In-Plane Anisotropy of Upper Critical Field in Sr_2RuO_4

Z. Q. Mao,[1,2,*] Y. Maeno,[1,2] S. NishiZaki,[1] T. Akima,[1] and T. Ishiguro[1,2]
[1]*Department of Physics, Kyoto University, Kyoto 606-8502, Japan*
[2]*Core Research for Evolutional Science and Technology of Japan Science and Technology Corporation (CREST-JST), Kawaguchi, Saitama 332-0012, Japan*
(Received 15 July 1999)

We investigated the behavior of the spin-triplet superconductor Sr_2RuO_4 ($T_c \approx 1.5$ K) under the magnetic fields parallel to the quasi-two-dimensional plane. The upper critical field H_{c2} exhibits a clear fourfold anisotropy of about 3% at 0.35 K. Furthermore, we detected an additional transition feature below H_{c2} in both the ac susceptibility and the specific heat. These second-transition features as well as the pronounced in-plane H_{c2} anisotropy disappear above 0.8 K or under intentional field misalignment of less than 1°. Most of these characteristics are consistent with the predicted emergence of the second superconducting phase with a line-node gap.

PACS numbers: 74.60.Ec, 74.25.Dw

After the discovery of superconductivity in the layered perovskite Sr_2RuO_4 [1], the possibility of p-wave superconductivity was proposed on the basis of the similarity of the Fermi liquid parameters of Sr_2RuO_4 to those of ^{3}He and of the presence of the ferromagnetic relative compound [2]. Successive experiments [3], as well as theory [4], have given substantial support for this expectation. In particular, the NMR experiment has revealed that the spin susceptibility remains totally unchanged through the superconducting transition temperature T_c [5], providing a definitive identification that Sr_2RuO_4 is a spin-triplet superconductor. Secondly, muon spin relaxation (μSR) measurement revealed that a spontaneous internal magnetic field develops below T_c [6], strongly suggesting that the superconducting state breaks time reversal symmetry. These two experimental results lead us to infer that the p-wave superconducting state represented by the two-component d vector $\boldsymbol{d} = \hat{z}(k_x + ik_y)$ with the nodeless gap $|\Delta| = (k_x^2 + k_y^2)^{1/2}$ ($\hat{z}$ and $k_x + ik_y$ are the spin and orbital parts of the wave function) is the most probable one among the possibilities examined theoretically [2].

In principle, the spin-triplet p-wave state may have multiple superconducting phases because of allowed spin and orbital degrees of freedom of the Cooper pairs, as seen in heavy Fermion superconductor UPt_3 [7] and analogously in superfluid ^{3}He [8]. The d-vector consisting of a two-component order parameter allows a state with different symmetry to be stabilized near H_{c2}. For Sr_2RuO_4, this state has a line-node gap, the presence of which should enhance the in-plane H_{c2} anisotropy [9]. Therefore, investigating the characteristics of the in-plane H_{c2} anisotropy and searching for the second transition from the nodeless to line-node gap state may be of decisive importance in confirming the superconducting order parameter of Sr_2RuO_4.

In this Letter, we report on the precise measurements of the angular dependence of the in-plane H_{c2} of Sr_2RuO_4. We indeed observed the in-plane H_{c2} anisotropy with fourfold symmetry, and it is noticeably enhanced below 0.8 K. In addition, we detected a feature which is attributable to the second transition at temperatures below 0.8 K in both ac susceptibility and specific heat measurements for fields parallel to the ab plane.

The single crystals of Sr_2RuO_4 used in this study were grown by a floating-zone method with an infrared image furnace. We measured angular dependence of the in-plane H_{c2} for two samples (denoted by A and B below) and specific heat under magnetic fields for one sample (C). Samples A (dimension $2.2 \times 2.0 \times 1.3$ mm^3) and C ($2.8 \times 4.8 \times 0.5$ mm^3) are as-grown crystals, and sample B ($1.9 \times 1.3 \times 0.5$ mm^3) was annealed in oxygen at 1050 °C for three weeks. For all three samples, the shortest dimension was parallel to [001]. The x-ray rocking curves of these samples all showed single crystal characters with the diffraction peak width [full width of half maximum (FWHM) $\approx 0.08°$] comparable to that of Si crystal (0.06°) in our diffractometer. The direction of the tetragonal crystallographic axes for these three samples was determined by x-ray Laue pictures. The side surface of sample A was aligned along the basal [100] axis by diamond polishing, whereas those of samples B and C were rotated from the [100] axis by about 25° and 55°, respectively. ac susceptibility measurements indicated a sharp superconducting transition with the midpoint at $T_c = 1.414$ K for sample A, 1.459 K for sample B, and 1.492 K for sample C.

