Anisotropy of the magnetic properties of c-axis-aligned $HgBa_2Ca_2Cu_3O_{8+\delta}$ powders

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We report the anisotropy of magnetic properties of c-axis-aligned $HgBa_2Ca_2Cu_3O_{8+\delta}$ powders embedded in epoxy. The alignment was done by applying a 7-tesla magnetic field at room temperature. The temperature dependence of the anisotropic ratio, $\chi_{\parallel c}(T)/\chi_{\perp c}(T)$, in the superconducting state was derived from data measured with zero-field cooling and field cooling for both parallel and perpendicular to the c axis at 30 G. The anisotropic ratio of about 3.05 was obtained at 5 K. The magnetization hysteresis loops $M(H)$ were measured up to ± 5 tesla at various temperatures. The magnetic flux irreversibility, calculated from $M(H)$ curves, decreases exponentially with increasing magnetic field, and the critical current density was estimated using the Bean model (i.e., $J_c = 32\Delta M/d$, where d was taken to be the average particle diameter of 2.5 μm). $J_c(H\|c)$ at 5 K in 0.5 tesla was found to be approximately 10^7 A/cm^2. The anisotropic ratios of the magnetic flux irreversibilities decrease rapidly with increasing magnetic field up to 0.5 tesla but decrease slowly in the field region higher than 0.5 tesla; the decrease of the ratios indicates that more significant activation of fluxoid in the c direction reduces $\Delta M(H\|c)$ rapidly. The data of $\Delta M_{\parallel c}$ and $\Delta M_{\perp c}$ in the low-temperature region below 30 K can be fitted by the exponential function $\Delta M(T) = a\exp(-T/T_0)$ with $T_0 = 14.2$ K, $a = 3.75$ emu/g for $H\|c$ and $T_0 = 18.2$ K, $a = 2.50$ emu/g for $H\perp c$ at 4 tesla, and in the high-temperature region above 30 K, the simple power law $\Delta M(T) = b(1-T/T_c)^n$ was observed with $n = 6.42$, $b = 32.9$ emu/g for $H\|c$ and $n = 4.65$, $b = 11.2$ emu/g for $H\perp c$ at 0.5 tesla.

I. INTRODUCTION

The discovery of superconductivity at 94 K in the $HgBa_2CuO_{4+\delta}$ system, a single-CuO_2-layer compound, by Putilin *et al.*[1] was enough to attract many investigators' attention, because many researchers expected that the highest T_c would occur in a mercury-based compound with more CuO_2 layers, as in thallium compounds. A successive increase of T_c is achieved in the mercury oxide family ($HgBa_2Ca_{n-1}Cu_nO_{2n+3+\delta}$, $n = 1,2,3,4$)[2–4] as shown by the extensive study of many investigators. Anyway, cuprate oxides which show high-T_c superconductivity have layer structures in which several kinds of oxide layers are periodically stacked along the c-axis. Physical properties in the layered crystals are highly anisotropic. In this respect, single crystals are preferable in studies of the intrinsic properties. However, there are no reports of growing single crystals. In particular, there are only some reports on the anisotropic properties for c-axis-aligned $HgBa_2CuO_{4+\delta}$,[5] oriented $HgBa_2CaCu_2O_{6+\delta}$ thin films[6] and aligned $(Hg,Pb)Ba_2Ca_2Cu_3O_{8+\delta}$.[7] To our knowledge, anisotropic properties of single-phase $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) have not been reported yet. Instead of making single crystals in this work, we have prepared c-axis-aligned Hg-1223 to investigate the Cu-O plane characteristics. The orientation was performed by applying a high magnetic field to the sample powder embedded in epoxy. We report the temperature dependence of magnetization at a low applied magnetic field and the field dependence of magnetization at various temperatures in both the parallel and the perpendicular orientation to the c-axis for the c-axis-aligned Hg-1223 powders. We also discuss the anisotropic nature of the susceptibility and the critical current densities calculated from the magnetic hysteresis loops.

