Upper critical field and anisotropy of the high-T_c $Bi_2Sr_2Ca_2Cu_3O_x$ phase

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The upper critical field (H_{c2}) of the 110-K $Bi_2Sr_2Ca_2Cu_3O_x$ phase has been obtained using high-quality whiskers and the measurement of the field-induced resistive transition up to 7.5 T. In the presence of magnetic fields parallel and perpendicular to the c axis, linear relations are obtained in H_{c2}-T curves defined at the 50% value of the extrapolated normal-state resistivity in the transition curves. According to the Werthamer-Helfand-Hohenberg theory and Ginzburg-Landau relations, the coherence lengths of $\xi_{ab}(0)=29$ Å and $\xi_c(0)=0.93$ Å are obtained. The anisotropy ratio of the coherence length is 31.

I. INTRODUCTION

One important feature of the high-T_c oxide superconductors is the degree of anisotropy of their superconducting properties derived from their layered crystal structure. It is essential for the understanding of the physical properties of these compounds to reveal what the significant factors for determining the anisotropy are. In the Tl and Bi systems, isostructural compounds with different numbers of CuO_2 planes are well known. These are considered to be a good model to examine the correlation between the degree of anisotropy and the number of CuO_2 planes. The evaluation of anisotropy for the cuprate superconductors has been made by upper critical field (H_{c2}), critical current density, resistivity, thermopower, fluctuation effects in conductivity, specific heat, electronic structure, and others. Among these, the upper critical field is intrinsic to the superconductor because H_{c2} is associated with microscopic currents on a length scale given by the vortex size.[1] For the $Tl_2Ba_2Ca_{n-1}Cu_nO_y$ ($n=1,2,4$) compounds, strong correlation between the upper critical field and the number of CuO_2 layers has been reported.[2] On the other hand, in the $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ ($n=1,2,3$) compounds, although they are the more widely studied system, only for the $Bi_2Sr_2CaCu_2O_x$ ($n=2$, 2:2:1:2 phase) has the anisotropy of H_{c2} (Ref. 1) been sufficiently studied. The anisotropy study had been limited to only the polycrystalline samples for the 110-K $Bi_2Sr_2Ca_2Cu_3O_x$ ($n=3$, 2:2:2:3 phase) compound[3–5] because large crystals of high quality have not previously been obtained.

In this paper, we report on the anisotropy of H_{c2} determined by the measurement of resistive transition curves in magnetic fields for $Bi_2Sr_2Ca_2Cu_3O_x$ with T_c over 100 K. We used $Bi_2Sr_2Ca_2Cu_3O_x$ whiskers for the measurement. We have previously reported on the preparation and properties of superconducting whiskers with the $Bi_2Sr_2CaCu_2O_x$ structure.[6,7] The $Bi_2Sr_2Ca_2Cu_3O_x$ whiskers with dimensions of ~ 300 μm wide, ~ 5 μm thick, and ~ 4 mm long have been obtained by annealing the $Bi_2Sr_2CaCu_2O_x$ whiskers in a Ca- and Cu-rich Bi-Sr-Ca-Cu-Pb-O powder.[8,9] The magnetic fields up to 7.5 T are applied parallel and perpendicular to the CuO_2 plane. An anisotropy factor of 31 has been obtained for H_{c2} defined at the conventional 50% value of the extrapolated normal-state resistivity in the magnetoresistance curves. We will discuss the degree of anisotropy compared with the $Bi_2Sr_2CaCu_2O_x$ compound.

II. EXPERIMENTAL

The $Bi_2Sr_2CaCu_2O_x$ whiskers were prepared by heating glassy plates in a stream of O_2 gas, as previously described.[6,7] Typically the $Bi_2Sr_2CaCu_2O_x$ whiskers were placed in a powder with the composition of $Bi_2Sr_2Ca_4Cu_6Pb_{0.5}O_x$, which had been calcined at 820 °C for 20 h. The sample containing the whiskers was annealed at 840 °C for 120–180 h in air. After cooling to room temperature, the whiskers were removed mechanically. Characterization of the annealed whisker performed by electron-microprobe analysis, x-ray diffraction, susceptibility measurement, and resistivity-temperature curve confirmed the formation of the $Bi_2Sr_2Ca_2Cu_3O_x$ whiskers.[8,9] It has been reported that the addition of small amounts of lead enhances the growth of the $Bi_2Sr_2Ca_2Cu_3O_x$ phase by promoting the nucleation of the $Bi_2Sr_2Ca_2Cu_3O_x$ phase and the diffusivity of calcium and copper.[10] We added small amounts of lead to the calcined powder and confirmed the incorporation of lead into the whiskers using an electron-probe microanalyzer. The resistivity decreases sharply at 110 K, and the zero-resistance state is achieved at 106.5 K. The Meissner curve shows a sharp decrease at 110 K without any signal around 80 K due to the $Bi_2Sr_2CaCu_2O_x$ phase. The resistivity of the whisker is 380 $\mu\Omega$ cm at room temperature and decreases linearly against temperature down to 130 K.