The angular dependence of the in-plane H_{c2} was determined by ac susceptibility using a dilution refrigerator (Oxford Instruments, model Kelvinox TLM) for sample A and a ^{3}He refrigerator for sample B. Both refrigerators are equipped with double-axis rotators. The ac susceptibility was measured by a mutual-inductance method with an ac field of 0.05 mT at a frequency of 700 Hz for sample A and 1.6 kHz for sample B. The ac field was maintained parallel to the [001] direction, thus perpendicular to the dc field (H_{dc}) for H_{dc}//the ab plane. The specific-heat measurements under magnetic fields for sample C were conducted by a relaxation method using another dilution refrigerator equipped with a single-axis rotator. Details of the specific-heat experiments will be published elsewhere [10]. Below, we will mainly focus on the ac susceptibility measurements.

To specify the direction of the field with respect to the crystalline axes, we adopt the polar angle θ, for which $\theta = 0°$ is along the [001] direction, and the azimuthal angle ϕ, for which $\phi = 0°$ with $\theta = 90°$ is along the [100] direction. The ab plane of the sample was aligned exactly parallel to H_{dc} by changing θ for each ϕ while observing the change in the ac susceptibility; the alignment was repeated whenever ϕ was changed. The accuracy of the exact parallel alignment for our experiment was as high as 0.02°. The in-plane H_{c2} measured using the present method with the accuracy of $\Delta\theta = -0.00 \sim +0.02°$ guarantees the precision in $\delta H_{c2}/H_{c2}$ of better than 0.1% at low temperatures.

Figure 1 shows the angular dependence of in-plane H_{c2} of both samples A (closed circles) and B (open diamonds) measured at $T = 0.10$ and 0.35 K, respectively. Here we define H_{c2} as the intersection of the linear extrapolation of the most rapidly changing part of χ' (the in-phase component of ac susceptibility) and that of normal state χ' [Fig. 2(a)]. Both samples clearly show a fourfold anisotropy. The maximum in H_{c2} appears in the diagonal directions ([110] and [−110]), and the minimum in H_{c2} in the principal basal directions ([100] and [010]), corresponding to the Ru-O bonding directions. The magnitude of the anisotropy is $\Delta H_{c2}/H_{c2}(110) = 0.026$ [ΔH_{c2} is defined as $H_{c2}(110)$-$H_{c2}(010)$] for sample A at 0.10 K and 0.028 for sample B at 0.35 K. Here it is worth noting that although the crystallographic axes of samples A and B have different orientation with respect to the physical surfaces as described above, they exhibit the same symmetry in the in-plane H_{c2} anisotropy. This fact excludes the possibility that the in-plane H_{c2} anisotropy shown in Fig. 1 is caused by surface superconductivity as observed in UPt_3 [11].

The inset in Fig. 1 shows the variation of the absolute magnitude of the in-plane H_{c2} anisotropy with temperature for sample B. Each data point was taken by sweeping the field at constant temperature. A rapid increase in ΔH_{c2} occurs below 0.8 K. The variation is much more gradual for $T > 0.8$ K, and ΔH_{c2} tends to be negative for $T > 1.15$ K before it approaches zero at T_c.

Anisotropic H_{c2} was observed previously in cubic materials such as clean Nb, V [12], and V_3Si [13], and recently in borocarbides such as $LuNi_2B_2C$ [14] and in high-T_c cuprates [15]. In these materials the in-plane H_{c2} anisotropy arises from the anisotropy of the Fermi surface (FS) and/or of the superconducting pairing interaction. The absolute magnitude of the anisotropy due to these effects generally shows a monotonic decrease with increasing temperature, unless superconductivity competes with magnetic ordering, for example, in $TmNi_2B_2C$ [16]. This is in contrast with the present observation in Sr_2RuO_4, and in particular, the enhanced H_{c2} anisotropy below 0.8 K as shown in the inset of Fig. 1 is suggestive of a different origin.