II. EXPERIMENTAL DETAILS

The source material for high-pressure synthesis was a mixture of precursor materials of $Ba_2Ca_2Cu_3O_7$ and yellow HgO. The precursor materials were prepared by calcining a well-ground mixture of $BaCO_3$, $CaCO_3$, and CuO powders with the nominal composition, at 930 °C for 20 h in O_2. After regrinding and mixing with yellow powdered HgO, the pressed pellets were sealed in a gold capsule of 4 mm diameter × 6 mm length. The sample capsule was heated in an internal graphite tube heater at 850 °C for 1 h under a pressure of 5 GPa. The sample was subsequently quenched to room temperature before the pressure was released. Finally the sample was annealed at 300 °C for 5 h in flowing oxygen in a similar way as in Ref. 8. The sintered single-phase superconducting pellets were ground to a powder with average microcrystalline grain size 2–3 μm, mixed with the monomers of epoxy resin (Cemedine EP-007) in a Teflon tube of diameter 4 mm with typical powder:epoxy ratio of 2:3, then aligned for 14 h in a 7-T Bruker superconducting magnet at room temperature using the anisotropic normal-state magnetic susceptibility. The degree of c-axis alignment is checked from the intensities of the tetragonal (00*l*) line of the pattern. The x-ray powder diffraction (XRD) patterns were obtained using a Rigaku RINT 1000 diffractometer with monochromated Cu $K\alpha$ radiation. Magnetic susceptibility was measured from 160 to 5 K under a field of 30 G, and magnetic hysteresis

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loops were obtained up to ±5 T using a Quantum Design Inc. superconducting quantum interference device magnetometer.

III. RESULTS AND DISCUSSION

Figure 1 shows the powder x-ray diffraction pattern of the Hg-1223 compound with three Cu-O layers for both randomly oriented powders and *c*-axis-aligned powders embedded in epoxy. All peaks can be identified by the Hg-1223 tetragonal structure with $a = 3.852$ Å and $c = 15.792$ Å. The (00*l*) peaks are predominant in the aligned sample, where the degree of *c*-axis alignment was checked by the equation $P(006) = 1 - \beta$, where

$$\beta = (I_{110}/I_{006})^{\text{aligned}} / (I_{110}/I_{006})^{\text{unaligned}} ,$$

and I_{110} and I_{006} are the relative intensities of the (110) and (006) peaks. The value of $P(006)$ was determined to be 0.994. Rocking-curve analysis of the (006) reflection of the sample reveals full width at half maximum (FWHM) of about 3.5° as shown in the inset of Fig. 1(b). We can also confirm the anticipated *c*-axis orientation along the applied field at room temperature under ambient pressure.

Figure 2 shows the temperature dependence of the magnetic susceptibility $\chi(T)$ for the *c*-axis-aligned Hg-1223 sample field cooled (FC) and zero-field cooled (ZFC) with the low field of 30 G parallel and perpendicular to the *c* axis. A superconducting transition temperature T_c of 131 K was observed for this sample. Unlike a bulk

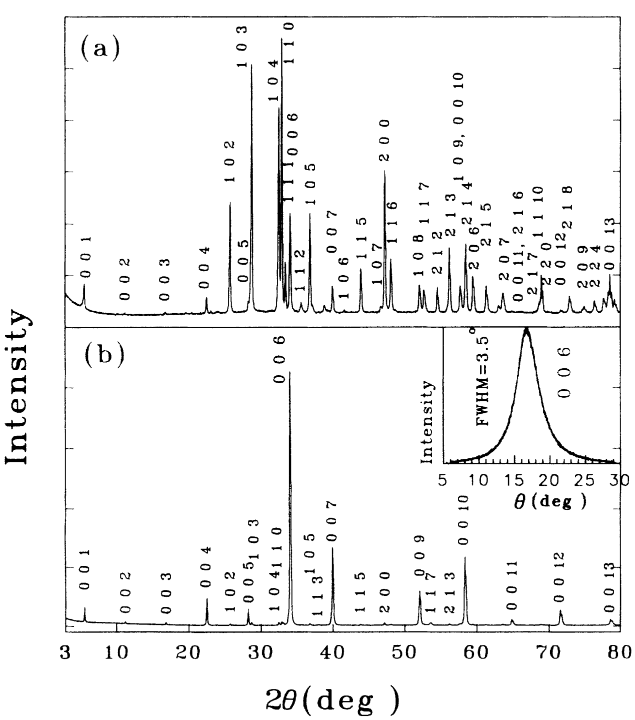

FIG. 1. (a) X-ray diffraction patterns for randomly oriented Hg-1223 powder. (b) XRD pattern of aligned Hg-1223 powders in epoxy. [The inset displays the θ rocking curve with FWHM = 3.5° measured at (006).]

