Anisotropic superconducting properties of $Ba_2YCu_3O_{7-y}$

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The upper critical magnetic field H_{c2} of $Ba_2YCu_3O_{7-y}$ single crystals is estimated from the resistive transition curves as a function of temperature and field direction. H_{c2} exhibits a large anisotropy between the c axis and the a-b plane. The H_{c2} data have linear temperature dependence, giving well-defined dH_{c2}/dT values: -0.56 T/K for the c axis and -3.3 T/K for the a-b plane. The angular dependence of H_{c2} is in good agreement with the effective-mass model when the ratio $M_\perp/M_\parallel = 60$, which is comparable to resistivity anisotropy in the normal state. On the other hand, no signs of anisotropy in the a-b plane can be recognized. This indicates that supercurrent flows dominantly in the Cu—O sheets, and that the Cu—O chains with oxygen deficiency are less conductive.

I. INTRODUCTION

Superconductivity above 90 K has recently been discovered in $Ba_2YCu_3O_{7-y}$ (Ba-Y-Cu-O), which has an orthorhombic oxygen-deficient perovskite structure.[1] This structure consists of sheets of oxygen arranged in square pyramids parallel to the a-b plane, and chains of square planes also exist between the sheets. Namely, the Cu—O bonds form both sheets and chains parallel to the a-b plane.[2-4] Thus, Ba-Y-Cu-O is low dimensional in its crystal structure, in common with the earlier-discovered 40-K superconducting system $[La,Ba,(Sr)]_2CuO_4$ (Refs. 5 and 6) with K_2NiF_4-type structure. We think it is crucial for high-T_c behavior that the crystal structures of these oxides have such a low-dimensional character. Therefore, it is important for solving the origin of the high T_c to study the effect of the anisotropic crystal structure on the superconducting properties, including the relation of the Cu—O sheets and chains to the upper critical magnetic field.

Various superconducting properties have recently been studied using Ba-Y-Cu-O single crystals and single-crystalline thin films, and considerable anisotropy has been observed in resistivity,[7,8] critical current density,[7,9] and lower and upper critical magnetic fields.[9-14] In particular, the Ba-Y-Cu-O upper critical field H_{c2} has been examined in detail by a number of workers, and it has been found that H_{c2} for the a-b plane is 6 to 7 times larger than that for the c axis.[11,12,14] On the other hand, H_{c2} anisotropy in the a-b plane has not been studied yet because it was thought that its anisotropy could not be determined owing to (110) microtwinned structure. However, H_{c2} anisotropy in the a-b plane is an important property which gives a clue to solving the problem of whether supercurrent flows dominantly in Cu—O sheets or in the Cu—O chains.

In this paper, we report the effect of the anisotropic crystal structure of $Ba_2YCu_3O_{7-y}$ on its superconducting properties. The upper critical magnetic field H_{c2} was estimated from the resistive transition curves as a function of temperature and field direction. Large H_{c2} anisotropy was found between the c axis and the a-b plane. We also point out that if H_{c2} anisotropy exists in the a-b plane, it should appear in the H_{c2} angular dependence even when Ba-Y-Cu-O crystals are twinned, thus showing that H_{c2} anisotropy in the a-b plane is absent.

II. EXPERIMENTAL PROCEDURE

Single crystals were grown by the CuO flux method using Y_2O_3 (99.9%), $BaCO_3$ (99.99%), and CuO (99.9%) powders.[15] The grown crystals were plate shaped with a typical dimension of about $1\times2\times0.1$ mm^3. It was found that the largest crystal face of the plate-shaped crystals was perpendicular to the c axis. These samples were annealed at 500 °C for 50 to 100 h in a flow of oxygen. Microtwinning in the [110] direction, which did not exist in as-grown crystals, was observed in annealed samples. This is ascribed to the structural transformation from tetragonal to orthorhombic symmetry caused by oxygen inclusion. Although the crystal structure was clearly observed, crystal orientation in the a-b plane remained undistinguished owing to microtwinned structure. Therefore, the two basic directions in these crystals are referred to as the a^* axis and the b^* axis, which are along the longer side and the shorter side of plate-shaped crystals, respectively. Optical polarizing microscopic observation revealed that many domains with widths of several μm were arranged alternately in the a^*-b^* plane. Therefore, the a axis in nearly half of the domains and the b axis in the other half were parallel to the a^* axis.