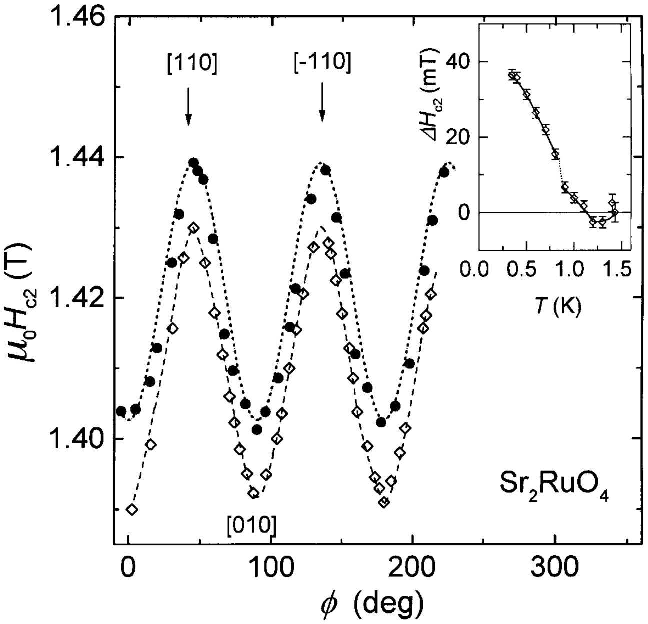

FIG. 1. The angular dependence of the in-plane H_{c2}. Closed circles: data of sample A measured at 0.10 K; open diamonds: sample B at 0.35 K. The crystallographic axes of samples A and B have different orientations with respect to the physical surfaces (see text). The inset shows the variation of the in-plane H_{c2} anisotropy with temperature for sample B, $\Delta H_{c2} = H_{c2}(110) - H_{c2}(010)$. The curves are guides to the eye.

Next, let us make further discussion on the possibility of the H_{c2} anisotropy induced by the line-node state. For the two-component d vector, the line-node state near H_{c2} is expected because the presence of line nodes can considerably decrease the kinetic energy generated by superconducting screening current, and hence the orbital depairing effect. It is naturally deduced that the line

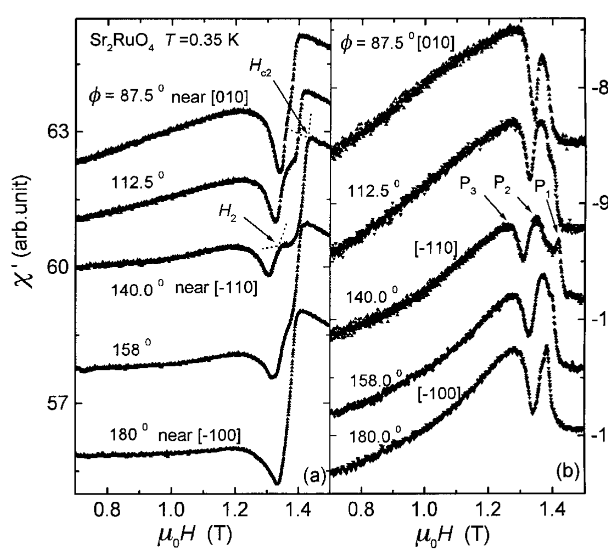

FIG. 2. ac susceptibility as a function of H_{dc} measured at different angles of ϕ for sample B. (a) χ'; (b) χ''. Features P_1, P_2, and P_3 are described in the text. H_2: The transition field corresponding to P_2.

nodes should appear in the in-plane direction perpendicular to the field and run along k_z. From the theoretical considerations for the allowed symmetries of the pairing states [9,17], this line-node state is expressed by $\boldsymbol{d} = \hat{z}k_{x'}$ with the gap $|\Delta| = |k_{x'}|$, where x' is always along the external field direction, and hence rotates with the field. We anticipate the in-plane H_{c2} anisotropy to be enhanced in the line-node state, provided that the density of state at FS is anisotropic. Agterberg [9] calculated such in-plane H_{c2} anisotropy using Ginzberg-Landau (GL) theory with a two-component superconducting order parameter. Our experimental observation on the in-plane H_{c2} anisotropy is in qualitative agreement with this theoretical prediction.