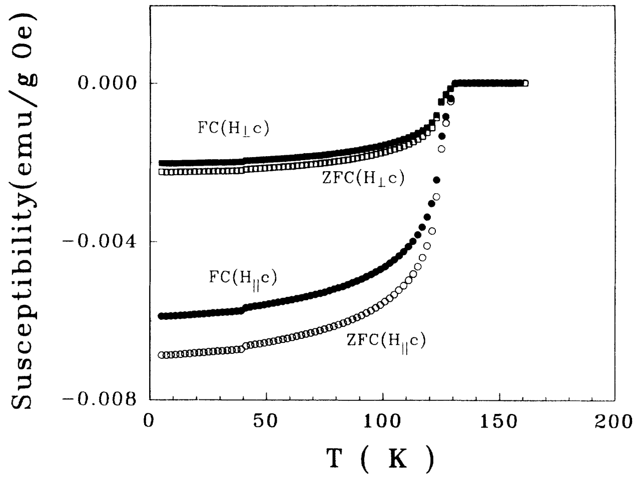

FIG. 2. Temperature dependence of magnetic susceptibility for both the parallel and the perpendicular directions to the *c* axis.

sample, the diamagnetic signals in both directions decrease monotonically upon increasing temperature even at temperature far below T_c; this can occur simply from London penetration at isolated grain surfaces. A fairly high ZFC diamagnetic field-shielding signal $-\chi_{\parallel c}^{\text{ZFC}} = 0.47$ is obtained for the applied field parallel to the *c* axis, using the x-ray density $\rho = 5.8$ g/cm^3 and powder mass $m = 35.8$ mg. The large value of the diamagnetic signal is fully expected when the surface screening current of the microcrystalline grains is around the Cu-O superconducting *ab* plane. For the FC (field expulsion) data, a somewhat smaller value of $-\chi_{\parallel c}^{\text{FC}} = 0.40$ is obtained for $H \parallel c$ due to the flux pinning inside the grain. For an applied field perpendicular to the *c* axis, low diamagnetic signals for ZFC and FC samples are expected for this layered structure.

Figure 3 shows the temperature dependence of the anisotropic ratios $\chi_{\parallel c}(T)/\chi_{\perp c}(T)$, for ZFC and FC for the aligned powder sample of Hg-1223. The anisotropic ratio

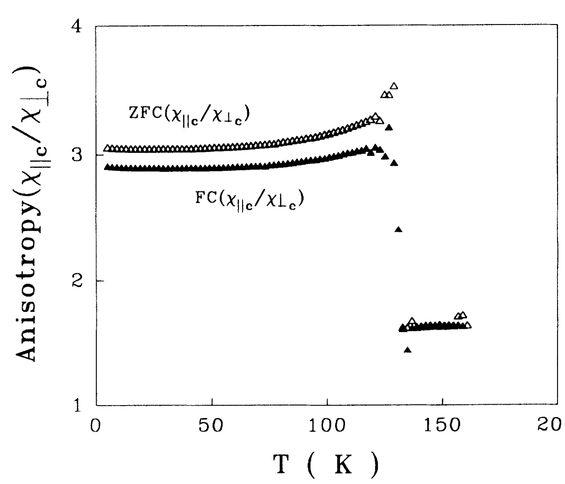

FIG. 3. Temperature dependence of anisotropic ratios of magnetic susceptibility for ZFC and FC samples.

for FC is slightly smaller than that for ZFC, which is due to the flux-pinning effect; this effect is dominant parallel to the c axis. The anisotropic ratio of about 3.05 is observed at 5 K for ZFC. This value is lower than that of 9.8 observed for c-axis-aligned $(Bi,Pb)_2Ca_2Sr_2Cu_3O_{10}$ powders,[9] but higher than that of 2.5 observed for c-axis-aligned $YBa_2Cu_3O_7$ powders[10,11] at a low temperature. This indicates that the mercury copper oxide family is an intermediately anisotropic superconductor, as expected from the structure with the copper oxide planes linked by the O-Hg-O chains. As the temperature increases, the anisotropic ratios increase from about 3.05 at 5 K to 3.5 around T_c. This probably indicates that a reduced diamagnetic signal, due to the London penetration depth which increases more significantly perpendicular to the c axis, pushes these ratios up. As the temperature approaches T_c, a paramagnetic signal starts to appear in both $\chi_{\parallel c}$ and $\chi_{\perp c}$. A normal-state anisotropic ratio around 1.6 is observed for aligned Hg-1223.

In order to obtain information about the anisotropic nature of the critical current density, we measured magnetization loops $M(H)$ for the aligned Hg-1223 powders with an applied magnetic field up to ± 5 T. For eight distinct temperatures, Figs. 4(a)–4(d) present the resultant hysteresis loops in an applied field parallel and perpendicular to the c axis of aligned Hg-1223.