The superconducting transition was determined from the resistive measurement using the dc four-probe method with current parallel to the a^* axis. The current density was about 3 A/cm^2. Electrical contacts were made with silver paste. For the study of the anisotropic critical field, a rotating sample holder was used in a superconducting solenoid. Samples were rotated in the a^*-c and a^*-b^* planes. Measurements were carried out by sweeping temperature at several values of magnetic field and for a series of sample rotation angles. Magnetic fields were applied up to 12 T with a superconducting magnet and up to 26 T with a hybrid magnet. (The high field data were taken by a hybrid magnet at the Institute for Materials

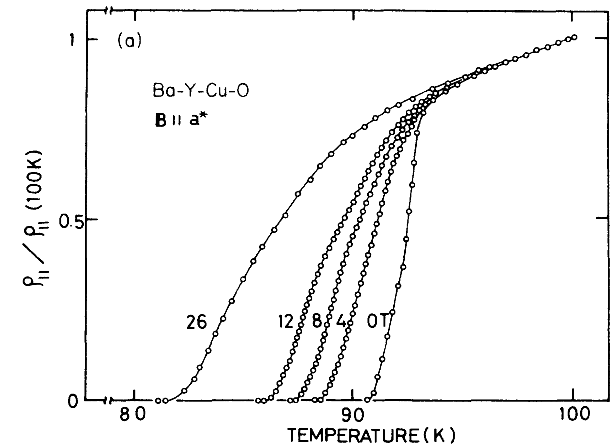
Research at Tohoku University.) Thermometry was carried out using calibrated carbon-glass thermometers. Experimental error in absolute temperature was estimated to be 0.2 K up to 12 T and 0.5 K at fields above 20 T.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The temperature dependence of resistivity in the a^*-b^* plane ($\rho_\parallel$) at zero magnetic field is shown in Fig. 1. $\rho_\parallel$ exhibited typical metallic temperature dependence, and decreased linearly down to 106 K, giving a ratio of $\rho_\parallel(300)/\rho_\parallel(106)=3.2$. Zero-resistance temperature extrapolated from the linear dependence data was 10 K. The superconducting transition began at 93 K and the resistivity became zero at 91 K.

Resistivity along the c axis ($\rho_\perp$) could not be measured using the conventional four-probe method because of the thin crystal (72 μm). The $\rho_\perp$ measurement was performed using current and voltage contacts attached to both surfaces of the crystal. The resistivity ratio $\rho_\perp/\rho_\parallel$ was estimated to be 70 at 300 K and 110 at 100 K. These values are about three times larger than those (~40 at 100 K) obtained for single-crystalline Ba-Y-Cu-O thin films.[7] This difference might be caused by the ambiguity of the measuring method for single crystals or by differences in sample quality. However, Ba-Y-Cu-O has a large resistivity anisotropy, and the anisotropy ratio is considered to be on the order of ten.

Superconducting resistive transitions in magnetic fields are shown in Figs. 2(a) and 2(b). A magnetic field was applied in the a^*-c plane and the angle ϕ between the magnetic field and the a^* axis was changed. When a field of 26 T was applied along the a^* axis ($\phi=0°$), the transition curve shifted to a lower temperature by 8 K. As the field direction changed from the a^* axis to the c axis, the curve shifted to a much lower temperature; and when the field was parallel to the c axis ($\phi=90°$), the zero resistance point shifted by 21 K at 12 T. These results indicate that Ba-Y-Cu-O has a large H_{c2} anisotropy in the a^*-c plane. When an applied magnetic field was varied in the a^*-b^* plane, the transition curves were almost independent of field direction.



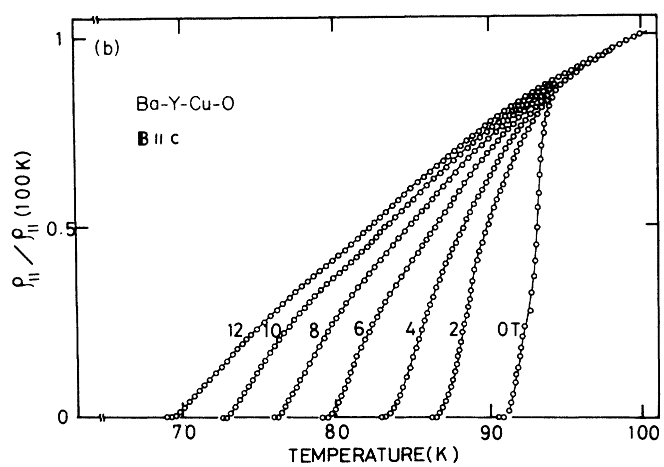


FIG. 2. Resistive transitions under the magnetic fields parallel to (a) the a^* axis and (b) the c axis.