If the line-node state near H_{c2} does appear, we naturally expect a second superconducting transition with decreasing field, because the fully gapped state which is most probably stable at lower fields has a different symmetry. We should emphasize here that the clear transition can occur only if the field is applied *exactly* parallel to the *ab* plane; otherwise the line-node formation is incomplete and only crossover behavior is expected. Let us next examine whether our ac susceptibility data display any feature reflecting the possible second superconducting transition. Figures 2(a) and 2(b) represent χ' and χ'' (the out-of-phase, dissipation component) as a function of dc field exactly parallel to the *ab* plane at some typical positions of ϕ for sample B. We can clearly see that both χ' and χ'' show distinct anisotropy with ϕ. When the field orients nearly along [010] [the top curves in Fig. 2(b)], the main dissipation peak corresponding to the superconducting transition is a single peak. With increasing ϕ, a shoulder peak gradually develops, and the main peak splits into two peaks (P_1 and P_2) for H_{dc} along the diagonal direction ([−110]). From [−110] to [−100], these two peaks merge into a single peak again. Apart from these two peaks, one other peak (P_3) was also observed. Yoshida *et al.* [18] has studied this peak and attributed it to the vortex synchronization pinning. Then the feature P_2 most probably corresponds to the expected transition. The presence of these three peaks in χ'' and their evolution with respect to the field orientation are reproducible in sample A.

Additionally, we checked the effect of intentional misalignment on the additional peak P_2 for sample B. We found that the misalignment of $\Delta\theta \sim 0.6°$ fully suppresses the satellite peak P_2 (not shown here). In contrast, the misalignment has only a minor influence on the "conventional" vortex peak P_3 as expected. It should be noted that the field misalignment has a strong effect also on the magnitude of the in-plane H_{c2} anisotropy. $\Delta H_{c2}/H_{c2}$ decreases from 0.028 with $\Delta\theta \leq 0.02°$ to 0.007 with $\Delta\theta = 0.60°$ and to a slightly negative value of -0.002 with $\Delta\theta = 1.20°$.

The temperature dependence of the transition field H_2 [see Fig. 2(a) for definition], corresponding to the additional feature P_2, in the direction of $H_{\mathrm{dc}}//[110]$ for sample B is shown in the phase diagram of Fig. 3. The

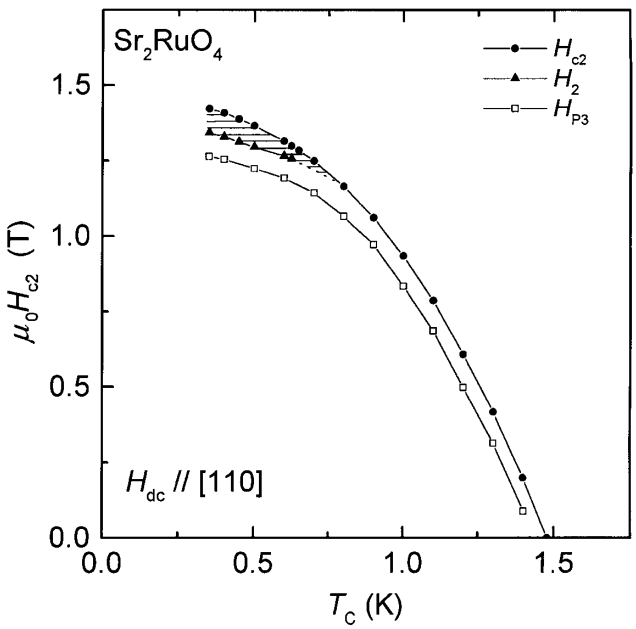

FIG. 3. The phase diagram for $H_{\mathrm{dc}}//[110]$. H_2: the transition field corresponding to P_2 [its definition is shown in Fig. 2(a)]. H_{P3}: the peak position of P_3 in χ''.

temperature dependence of P_3 (peak position) is also plotted in Fig. 3. It shows that the feature P_2 becomes undetectable at $T > 0.7$ K. The extrapolation of the curve for H_2 merges with that for H_{c2} at about 0.8 K. Experimentally, there is remarkable correlation between the feature P_2 and the pronounced in-plane H_{c2} anisotropy below 0.8 K (see the inset of Fig. 1), because both are simultaneously suppressed above 0.8 K or under slight field misalignment of less than 1°.

