperatures, 1200–1500 °C, for three days in air.

The T_c and $H_{c2\parallel c}(T)$ of the crystals were determined by ac susceptibility using a commercial ^{3}He refrigerator with a 2-T magnet. The ac susceptibility was measured by a mutual-inductance method with an ac field of 0.1 mT at a frequency of 1000 Hz, applied in the same direction as the dc field. The misalignment of the crystals for the $H_{c2\parallel c}$ measurement was less than 4°. Since $H_{c2}(T)$ is much less sensitive to the field direction for $H\parallel c$ compared with $H\parallel ab$, the misalignment of less than 4° will not have a substantial influence on the value of $H_{c2\parallel c}(T)$. The resistivity was measured by a standard four-probe method.

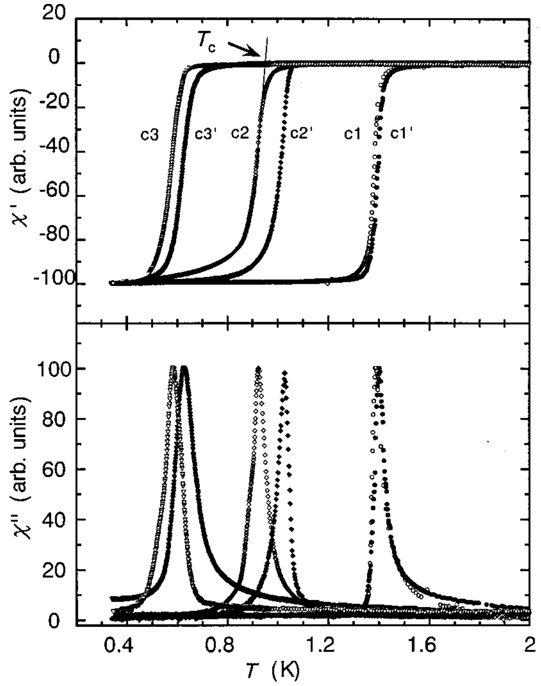

FIG. 1. ac susceptibility of some as-grown and annealed crystals of Sr_2RuO_4. $C1$, $C2$, and $C3$: as-grown crystals; $C1'$, $C2'$, and $C3'$ obtained by annealing $C1$, $C2$, and $C3$ at 1500 °C for three days in air. χ': in-phase component and χ'': out-of-phase, dissipative component of the susceptibility.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the ac susceptibility data of some typical as-grown and annealed crystals. $C1$, $C2$, and $C3$ are as-grown crystals, while $C1'$, $C2'$, and $C3'$ are obtained by annealing $C1$, $C2$, and $C3$ at 1500 °C. Here, we define T_c as the intersection of the linear extrapolation of the most rapidly changing part of χ' and that of normal state χ'. From Fig. 1, it can be seen that the enhancement in T_c by annealing for the crystal with as-grown T_c of 1.408 K is much less than that for the crystals with $T_c = 0.618$ K and 0.953 K. This indicates that the defects in the crystals with lower T_c are more severe than that in the crystals with higher T_c. The annealing reduces the defects in the crystals with lower T_c to some extent. Therefore we can say that the defects are really the main factor to determine T_c for crystals with very low levels of impurity elements.

Y. Inoue *et al.*[8] have studied features of microstructure in Sr_2RuO_4. They pointed out that the defects in Sr_2RuO_4 are mainly located in the modulated structure along the c direction and the layered defects distributed locally. Especially for the crystal with much lower $T_c(\sim 0.4\,\mathrm{K})$, a lot of modulated structures with various periods were found.

We measured the resistivity of some as-grown and annealed crystals with different T_c ranging from 1.5 to 0.6 K. Figure 2 shows the dependence of T_c on residual resistivity ρ_0 for these crystals (open circles). Solid circles were obtained by crystals with different amount of impurities.[2] The crystals for points 3 through 6 are cleaved from the same region of a crystal block and annealed at four different temperatures ranging from 1200 °C to 1500 °C. The crystals for points 9 and 10 were cut from the different regions of the same batch and they had the same T_c. The ρ_0 was deter-