The magnetoresistance was measured by a standard four-probe method using a dc current of 0.05–0.5 mA along the *ab* plane. The electrical contact was made by using gold wires of 25 μm in diameter with silver epoxy. A magnetic field up to 7.5 T was applied parallel and perpendicular to the *c* axis with a superconducting solenoid. The current was always perpendicular to the magnetic field. The accuracy of the alignment of magnetic field and sample orientation is approximately 1°. The $Bi_2Sr_2Ca_2Cu_3O_x$ whisker has some steps on the surface because of erosion during the annealing of the calcined powder.[9] The result of scanning tunnel microscope (STM) observation indicates that the plateaus on the both sides of the step are flat and smooth, and they are mutually parallel. Therefore, the magnetic field was actually aligned parallel and perpendicular to the *c* axis within the experimental error of one degree.

III. RESULTS AND DISCUSSION

Figure 1 shows the resistive superconducting transition under the magnetic fields (H) up to 7.5 T perpendicular and parallel to the *c* axis. As observed in other superconducting cuprates, the onset of superconductivity is far less sensitive to the field than the foot of the transition. A remarkable field-broadened transition is observed when the field is parallel to the *c* axis (**H**||**c**). On the other hand, transition curves are less sensitive in perpendicular fields (**H**⊥**c**).

These data for **H**||**c** axis and **H**⊥**c** axis in the low-resistivity region replotted as $\log_{10}\rho$ vs T^{-1} are shown in Figs. 2 and 3. Palstra *et al.*[11] have reported that the resistivity (under 1% of the normal-state resistivity) is thermally activated and described by an Arrhenius law, $\rho=\rho_0\exp(-U_0/T)$, for the 2:2:1:2 single crystal. As shown in Fig. 2, the resistivity depends exponentially on T^{-1} over the wide resistivity range for the $Bi_2Sr_2Ca_2Cu_3O_x$ whisker, resulting in thermally activated behavior. The same behavior is obtained for the **H**⊥**c** axis plotting (Fig. 3). We have calculated the activation energy U_0 by fitting the Arrhenius law. The U_0 values are 1500, 940, 750, 700, 620, and 580 K for the **H**||**c** axis field of 0.5, 1.5, 3, 4.5, 6, and 7.5 T, and 2000, 1600, 1450, 1350, and 1280 K for the **H**⊥**c** axis field of 1.5, 3, 4.5, 6, and 7.5 T, respectively. Moreover, the U_0 values are expressed by a power law: $U_0=1100H^{-0.30}$ K for $1.5<\mathbf{H}(\|\mathbf{c}\text{ axis})<7.5$ T, and $U_0=2200H^{-0.27}$ K for $1.5<\mathbf{H}(\perp\mathbf{c}\text{ axis})<7.5$ T. The anisotropy in U_0 (factor of 2) is comparable to the 2:2:1:2 single crystal.[11] However, the U_0 values are two times larger than that for the 2:2:1:2 phase. It is known that U_0 strongly depends on microstructural defects and can be enhanced by the introduction of effective pinning centers. If the single crystals are perfect, they would contain no pinning centers, unless they have intrinsic pinning centers.[12] In order to reveal the origin of the difference of U_0, microstructural effects or intrinsic pinning, between $Bi_2Sr_2Ca_2Cu_3O_x$ and $Bi_2Sr_2CaCu_2O_x$, microstructual studies are necessary.