From the experimental results in Fig. 2, it was found that Ba-Y-Cu-O exhibits a broad resistive transition under the magnetic field and that the broadness increases with increasing field strength. Since these gradual transitions to the normal states made it difficult to determine H_{c2} definitely, H_{c2} was defined as the magnetic field that breaks the zero-resistance state.

The H_{c2} temperature dependence for several field directions is shown in Fig. 3. The temperature dependences of H_{c2} are basically consistent with straight lines having different slopes up to 26 T except near T_c. Slope $|dH_{c2}/dT|$ decreases rapidly from 3.3 T/K at $\phi=0°$ to 0.56 T/K at $\phi=90°$, giving an anisotropy ratio of 5.9.

When the field direction was changed within the a^*-b^* plane, the slope had the same value of 3.3 T/K, independent of the field direction. In a previous paper,[10] we reported that some Ba-Y-Cu-O samples had two slopes in the temperature dependence of H_{c2}, depending on the field direction within the a^*-b^* plane. For this reason, it can be pointed out that edge-type planar faults[16] can cause spurious anisotropic characteristics in the a-b plane. In

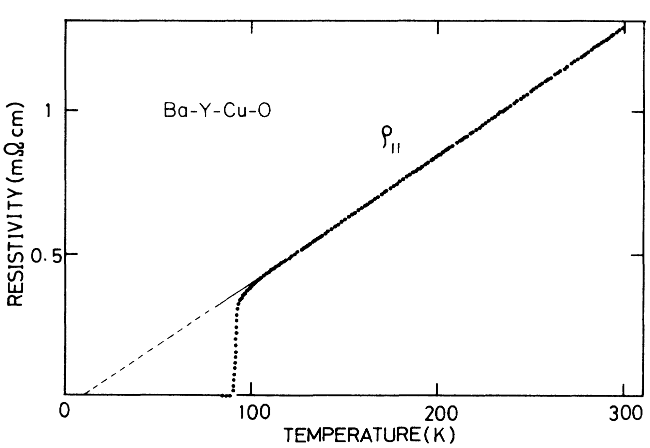


FIG. 1. Temperature dependence of resistivity in the a^*-b^* plane under zero magnetic field.

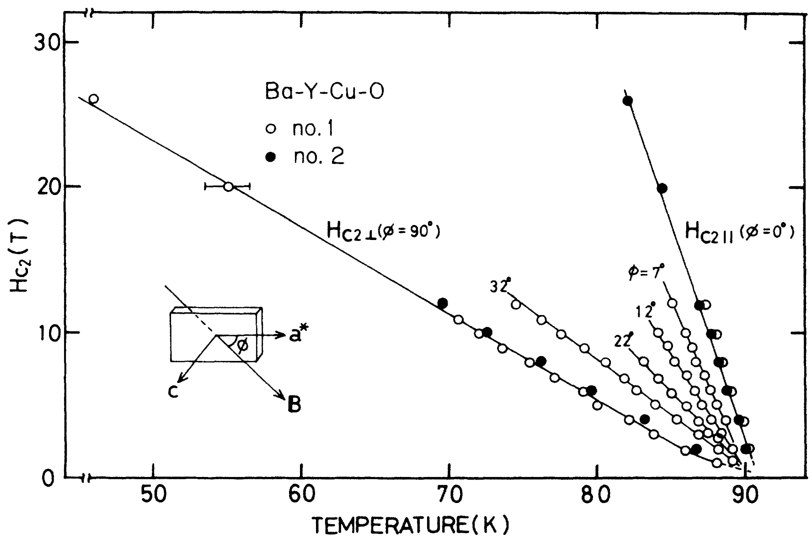


FIG. 3. Temperature dependence of H_{c2} for several field angles ϕ, where ϕ is the angle of field to the a^* axis.

fact, the high resistivity of the sample (by a factor of 20 higher than the present result) in the previous measurement suggests the probable inclusion of such planar defects.

First, let us consider H_{c2} anisotropy in the a-b plane. H_{c2} anisotropy in the a-b plane cannot be clarified precisely because Ba-Y-Cu-O has (110) microtwinned structure. However, it can be roughly estimated from the following discussion for the angular dependence of H_{c2} in the a^*-b^* plane. If H_{c2} anisotropy existed in the a-b plane, H_{c2} would depend on field direction, and exhibit angular dependence shown by the solid line in the inset in Fig. 4. Moreover, because the crystal is twinned, and the a axis in half of the domains and the b axis in the other half are parallel to the a^* axis, one should consider the superposed angular dependence of the symmetric solid and broken lines. When H_{c2} is defined by the zero-resistance point in the transition curve, it changes from point i to j to k, that is, it has a peak at $\theta = 45°$, because transition to the normal state occurs first in the domains where superconductivity is more easily broken under a magnetic field. When H_{c2} is defined by the onset point, it has a dip at $\theta = 45°$. Thus, anisotropy in the a-b plane should appear in the angular dependence of H_{c2} even when crystals are twinned.