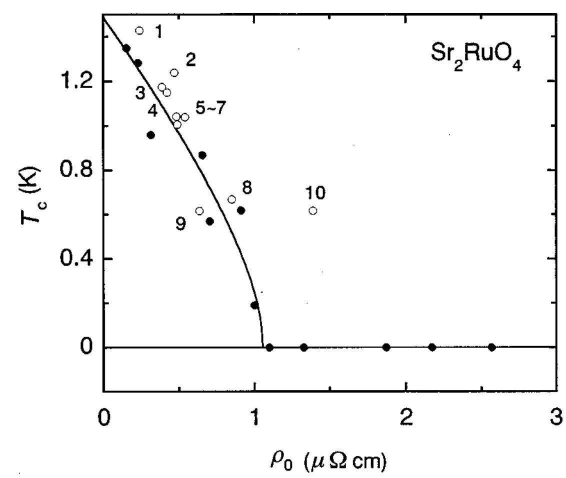

FIG. 2. Dependence of T_c on residual resistivity ρ_0. Open circles: results from the present work; solid circles: data for impurity effect taken from Ref. 2; the solid line: a fit of the Abrikosov-Gor'kov pair-breaking function to the solid circles (Ref. 2); the meaning of numbers 1–10 are described in the text.

mined by fitting the resistivity data between 4.2 and 25 K to the formula $\rho = \rho_0 + AT^2$. As mentioned above, this impurity suppression on T_c (solid circles) can be fitted well by the modified AG function,[2] which is given by the solid line in Fig. 2. For the open circles, we can see clearly that the decrease of T_c follows almost the same tendency as the fitting curve with increasing ρ_0 except for point 10. It is unlikely that the deviation of this point from the fitting curve is caused by measurement errors, because the samples for points 9 and 10 had almost the same room temperature resistivity. Hence, we believe that the deviation of point 10 from the fitting curve actually comes from the inhomogeneity of defects for crystals with such low T_c. This kind of inhomogeneity characteristic of defects has been observed by transmission electron microscope, as remarked above. We therefore conclude that the lattice defect is also an additional strong pair breaker in addition to impurity elements in Sr_2RuO_4.

To study the influence of defects on $H_{c2}(T)$ and characterize how $\xi_{ab}(0)$ varies with T_c, we measured $H_{c2\parallel c}(T)$ for eight samples with different T_c by ac susceptibility. Figure 3 shows a typical set of ac susceptibility data measured under different external dc magnetic fields for the sample with the highest T_c $(T_c = 1.489\,\mathrm{K})$. The T_c definition used here is the same as the one we described above. Figure 4 shows the data of $H_{c2\parallel c}(T)$ for six samples. As seen in Fig. 4, the $H_{c2}(T)$ curves simply shifts downward with decreasing T_c. Since the lowest temperature attained with our ^{3}He refrigerator is ~0.3 K, we do not have any data points for temperatures lower than 0.3 K. It is not easy to estimate $H_{c2\parallel c}(0)$ with high precision directly just by extrapolation of the experimental data points. Therefore, to estimate $H_{c2}(0)$ for each curve, we adopted the following formula,

$$H_{c2}(0) = -0.6795(dH_{c2}/dT)_{T=T_c}T_c, \quad (1)$$

which is derived in a recent theory of a p-wave superconductor.[7] This equation shows only a little difference

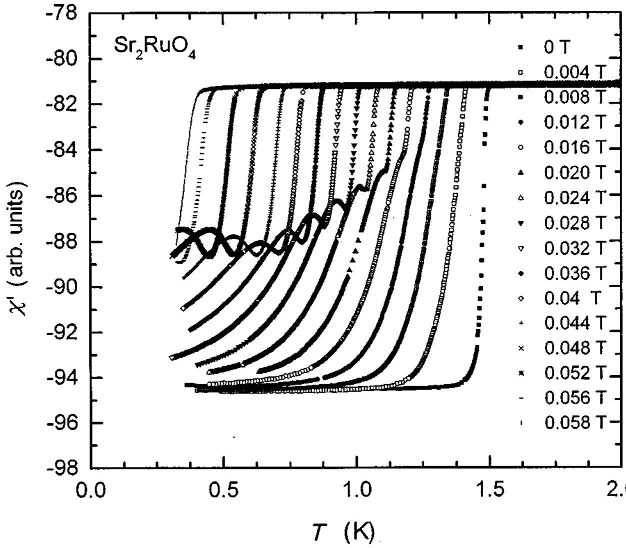

FIG. 3. Temperature dependence of ac susceptibility of Sr_2RuO_4 measured under different external dc magnetic fields for the sample with the highest T_c ($T_c = 1.489\,\mathrm{K}$).