The strong broadening of the transition curve in a magnetic field leads to quite different temperature dependence of H_{c2}, so the slopes of the $H_{c2}-T$ curve at T_c will depend strongly on the method of evaluation. Some definitions for H_{c2} from the magnetoresistance curve have been reported: $\rho(T)/\rho_N(T)=0.15$, 0.3, 0.5, 0.6, and 0.9, and $\rho=0$, which was obtained by extrapolation of the

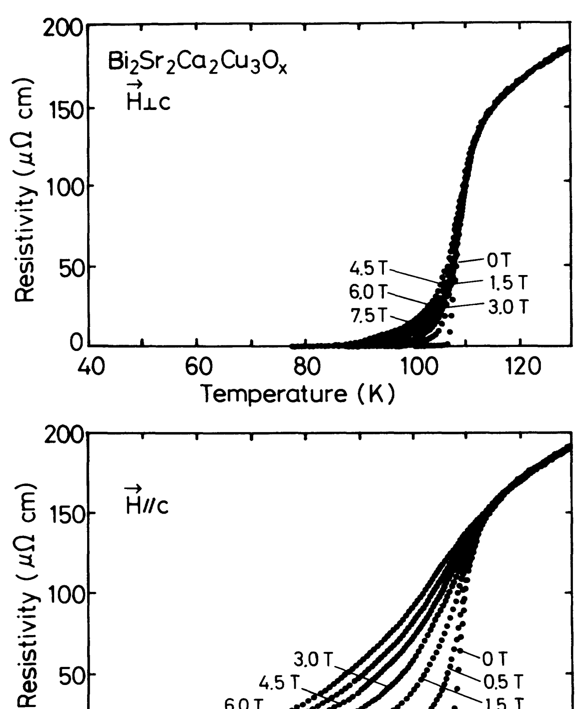

FIG. 1. Resistive transitions of the $Bi_2Sr_2Ca_2Cu_3O_x$ whisker in various magnetic fields perpendicular and parallel to the *c* axis.

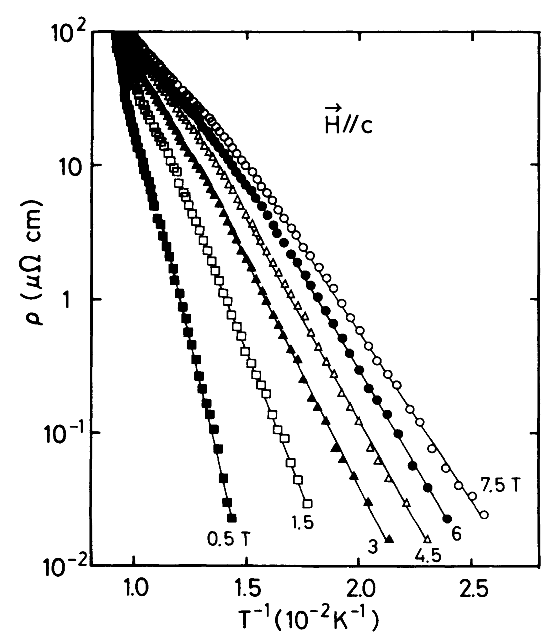

FIG. 2. Arrhenius plot of the resistivity of the $Bi_2Sr_2Ca_2Cu_3O_x$ whisker in magnetic fields parallel to the *c* axis.

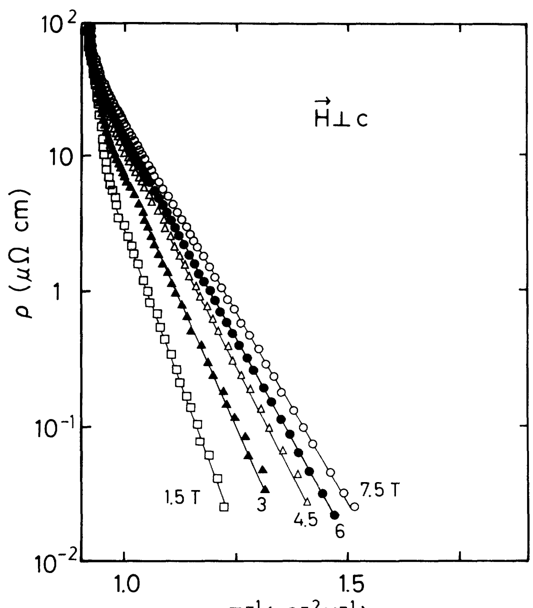

FIG. 3. Arrhenius plot of the resistivity of the $Bi_2Sr_2Ca_2Cu_3O_x$ whisker in magnetic fields perpendicular to the c axis.

