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Electrical properties of high-T_c superconducting single-crystal $Eu_1Ba_2Cu_3O_y$

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The normal resistivity and H_{c2} of single-crystal $Eu_1Ba_2Cu_3O_y$ with $T_c = 95$ K and transition width of 0.25 K were measured. The crystal has orthorhombic and twinning structure with the *a* and *b* axes interchanged. H_{c2} shows anisotropic characteristics, the ratio of $(dH_{c2}/dT)_{T_c}$ between the *c* axis and the *a*-*b* plane is about 4, and $H_{c2}(0)$ is large, estimated to be 190 T. The $Eu_1Ba_2Cu_3O_y$ behaves as a quasi-two-dimensional superconductor. It is unambiguously evident in the temperature dependence of the normal resistivity that $d\rho/dT$ is anomalously large and that the temperature-dependent curve has a bulge shape.

Since superconductivity near 30 K was found by Bednorz and Müller,[1] extensive studies have concentrated on the search for new high-T_c superconducting metal oxide materials. The first superconducting material with T_c above liquid-nitrogen temperature was discovered in a mixed-phase Y-Ba-Cu-O system by Wu *et al.*,[2] and Hikami, Hirai, and Kagoshima,[3] and the high-T_c phase was identified to be oxygen-deficient perovskite $Y_1Ba_2Cu_3O_y$ (1:2:3 structure) by several groups independently.[4-6] Furthermore, high T_c above 90 K was also observed in a series of L-Ba-Cu-O compounds where Y in $Y_1Ba_2Cu_3O_y$ is replaced by lanthanide elements.[7-15] So far, almost all studies have used sintered powder samples for experimental measurements. The few papers studying single-crystal samples were mainly concerned with superconducting transition measurements in a magnetic field, which showed a large H_{c2} and H_{c1} anisotropy and high estimated value of $H_{c2}(0)$ in Y-Ba-Cu-O crystal,[16-18] and no detailed study to clarify intrinsic transport phenomena in the normal state using single-crystal samples has been reported.

In this Communication, we study the electrical properties of high-quality single-crystal $Eu_1Ba_2Cu_3O_y$, and find a large anisotropy in H_{c2} and unusual behavior in the normal-state resistivity. The reason we chose $Eu_1Ba_2Cu_3O_y$ is because it has the hightest T_c and the narrowest transition width among L-Ba-Cu-O compounds in sintered powder form.[7,11] We also make a comparison of electrical properties between $Eu_1Ba_2Cu_3O_y$ and $Y_1Ba_2Cu_3O_y$.

$Eu_1Ba_2Cu_3O_y$ single crystals were grown from molten Eu-Ba-Cu-O compounds.[16,19] As-grown $Eu_1Ba_2Cu_3O_y$ crystals were annealed in an oxygen atmosphere at 900–950 °C for 5–10 h, and cooled down to room temperature. The crystal structure and the lattice constants were determined using Weissenberg photographs and a four-circle x-ray diffractometer. Chemical compositions Eu, Ba, and Cu were determined to be 1:2:3 using an energy dispersion type electron-probe microanalyzer (EPMA).[20] Sample resistivity was measured using the low-frequency (73 Hz) ac four-terminal method. Silver films were evaporated on the samples as lead terminals. Gold wire leads were attached to the terminals with silver paste. Angle-dependent H_{c2} measurements were carried out by rotating a sample holder (Vacuum Metallurgical Co. Ltd.) with a Hall generator (Lake Shore Cryotronics, Inc.) in a magnetic field. The temperature was determined by a calibrated Pt resistance thermometer or carbon-glass thermometer in the magnetic field.