Figure 4 shows the angular dependence of H_{c2} defined by the zero-resistance point and by the 85% resistance point. These are almost angular independent. Therefore, H_{c2} anisotropy in the a-b plane cannot be recognized. The Ba-Y-Cu-O crystal structure has both Cu—O sheets and Cu—O chains parallel to the a-b plane. Furthermore, in orthorhombic Ba-Y-Cu-O samples with $T_c = 90$ K, Cu—O chains have 10% to 20% O deficiency. Therefore, since anisotropy cannot be recognized, it is concluded that the supercurrent flows dominantly in the Cu—O sheets, and chains with O deficiency are less conductive.

H_{c2} at 87.5 K in the a^*-c plane is plotted as a function of the field angle ϕ in Fig. 5. It is clear from this figure that H_{c2} decreases rapidly with increasing ϕ. Various properties of superconductors with anisotropic electronic structures have been frequently analyzed using the effective-mass model. In this model, the effective mass in the Ginzburg-Landau (GL) equations is replaced with an effective-mass tensor in the order to take into account the anisotropy of the electronic structure. The effective-mass model succeeds in explaining the H_{c2} angular dependence

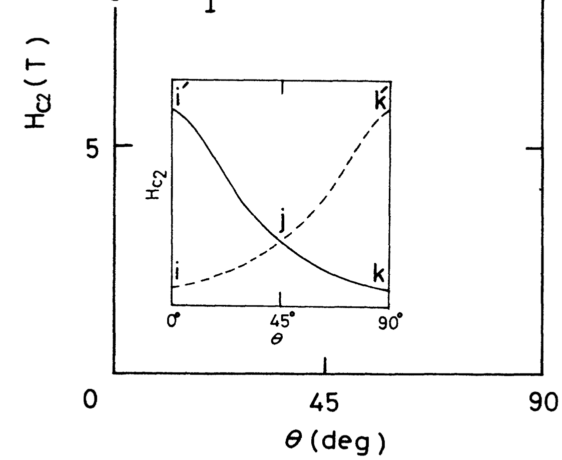


FIG. 4. Angular dependence of $H_{c2}(\theta)$ in the a^*-b^* plane, where θ is the angle of field to the a^* axis. The inset shows the angular dependence of H_{c2} with anisotropy in the a-b plane.

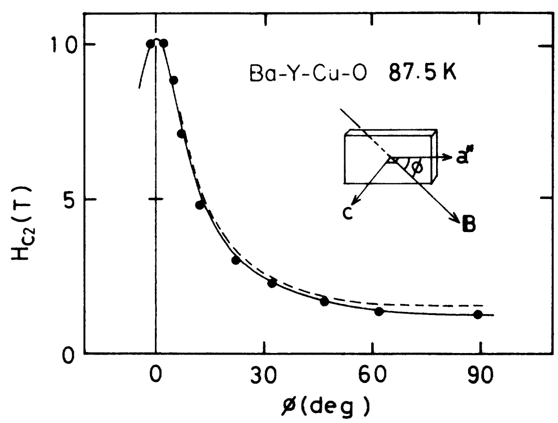


FIG. 5. Angular dependence of H_{c2} in the a^*-c plane. The solid line is the theoretical curve in the effective-mass model with $M_\perp/M_\parallel=60$. The broken line shows the $H_{c2}(\phi)$ extrapolated from the straight line which intersects the T axis in Fig. 3 at $T=T_c$ (91 K) and has the same slope as linear part in H_{c2}-T curve.

of layered superconductors, such as 2H-NbS_2 (Ref. 17) and 2H-$NbSe_2$,[18] which have two-dimensional (2D) electronic structures. For a superconductor with a 2D electronic structure the effective-mass model predicts an angular dependence of $H_{c2}(\phi)$ as follows:

$$H_{c2}(\phi)=H_{c2}(0)/[\cos^2\phi+(M_\perp/M_\parallel)\sin^2\phi]^{1/2} ,$$

where $M_\parallel$ and $M_\perp$ are the effective mass for the motion parallel and perpendicular to the a-b plane. The angular dependence of the Ba-Y-Cu-O H_{c2} is in good agreement with the theoretical curve (solid line) in Fig. 5 with $M_\perp/M_\parallel=60$, which is comparable to the resistivity anisotropy $\rho_\perp/\rho_\parallel$ in the normal state. Therefore, the Ba-Y-Cu-O critical field anisotropy can be explained using the effective-mass model.