linear part of transition curve, where $\rho_N(T)$ is the extrapolated normal-state resistivity. Palstra *et al.*[1] have represented that the angular dependence of H_{c2} defined by $\rho(T)/\rho_N(T)=0.5$ shows a good correspondence to the anisotropic Ginzburg-Landau (GL) theory for the 2:2:1:2 single crystal. Therefore, we chose $\rho(T)/\rho_N(T)=0.5$ for determining H_{c2}. Figure 4 shows the temperature dependence of the upper critical field. The $Bi_2Sr_2Ca_2Cu_3O_x$ whisker shows a linear relation for the H_{c2}-T curve for the alignments **H**$\|c$ and **H**$\perp c$. The H_{c2}-T curves with a slightly upward curvature near T_c have been observed for $YBa_2Cu_3O_x$ (Refs. 13 and 14), $Bi_2Sr_2CaCu_2O_x$ (Ref. 15), $Tl_2Ba_2Ca_{n-1}Cu_nO_x$ ($n=1,2,4$) (Refs. 2 and 16), and

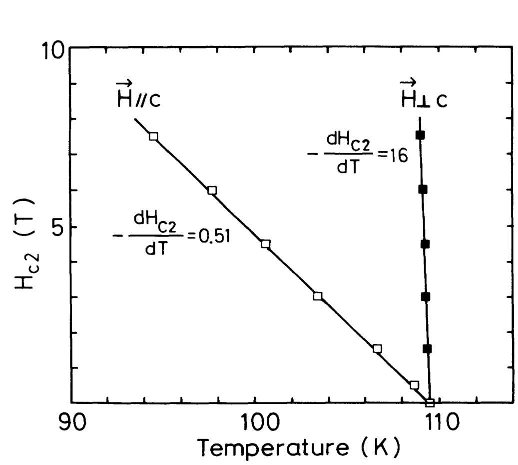

FIG. 4. Temperature dependence of upper critical field H_{c2} defined at the conventional 50% value of the extrapolated normal-state resistivity in the magnetoresistance curves.

$Nd_{1.85}Ce_{0.15}CuO_x$ (Ref. 17) single crystals or thin films. However, a linear relation is also observed for $Bi_2Sr_2CaCu_2O_x$ thin films.[18] Suzuki and Hikita[19] have reported H_{c2}-T behavior for $La_{2-x}Sr_xCuO_4$ ($x=0.1,0.15,0.3$) thin films, which show slightly downward curvature, near linear relation, and upward curvature, respectively. In these samples, $La_{1.85}Sr_{0.15}CuO_4$ compound shows the highest T_c value, i.e., has most optimum hole concentration. Han *et al.*[5] have examined the H_{c2}-T behavior for various doped $Bi_2Sr_2Ca_2Cu_3O_x$ polycrystalline samples and suggested that increases sample quality leads to a more linear H_{c2} relation and second phase contributions may play a crucial role in the curvature. The H_{c2}-T behavior defined by $\rho(T)/\rho_N(T)=0.5$ would be influenced by hole concentration, sample quality, and existence of impurity phase. Over doping of holes, low sample quality, and twin boundary in $YBa_2Cu_3O_x$ (Ref. 20) tend to give an upward curvature. The linear relation in H_{c2}-T curve for the $Bi_2Sr_2Ca_2Cu_3O_x$ whisker assures of its high quality and indicates that the sample has a hole concentration near the optimum one.

The values of $-dH_{c2}/dT$ near T_c for **H**$\|$**c** axis and **H**$\perp$**c** axis are 0.51 and 16 T/K, respectively. Using these values, we obtain values of $H_{c2}(0)=39$ and 1210 T by applying the Werthamer-Helfand-Hohenberg (WHH) theory,[21] $H_{c2}(0)=0.69T_c(dH_{c2}/dT)$. The effectiveness of the application of the WHH theory has been reported by Tajima *et al.*[14] They have directly measured H_{c2} for the $YBa_2Cu_3O_x$ single crystal at 4.2 K by applying a pulsed magnetic field up to 50 T, and observed a good agreement with a prediction of WHH theory. The $H_{c2}(0)$ values are used to calculate the coherence length (ξ) from the Ginzburg-Landau relation:

$$\xi_{ab}^2(0)=\Phi_0/2\pi H_{c2}^{\|c}(0)$$

and

$$\xi_c(0)=\Phi_0/2\pi H_{c2}^{\perp c}(0)\xi_{ab}(0) ,$$

where Φ_0 is the flux quantum. We then obtain $\xi_{ab}(0)=29$Å and $\xi_c(0)=0.93$ Å, and an anisotropy ratio of 31. It should be noted that the coherence lengths would be overestimated because the H_{c2} values are estimated from the field-broadened transition curves, which involve thermally activated resistivity as shown in Figs. 2 and 3. The intrinsic coherence lengths would be shorter than the values obtained here. However, it is significant to compare the values of coherence lengths and the anisotropy with that for other compounds.