The crystal is a roughly rectangular prismatic with typical dimensions of $0.5 \times 0.5 \times 0.05$ mm^3. The largest facet is the *a*-*b* plane, which is perpendicular to the *c* axis. The as-grown crystals showed low T_c or no superconducting transition above 10 K. From Weissenberg photographs the crystallographic symmetry of these samples was found to be tetragonal. Lattice constants of the typical as-grown samples are 3.866 Å for *a* and *b* axes and 11.735 Å for the *c* axis. By contrast, oxygen annealed crystals are orthorhombic ($a/b = 1.015$) and showed a sharp superconducting transition above 90 K. Figure 1 shows a polarized optical microscope (POM) photograph of the oxygen-annealed crystal at room temperature by the reflection mode. A number of black and white lines at 45° to the *a* and *b* axes are observed in the crystal, clearly indicating that a twin structure with interchanged *a* and *b* axes grew

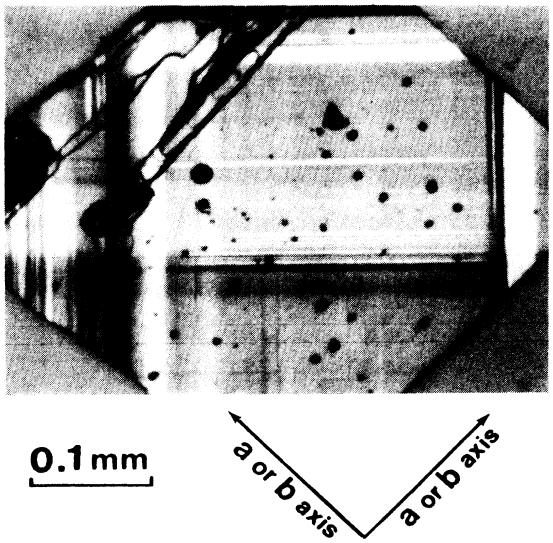

FIG. 1. Polarized optical microscope photograph of the oxygen annealed crystal $Eu_1Ba_2Cu_3O_y$ by reflection mode.

in the cooling process. This explanation is supported by $\mathrm{Eu_1Ba_2Cu_3O_y}$ powder x-ray studies indicating the phase transition between tetragonal and orthorhombic observed range between 650 and 350 °C. Therefore, the anisotropic electrical properties of the *a* and *b* axes cannot be expected in our samples. It is worthwhile noting that white and black contrasts in POM observation were changed by rotating the sample in the *a*-*b* plane. Optical reflectivity may differ between the *a* and *b* axes.

The temperature-dependent resistivity of a typical oxygen-annealed sample measured along the *a*-*b* plane is shown in Fig. 2 and material parameters are summarized in Table I. The very sharp superconducting transition observed at 95 K with $\Delta T_c = 0.25$ K proved high-quality crystals, where ΔT_c is defined as the temperature width between 90% and 10% of normal resistance at 95.5 K. Temperature-dependent resistivity in the normal state is discussed later.

Figure 3(a) shows the angle θ dependence of T_{c0} and $T_{c\,\mathrm{mid}}$ in the 5-T magnetic field, where T_{c0}, $T_{c\,\mathrm{mid}}$, and θ are defined as the temperatures of zero resistance and of the half value of the resistivity at 95.5 K, and as the angle between the magnetic field direction and the *c*-axis plane of the sample shown in Fig. 3, respectively. Anisotropic H_{c2} between the *a*-*b* plane and *c* axis was observed. In the magnetic field, the resistivity transition appeared sharply down to zero and did not show the large tail which was often observed in sintered powder samples. A small transition tail was sometimes observed. This could be due to the penetration of magnetic fluxes into the sample along twin lines. Therefore, T_{c0} is adopted as zero resistance temperature shown in Fig. 3(b) instead of T_{c0}^*. When adopting the redefined T_{c0}, the T_{c0} of θ dependence is symmetric with the value at $\theta = 0°$.

Figure 4 shows the temperature dependence of $H_{c2\perp}$ and $H_{c2\parallel}$, which are defined as H_{c2s} at $\theta = 0°$ and $\theta = 90°$, respectively. The value of H_{c2} ($T_{c\,\mathrm{mid}}$), which is normally used for sintered powder samples, is also shown in Fig. 4 for comparison with the other data. The temperature dependence of H_{c2} in the present measured range exhibits the slightly upward curvature often observed in layered superconductors.[21] This suggests that the sample behaves like a two-dimensional superconductor. The values of $dH_{c2\perp}/dT$ and $dH_{c2\parallel}/dT$ are roughly estimated to be -0.7 T/K at $t = 0.93$ and -3.0 T/K at $t = 0.98$, where t is T/T_c. The anisotropic H_{c2} ratio between the *c* axis and *a*-*b* plane is about 4. These values of $dH_{c2\perp}/dT$,

TABLE I. Material parameters for $\mathrm{Eu_1Ba_2Cu_3O_y}$ single crystal.