The ratio $H_{c2}(0°)/H_{c2}(90°)$ is 7.8 at 87.5 K, which is larger than that (5.9) of dH_{c2}/dT by 1.9. This is caused by the gradual change of H_{c2} in the $H_{c2}(90°)$-T curve near T_c (Fig. 3). Therefore, when $H_{c2}(\phi)$ at 87.5 K is extrapolated from the straight line which intersects the T axis in Fig. 3 at $T=T_c$ (91 K) and has the same slope at the linear part in $H_{c2}(\phi)$-T curve, the $H_{c2}(\phi)$ data (broken line) in Fig. 5 deviate slightly from the theoretical curve (solid line) at large angles. Although further studies on this small deviation from the theoretical curve are needed, it is considered that H_{c2} anisotropy can be explained by the effective-mass model.

In the above discussion, it was found that H_{c2} exhibits a large anisotropy in the a^*-c plane, while anisotropy in the a-b plane cannot be recognized. Also, GL coherence length of Ba-Y-Cu-O has the same anisotropy. We next estimate the GL coherence length $\xi_\parallel$ and $\xi_\perp$, where the suffix $\parallel$ and $\perp$ mean parallel and perpendicular to the a-b plane. Using the Werthamer-Helfand-Hohenberg (WHH) theory for type-II superconductors,[19] the critical field at 0 K was estimated using the relation $H_{c2}(0)=0.69T_c\,|dH_{c2}/dT|$. $H_{c2\perp}(0)$ and $H_{c2\parallel}(0)$ were 35 and 210 T, respectively. The GL coherence length was calculated from the relations $H_{c2\perp}(0)=\phi_0/2\pi\xi_\parallel^2$ and $H_{c2\parallel}(0)=\phi_0/2\pi\xi_\parallel\xi_\perp$, to be $\xi_\perp=5.1$ Å and $\xi_\parallel=31$ Å.

The obtained $\xi_\perp$ is less than the spacing (8.3 Å) of the Cu–O sheets separated by the Cu–O chain, and is greater than the spacing (3.4 Å) between the Cu–O planes adjacent to the Y plane. According to the Josephson-coupled layer model,[20] the 3D-2D crossover is expected when $\xi_\perp < s/\sqrt{2}$, where s is the interlayer spacing. In Ba-Y-Cu-O, one of the above-described two spacings is considered as s, and the possibility of the 3D-2D crossover depends on the value of s. Namely, the crossover to a 2D behavior is expected if s is the former spacing ($s=8.3$ Å), while superconductivity in Ba-Y-Cu-O remains three dimensional at low temperatures if s is the latter ($s=3.4$ Å). However, the interlayer spacing is closely related to the problem of whether superconductivity occurs in each Cu–O sheet independently, which has not been clarified yet. Therefore, the problem of the possibility of the 3D-2D crossover in Ba-Y-Cu-O superconductivity remains unsolved at present.

IV. SUMMARY

The upper critical magnetic field in $Ba_2YCu_3O_{7-y}$ was estimated from the resistive transition curves as a function of temperature and field direction. The temperature dependences of the H_{c2} are basically consistent with straight lines with different slopes. The values $dH_{c2\perp}/dT$ and $dH_{c2\parallel}/dT$ were -0.56 and -3.3 T/K, giving a ratio of 5.9. $H_{c2\perp}(0)$ and $H_{c2\parallel}(0)$ were estimated to be 35 and 210 T, according to the WHH theory. Using these values, the GL coherence length was calculated to be $\xi_\perp=5.1$ Å, $\xi_\parallel=31$ Å.

H_{c2} exhibited large anisotropy in the a^*-c plane. Angular dependence of H_{c2} was explained by the effective-mass model with the ratio $M_\perp/M_\parallel=60$, which is comparable to the resistivity anisotropy in the normal state. On the other hand, the anisotropy of H_{c2} in the a-b plane could not be recognized. This indicates that the supercurrent flows dominantly in the Cu–O sheets, and the Cu–O chains with O deficiency are less conductive. The H_{c2} anisotropy of $Ba_2YCu_3O_{7-y}$ is associated with the Cu–O sheets.

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