Critical temperatures, $-dHc_2/dT$, coherence lengths, and anisotropy ratios for $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ [$n=2$ (Ref. 1), 3] and $Tl_2Ba_2Ca_{n-1}Cu_nO_x$ ($n=1,2,4$) (Refs. 2 and 16) compounds are listed in Table I. These values are obtained by the same definition of H_{c2} [$\rho(T)/\rho_N(T)=0.5$] and the same analysis with WHH theory and GL relations. The $\xi_{ab}(0)$ value of 29 Å in the present $Bi_2Sr_2Ca_2Cu_3O_x$ whisker is almost the same as the value of 27 Å for the $Bi_2Sr_2CaCu_2O_x$ single crystal.[1] The small

TABLE I. Critical temperature, $-dHc_2/dT$, coherence lengths, and anisotropy ratio for $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ ($n=2,3$) and $Tl_2Ba_2Ca_{n-1}Cu_nO_x$ ($n=1,2,4$) compounds.

Compounds	T_{c0} (K)	$-dH_{c2}^{\parallel c}/dT$ (T/K)	$-dH_{c2}^{\perp c}/dT$ (T/K)	$\xi_{ab}(0)$ (Å)	$\xi_c(0)$ (Å)	Anisotropy ratio	Ref.
$Bi_2Sr_2Ca_2Cu_3O_x$	106.5	0.51	16	29	0.93	31	Present
$Bi_2Sr_2CaCu_2O_x$	81	0.75	45	27	0.45	60	1
$Tl_2Ba_2CuO_x$	86	0.36	5	52	3	14	2
$Tl_2Ba_2CaCu_2O_x$	97	0.4	1.8	31	6.8	4.5	2
$Tl_2Sr_2Ca_3Cu_4O_x$	93	0.25	1.1	45	10	4.4	2,16

$\xi_c(0)$ value (0.93 Å) and the large anisotropy ratio (31) for the $Bi_2Sr_2Ca_2Cu_3O_x$ whisker indicates that this compound is expected to show strong two-dimensional properties as in the case of the $Bi_2Sr_2CaCu_2O_x$ compound. The anisotropy ratio of the Tl-system compounds is much smaller than that of the Bi-system compounds, although they have an analogous structure. Therefore, the kind of "blocking layer" that separates the CuO_2 layers is one of the intrinsic factors for determining the degree of anisotropy. For the $Tl_2Ba_2Ca_{n-1}Cu_nO_x$ ($n=1,2,4$) compounds, Mukaida *et al.*[2] have reported that the $\xi_c(0)$ decreases as the number of CuO_2 layers decreased, while the $\xi_{ab}(0)$ is almost independent of n. Although the coherence lengths, especially $\xi_c(0)$, would be overestimated due to misalignment, the same tendency is observed for the $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ ($n=2,3$). These results suggests that the ratio of thickness between "blocking layer (Bi_2O_2)" and "mediating layer,"[22] which contains CuO_2 layers inside the blocking layer would be another important factor for determining the degree of anisotropy.

In conclusion, we have measured the magnetoresistance for the $Bi_2Sr_2Ca_2Cu_3O_x$ whisker. Linear relation is obtained in H_{c2}-T curve defined at $\rho(T)/\rho_N(T)=0.5$, and according to the WHH theory and the GL relations, the coherence lengths of $\xi_{ab}(0)=29$ Å and $\xi_c(0)=0.93$ Å are obtained for the $Bi_2Sr_2Ca_2Cu_3O_x$ phase. The large anisotropic factor of coherence length (31) and the small $\xi_c(0)$ value indicate that the $Bi_2Sr_2Ca_2Cu_3O_x$ compound is expected to show strong two-dimensional properties.

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