Measured parameters	
T_c midpoint	94.8 K
ΔT_c	0.25 K
$\rho(270K)$	0.72 mΩ cm
$\rho(100K)$	0.41 mΩ cm
$d\rho/dT$	1.5 μΩ cm/K
$dH_{c2\perp}/dT$	−0.7 T/K
$dH_{c2\parallel}/dT$	−3.0 T/K
Derived parameters	
$H_{c2\parallel}(0)$	190 T
$H_{c2\perp}(0)$	45 T
$\xi_{\parallel}(0)$	27 Å
$\xi_{\perp}(0)$	6 Å

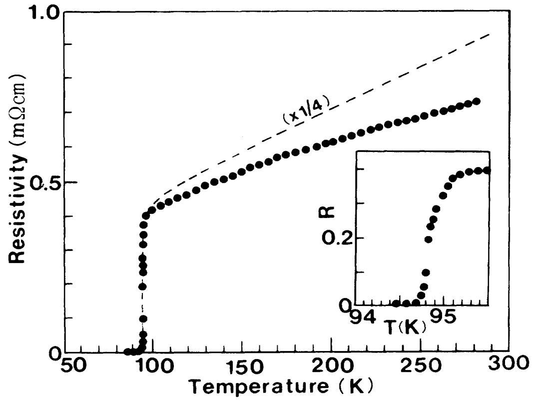

FIG. 2. The resistivity vs temperature for the $\mathrm{Eu_1Ba_2Cu_3O_y}$ single crystal. Inset: expansion of the region near T_c. The dashed line is resistivity for the sintered powder sample of $\mathrm{Eu_1Ba_2Cu_3O_y}$. The resistivity values of the powder sample at 100 and 270 K are 1.68 mΩ cm and 3.50 mΩ cm, respectively.

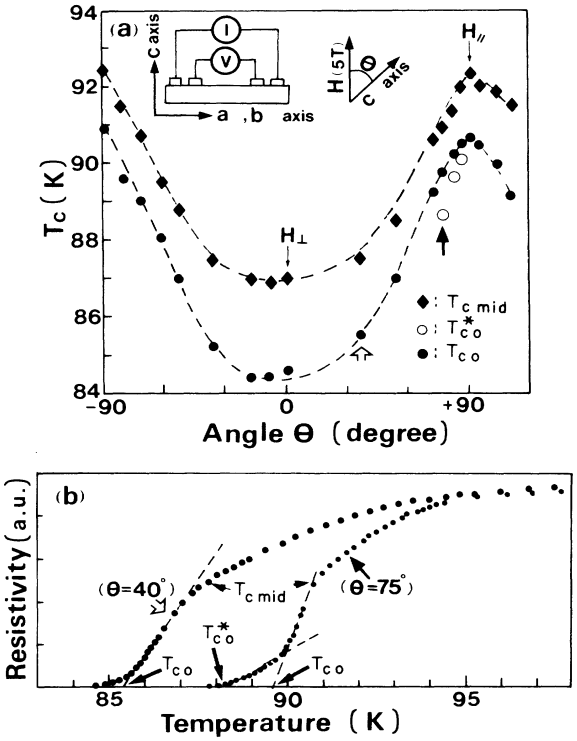

FIG. 3. The anisotropic H_{c2} measurement results between *c* axis and *a*-*b* plane in magnetic field at 5 T. (a) Angle θ vs T_c curve. Three kinds of T_c are defined $T_{c\,\mathrm{mid}}$, T_c0, and T_{c0}^* as shown in Fig. 2(b). The dashed lines are a guide for the eyes. (b) The resistivity transition curves for two examples at $\theta = 40°$ (⇧) and $\theta = 75°$ (↑). Three defined T_c points are also shown.