in the coefficient from the Werthamer-Helfand-Hohenberg (WHH) formula[9] for conventional superconductors,

$$H_{c2}(0) = -0.693(dH_{c2}/dT)_{T=T_c}T_c. \tag{2}$$

The open symbols shown on the vertical axis of Fig. 4 display $H_{c2}(0)$ estimated by Eq. (1). From the rough extrapolation of the experiment curves, we found that these estimated values of $H_{c2}(0)$ are in reasonable agreement except for the sample with the highest T_c. To evaluate the error in this estimation, we used Eq. (1) to check the $H_{c2\parallel c}(T)$ data thoroughly measured by Yoshida *et al.*[10], Mackenzie *et al.*,[11] and Riseman *et al.*[12] where the precise estimation of $H_{c2\parallel c}(0)$ is available from the extrapolation of experimental curves because they extended the measurements to much lower temperatures (<0.3 K). We found that the discrepancy between the $H_{c2\parallel c}(0)$ obtained by theoretical estimation and the one gained by extrapolation from experimental curve is less than ~2 mT. However, for the sample with the highest

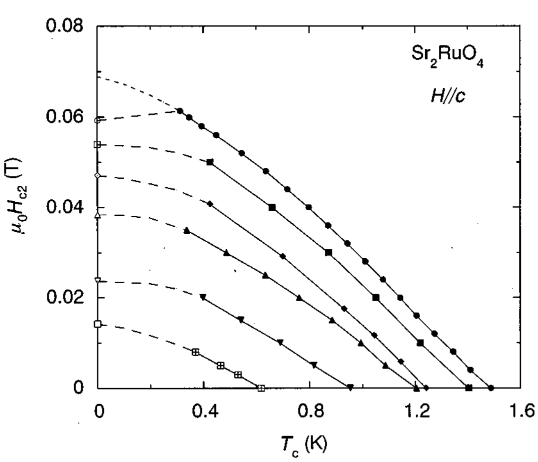

FIG. 4. Temperature dependence of H_{c2} for six crystals of Sr_2RuO_4 with different T_c. The open symbols are $H_{c2}(0)$ estimated by a recent theory of *p*-wave superconductivity (Ref. 7).

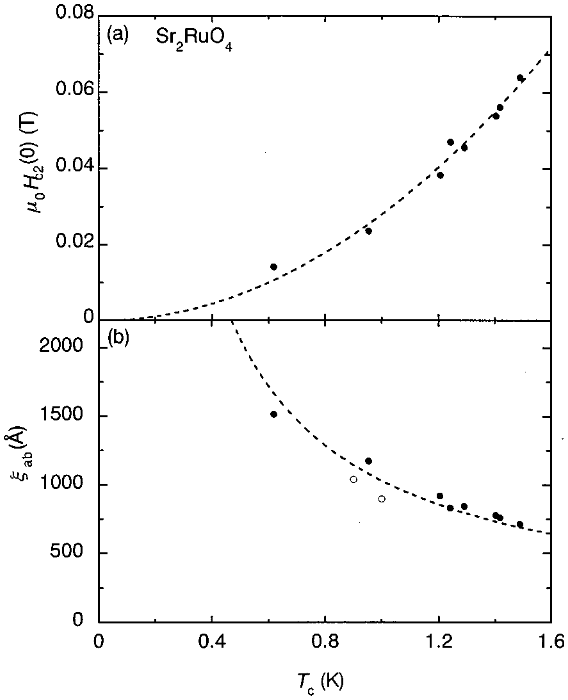

FIG. 5. (a) The estimated $H_{c2\parallel c}(0)$ as a function of T_c; (b) the in-plane coherence length $\xi_{ab}(0)$ as a function of T_c. The open circles are the previous data of Yoshida *et al.* (Ref. 9) and Mackenzie *et al.* (Ref. 10). Broken curves are fits to the data described in the text.

T_c, the error for the estimated $H_{c2}(0)$ is appreciably larger than 2 mT. So we just take the intersection of smooth extrapolation of the experimental curve and the vertical axis as the $H_{c2}(0)$ for this sample.