To further characterize this additional transition feature, we performed specific heat measurements for sample C under fields parallel to [110] as shown in the main panel of Fig. 4. The accuracy of the field alignment was $\Delta\phi \approx 3°$ and $\Delta\theta \approx 0.3°$. The temperature dependence of C_e/T (C_e: electronic contribution of the specific heat) with $H > 1.2$ T shows an anomalous behavior compared with the data for $H < 1.2$ T. The variation of C_e/T with T is nearly T-linear at low temperatures and shows a conventional downward concave character as temperature approaches $T_c(H)$ for $H < 1.2$ T, while for $H > 1.2$ T the C_{e}/T shows a sharp additional increase somewhat below $T_c(H)$. We also found that misalignment of less than 1° can fully suppress this anomalous behavior, as shown in the inset of Fig. 4. Obviously this unusual behavior in C_e/T with $H > 1.2$ T can be ascribed to the substantial entropy release from the additional transition, which is revealed by ac susceptibility measurements (it occurs only with $H > 1.2$ T; see Fig. 3). The relative amount of the entropy release induced by the additional transition at 1.4 T is ≈9% of the total entropy release associated with the superconducting transition. This fact confirms that the additional transition is a thermodynamic transition, not merely a vortex-lattice transition. The reason why we did not see

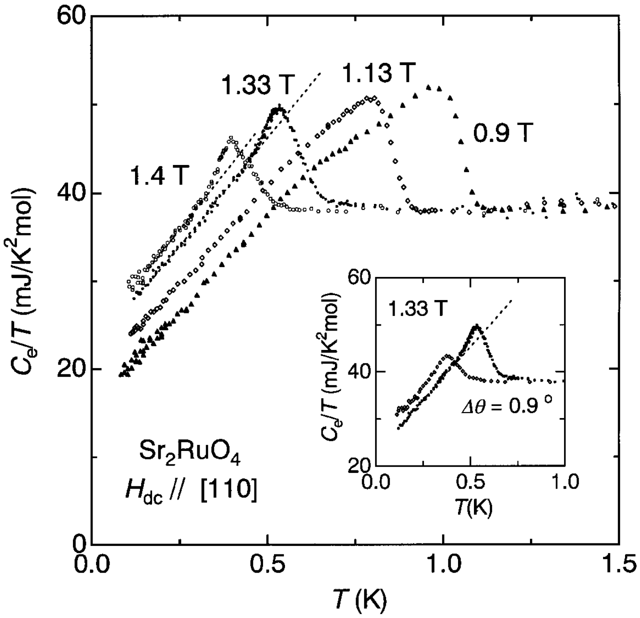

FIG. 4. Temperature dependence of the specific heat divided by temperature of sample C with magnetic fields parallel to [110]. The inset shows the effect of an intentional slight field misalignment. The dotted lines are guides to the eye.

a clear splitting in specific heat jump may be due to the larger uncertainty in the field alignment.

Combining the results of specific heat and ac susceptibility, it is natural to interpret the peak P_2 as being due to the second superconducting transition. To our knowledge, the only plausible explanation available for the second superconducting transition in Sr_2RuO_4 is due to the emergence of the line-node state [9]. In this case, the corresponding enhancement of the in-plane H_{c2} anisotropy is also naturally understood. Moreover, the point in the phase diagram where H_{c2} and the extrapolation of H_2 intersect may be regarded as the bicritical point.

Finally, we should point out that although the fourfold symmetry of the in-plane H_{c2} anisotropy observed experimentally is in qualitative agreement with the theoretical expectation by Agterberg [9], the temperature dependence of both the H_{c2} anisotropy and the second transition predicted by this theory is different from our experimental observations. In that theory, the second transition as well as the associated in-plane H_{c2} anisotropy should persist up to $T_c(H = 0)$. In comparison, our experiments show that the second transition feature appears only at low temperatures and that the in-plane H_{c2} anisotropy sharply reduced above 0.8 K. The reason for this discrepancy is not known at present.

In summary, we have observed the fourfold anisotropy of in-plane H_{c2} of Sr_2RuO_4, the magnitude of which shows a sharp decrease above 0.8 K or under slight field misalignment. We also observed the feature which is attributable to the second superconducting transition only in the H-T region where the in-plane H_{c2} anisotropy is enhanced. All of these results are consistent with the emergence of a new superconducting state with a line-node gap at $T < 0.8$ K in the field exactly parallel to the ab plane.

The authors would like to thank M. Sigrist, D. F. Agterberg, A. P. Mackenzie, and T. Oguchi for useful suggestions and discussions; T. Ando, H. Fukazawa, S. Sakita, T. Kawasaki, E. Ohmichi, and Y. Shimojo for their technical support.

*On leave from the University of Science and Technology of China (USTC), Hefei, China.

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