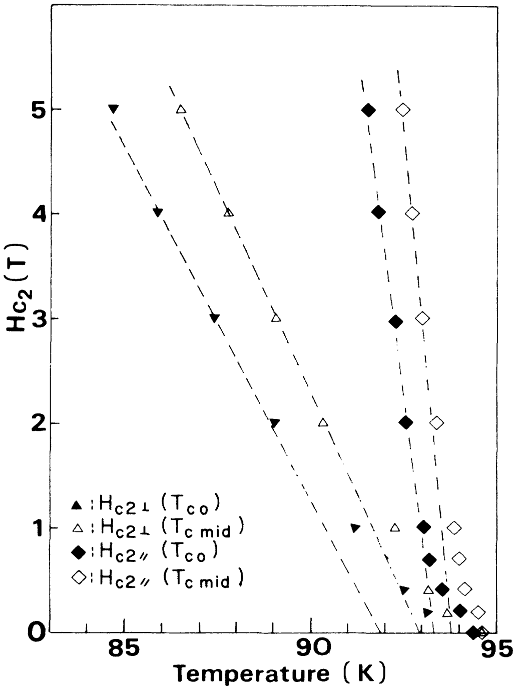

FIG. 4. Upper-critical field H_{c2} vs temperature T for single-crystal $Eu_1Ba_2Cu_3O_y$. $H_{c2}(T_{c0})$ is defined H_{c2} at T_{c0} shown in Fig. 2(b). $H_{c2}(T_{mid})$ is defined H_{c2} at $T_{c\,mid}$ which is defined at midpoint resistivity transition. The parallel (∥) means magnetic field applied parallel to a-b plane. The perpendicular (⊥) means magnetic field direction applied parallel to c axis. The dashed lines are guides for dH_{c2}/dT estimation.

$dH_{c2\parallel}/dT$, and anisotropy are almost the same as those of the high-T_c single-crystal $Y_1Ba_2Cu_3O_y$ reported by Iye, Tamegai, Takeya, and Takei.[17] These results indicate that the replacement of Y^{3+} by Eu^{3+} has virtually no effect on superconducting characteristics in the magnetic field.

By using the relation $H_{c2}(0) = 0.69T_c(dH_{c2}/dT)_{T_c}$,[22] $H_{c2\parallel}(0)$ of 190 T and $H_{c2\perp}(0)$ of 45 T were estimated roughly. The $H_{c2}(0)$ of 80 T,[23] 85 T,[24] and 148 T (Ref. 25) previously reported for sintered $Y_1Ba_2Cu_3O_y$ samples are in the range of these estimated values. Anisotropic coherent lengths $\xi_\parallel(0)$ and $\xi_\perp(0)$ were also estimated to be 27 and 6 Å, respectively, by using the relation that $H_{c2\perp} = \Phi_0/2\pi\xi_\parallel^2$ and $H_{c2\parallel} = \Phi_0/2\pi\xi_\perp\xi_\parallel$, where Φ_0 is the flux quantum. The value of $\xi_\perp$ is about half the c-axis lattice constant. Recent studies on the electronic band structure of $Y_1Ba_2Cu_3O_y$ have shown that the electrical conduction of high-T_c oxide superconductors is dominated by the layered and ribboned in-plane Cu(3d)-O(2p) interaction.[26,27] The crystal-structure analysis shows oxygen atoms in the L plane of $L_1Ba_2Cu_3O_y$ are missing and the conducting paths are separated by the L plane,[28] then the two-dimensional figure shows up. The distance between Cu-O planes separated by L is approximately 4 Å which is shorter than $\xi_\perp$. Two-dimensional superconducting layers can be weakly coupled by Josephson tunneling.[21] It should be noted that the H_{c2} anisotropy in $Eu_1Ba_2Cu_3O_y$ and $Y_1Ba_2Cu_3O_y$ is smaller than the H_{c1} anisotropy of 10 in single-crystal $Y_1Ba_2Cu_3O_y$.[18] At present, however, we have no quantitative data to explain the difference between H_{c1} and H_{c2} anisotropic values.