Figure 5(a) gives the estimated $H_{c2\parallel c}(0)$ data as a function of T_c. These $H_{2c\parallel c}(0)$ data can be fitted well with temperature squared dependence as shown by the broken curve, i.e.,

$$H_{c2\parallel c}(0) = aT_c^2, \tag{3}$$

where $a = 0.029T/\mathrm{K}^2$. Using the Ginzburg-Landau (GL) formula for an anisotropic three-dimensional superconductor,

$$H_{c2\parallel c}(0) = \frac{\phi_0}{2\pi\xi_{ab}(0)^2}, \tag{4}$$

where ϕ_0 is the flux quantum and $\xi_{ab}(0)$ is the in-plane GL coherence length, we obtained the relation between the experimental $\xi_{ab}(0)$ and T_c,

$$\xi_{ab}(0) = (\phi_0/2\pi a)^{1/2}(1/T_c). \tag{5}$$

Such variation of $\xi_{ab}(0)$ with T_c, shown by the broken curve, can be seen clearly from Fig. 5(b), where the previous data of Yoshida *et al.*[10] and Mackenzie *et al.*[11] are also included (open symbols); their data also follow the same tendency as the fitting curve.

For a BCS-type superconductor, the intrinsic coherence length ξ_0 is proportional to $1/T_c$, i.e.,

$$\xi_0 = \alpha\hbar v_F/k_BT_c, \tag{6}$$

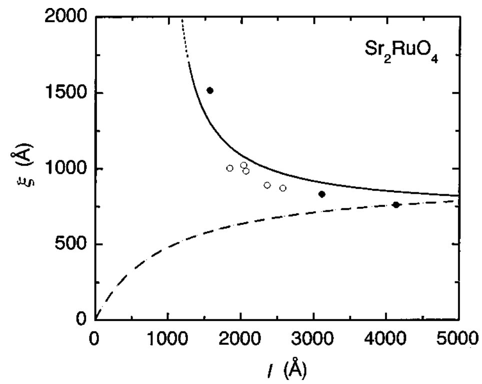

FIG. 6. The coherence length $\xi_{ab}(0)$ as a function of the mean-free-path l. The solid and extrapolated dotted lines are deduced from the solid line in Fig. 2 in terms of Eqs. (5) and (7). The solid circles: experimental points [measurements of both $H_{c2}(T)$ and ρ_0 were performed on the same sample for the three points]; the open circles: corresponding to points 3–7 in Fig. 2, the $\xi_{ab}(0)$ of which was not measured but estimated from Eq. (5); the dashed line: the relation of $\xi_{ab}(0)$ and l for conventional superconductors.

where $\alpha=0.18$, $\hbar=h/2\pi$ as h is the plank constant and ν_F is the Fermi velocity. Substituting Eq. (6) into Eq. (5) and using the average Fermi velocity measured by quantum oscillations,[13] we can estimate that $\alpha=0.14$ for Sr_2RuO_4, which is about 20% smaller than the BCS expectation.

We shall next discuss the relation between the $\xi_{ab}(0)$ and the mean-free-path l. As shown by Eq. (5), $\xi_{ab}(0)$ of Sr_2RuO_4 can be estimated once T_c is given. On the other hand, the mean-free-path l can be estimated from the residual resistivity ρ_0 using the following expression,

$$l=\frac{2\pi\hbar d}{e^2\rho_0\sum_i k_F^i}, \tag{7}$$

where d is the interlayer spacing of 6.4 Å, and the sum of k_F is over the three Fermi surface sheets $i=\alpha$, β, and γ, which are known from quantum oscillation measurements.[13] Therefore, from the dependence of T_c on ρ_0, the fitting solid line in Fig. 2, we can deduce the l dependence of $\xi_{ab}(0)$ in terms of Eqs. (5) and (7). This is shown by the solid line and extrapolated dotted line in Fig. 6. The solid circles are experimental points, and the open circles correspond to points 3–7 in Fig. 2, the $\xi_{ab}(0)$ of which was not measured but estimated from Eq. (5).