The electronic band-structure calculation also suggests that electrical properties should exhibit anisotropy between a and b axes.[26,27] However, Mitzi *et al.* recently pointed out that a one-dimensional feature is not essential for high-T_c 1:2:3 structure materials.[29] Although unable to measure anisotropic conduction between a and b axes because of the twinning structure, the anisotropic optical reflectivity observed in our preliminary POM study suggests anisotropy in the electronic structure.[30] To understand high-T_c mechanisms, it will be very important to investigate anisotropic conduction between a and b axes by using nontwinning single-crystal samples.

Unusual behaviors are observed at normal resistivity in Fig. 2. The resistivity ratio [$R_R = R(270\text{ K})/R(100\text{ K})$] of 1.8 is smaller than previously reported values,[7,12] and the $d\rho/dT$ value of 1.5 $\mu\Omega$ cm/K is extraordinarily large. These characteristics were observed in high-quality sintered powder materials. In Fig. 2, results for the sintered $Eu_1Ba_2Cu_3O_y$ powder sample are also shown. The single-crystal resistivity is about $\frac{1}{4}$ that of the sintered one, but RR is slightly smaller. Murphy *et al.* pointed out that the correlation between resistivity and RR was quite rough in sintered Eu- and Y-based samples, and suggested that intergrain resistivity may be important for sintered samples.[7] However, assuming anisotropic resistivity in the normal state of a single crystal, which is easily speculated from H_{c2} measurements, anomalous RR in sintered samples can be explained by the existence of microcrystals with various orientations, which could be strongly dependent on sintering processes.

It should be noted that resistivity of the single crystal decreases linearly with temperature down to about 170 K, and $d\rho/dT$ increases slightly with decreasing temperature down to T_c. Consequently, a downward temperature dependence called a bulge for resistivity appeared. The bulge is very often observed in dirty superconductors such as $A15$ materials,[31] and its origin has been explained in terms of strong electron-phonon coupling. However, the 1.5 $\mu\Omega$ cm/K value of $d\rho/dT$ in our sample seems too large to explain the bulge structure by electron-phonon coupling. Anomalously large $d\rho/dT$ was already pointed out by Lee and Read,[32] but it was not clear whether this characteristic was intrinsic in the normal-state resistivity or not because only data for sintered powder materials were available. The present work indicates that the large $d\rho/dT$ and the bulge structure are intrinsic in normal-state resistivity of $Eu_1Ba_2Cu_2O_y$, and could be essential in oxide superconductors with 1:2:3 structure.

To summarize, we have studied the normal and superconducting resistivity of single-crystal $Eu_1Ba_2Cu_3O_y$ with $T_c = 95$ K. Magnetic field measurements revealed that $(dH_{c2\parallel}/dT)/(dH_{c2\perp}/dT)$ anisotropy is about 4, and that a large $H_{c2}(0)$ of 190 T is estimated. It is unambiguously evident from the temperature dependence of the normal resistivity that $d\rho/dT$ is anomalously large, and that the temperature-dependent curve has a bulge shape. Further detailed investigations using various single-crystal samples will be necessary to elucidate the high-T_c mechanism.

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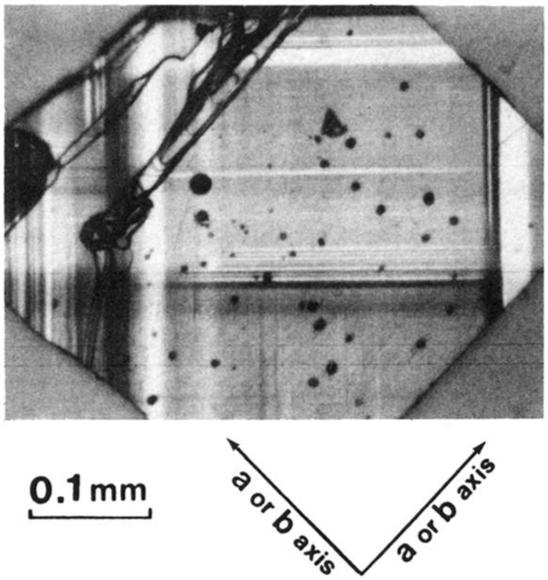

FIG. 1. Polarized optical microscope photograph of the oxygen annealed crystal $Eu_1Ba_2Cu_3O_y$ by reflection mode.