The results shown in Fig. 6 show that $\xi_{ab}(0)$ decreases with increasing l and the intrinsic coherence length ξ_0 is ~720 Å. This type of relation between the $\xi_{ab}(0)$ and l observed in Sr_2RuO_4 is completely different from that in conventional superconductors, in which Pippard coherence length ξ_P [comparable to $\xi_{GL}(0)$] and l are related by

$$1/\xi_P=1/\xi_0+1/\beta l, \tag{8}$$

as shown by the dashed line in Fig. 6, where β is a constant of the order of unity. For conventional superconductors, ξ_p decreases as l decreases. In contrast, $\xi_{ab}(0)$ in Sr_2RuO_4 increases rapidly as l decreases to ~900 Å. The reason why Eq. (8) is not applicable to Sr_2RuO_4 is simple, since Eq. (8) is based on the assumption that T_c changes little with l,

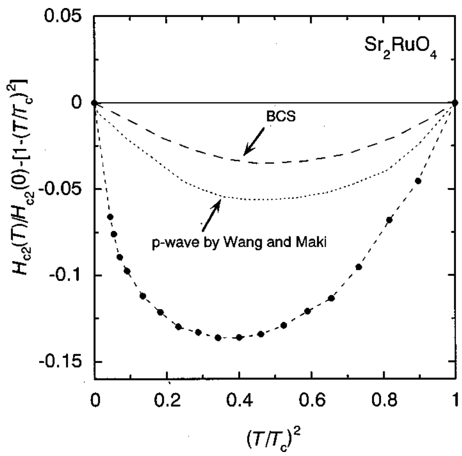

FIG. 7. Deviation of $H_{c2\parallel c}$ from the T^2 dependence for the crystal with the highest T_c (1.489 K) (closed circles). The dotted and dashed lines are, respectively, the deviation curves expected by a recent theory for a p-wave superconductor (Ref. 7) and by the BCS for the case of weak coupling.

whereas for Sr_2RuO_4 T_c strongly depends on l. In fact T_c as well as $H_{c2}(0)$ vanishes at $l\sim\xi_0$, thus resulting in the divergence in $\xi_{ab}(0)$. Therefore the $\xi-l$ relation for Sr_2RuO_4 represented in Fig. 6 is a manifestation of unconventional superconductivity.

Finally, let us examine the temperature dependence of $H_{c2\parallel c}$ and contrast it with the expectation for the isotropic p-wave superconductor,[7] as well as with the BCS prediction. Figure 7 shows the deviation of $H_{c2\parallel c}$ from T^2 dependence for the crystal with the highest T_c (1.489 K). The deviation curves predicted by both the p-wave and BCS theories for the case of weak coupling are displayed in this figure as well. For conventional s-wave superconductors, H_{c2} only shows a smaller deviation from the T^2 dependence with the maximum deviation magnitude less than 4%. (Here, we assume, for simplicity, that GL parameter κ does not depend on temperature.) This deviation is negative in weak coupling superconductors, such as Sn and Al, but positive in strong coupling superconductors, like Hg and Pb. It can be seen clearly that the experimental data for Sr_2RuO_4 show a much larger deviation from the T^2 dependence than that predicted by the BCS theory. This certainly manifests the feature of unconventional superconductivity for Sr_2RuO_4 from the other side. Yet, the expectation given by the p-wave theory also shows a substantial difference from the experiment result although the difference is less severe. This theory directly deals with the upper critical field, but does not consider orbital dependence of superconductivity,[14] which is probably needed for a more realistic model for Sr_2RuO_4.

IV. CONCLUSION

We have studied the suppression of T_c in Sr_2RuO_4 caused by lattice defects. Our results revealed that the defect is also a strong pair breaker like a nonmagnetic impurity element. We further found that $\xi_{ab}(0)$ evaluated from $H_{c2}(T)$ is proportional to $1/T_c$. The in-plane coherence length $\xi_{ab}(0)$ decreases with increasing l, which is opposite to the relation of $1/\xi_P=1/\xi_0+1/\beta l$ for conventional superconductors. This anomalous behavior reflects the characteristic of unconventional superconductivity of Sr_2RuO_4. In addition, we found that the deviation of $H_{c2}(T)$ from the T^2 dependence significantly differs from the BCS prediction, and also has a substantial difference from the present theoretical expectation for a *p*-wave superconductor. The orbital dependence of superconductivity must probably be taken into account in the current *p*-wave theory to give final interpretation on this large discrepancy.

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