The field dependence of the anisotropic ratios of $M_{i,\parallel c}(H)/M_{i,\perp c}(H)$ at different temperatures is extracted from the initial magnetization curve $M_i(H)$, as shown in Fig. 5. A rapid decrease of the ratios appears up to 0.5 T, while no appreciable change is seen in the high-field region above 0.5 T. This indicates that the flux pinning is more insensitive for $H \perp c$ than for $H \parallel c$ in a low field.

Also, the magnetic-flux irreversibility ΔM is calculated from the hysteresis loop both parallel and perpendicular to the c axis as a function of applied magnetic field at various temperatures shown in Fig. 6, where ΔM is the difference in magnetization $(M_+ - M_-)$ between the increasing and the decreasing field process. Critical current densities were then estimated using the Bean model,[12] i.e., $J_c = 32\Delta M/d$, where d was taken to be the average particle diameter of 2.5 μm. J_c for the magnetic field parallel to the c axis was estimated to be approximately $\sim 10^7$ A/cm^2 at 5 K at a magnetic field of 0.5 T. This value is comparable to the value reported for a bulk Hg-1223 sample by Schilling *et al.*[13] The ΔM for both directions

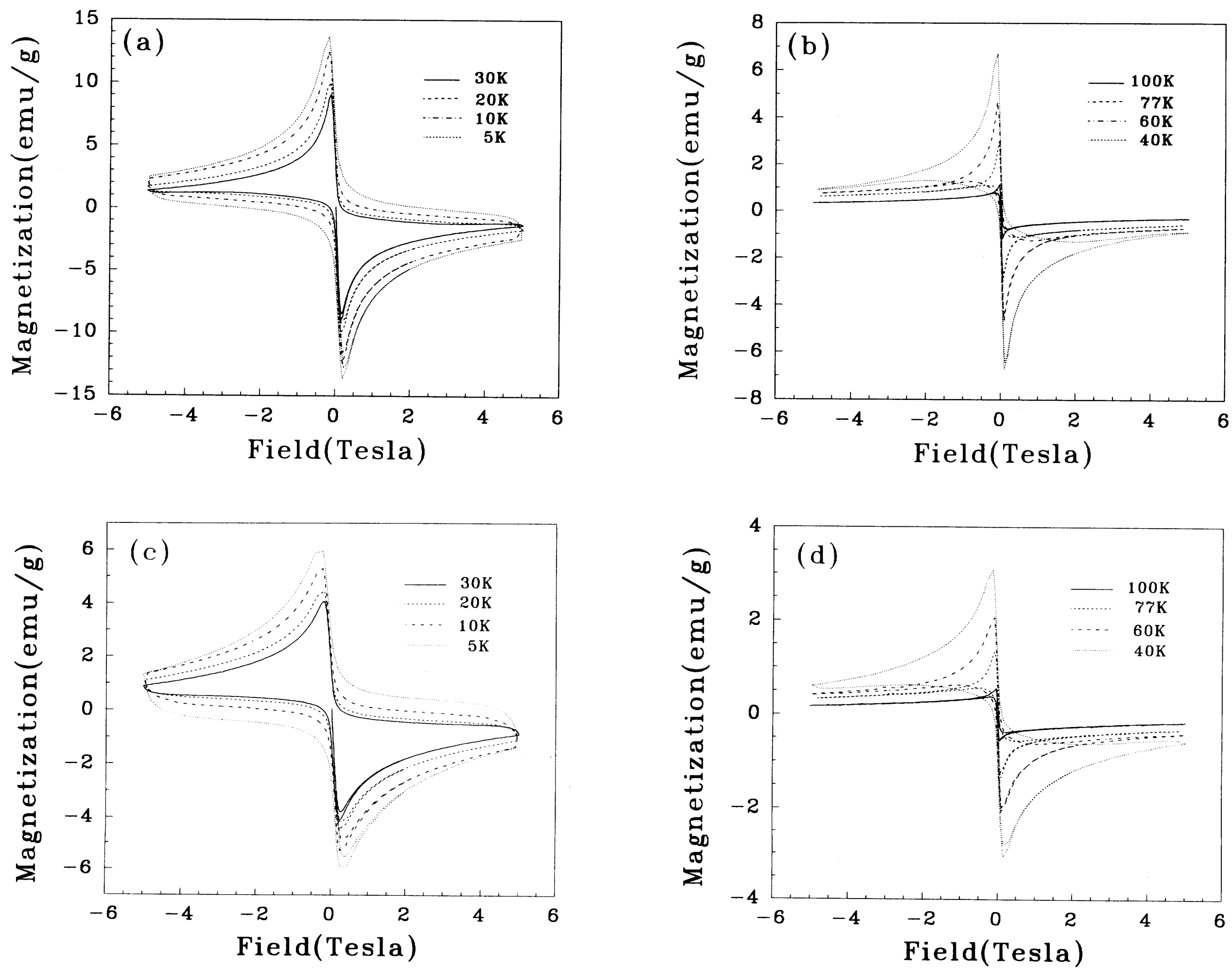

FIG. 4. Magnetization hysteresis loop measured at 5, 10, 20, 30, 40, 60, 77, and 100 K for aligned Hg-1223. (a) and (b) correspond to $H \parallel c$, whereas (c) and (d) correspond to $H \perp c$.

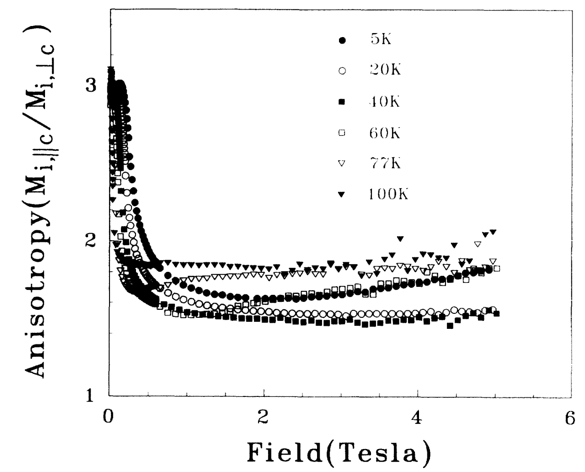

FIG. 5. Anisotropic ratio $M_{i,\|c}/M_{i,\perp c}$ of initial magnetization as a function of applied magnetic field at 5, 20, 40, 60, 77, and 100 K.

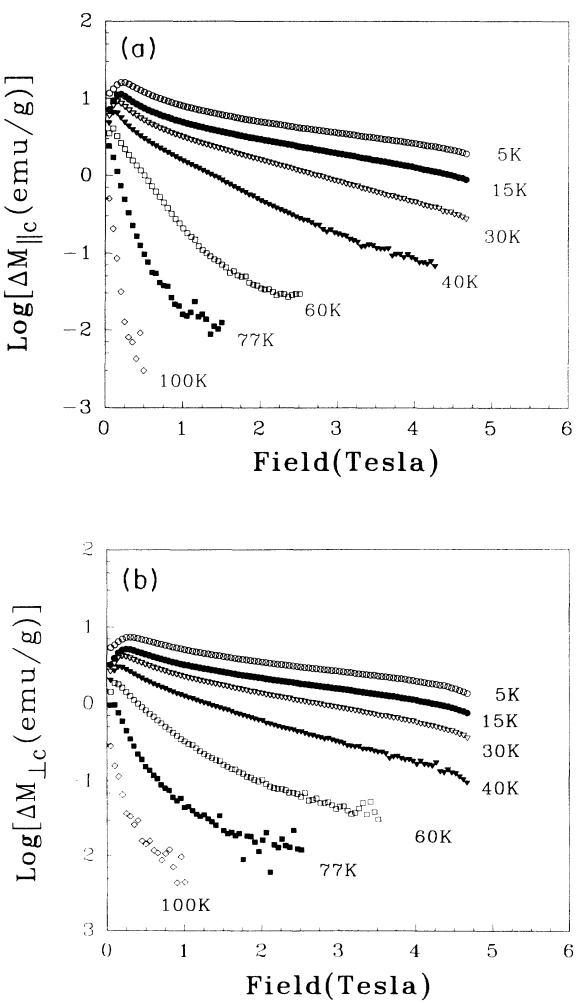

FIG. 6. (a) Magnetic-field dependence of the magnetic-flux irreversibility $\Delta M_{\|c}$ at 5, 15, 30, 40, 60, 77, and 100 K. (b) Magnetic-field dependence of the magnetic-flux irreversibility $\Delta M_{\perp c}$ at 5, 15, 30, 40, 60, 77, and 100 K.

decreases exponentially with increasing applied magnetic field. But ΔM perpendicular to the c axis is more insensitive to the applied field at all temperatures. In general, the activation energy is larger and more insensitive for $H \perp c$ than for $H \| c$. Therefore, ΔM decreases more quickly for magnetic fields parallel to the c axis. This can be attributed to the more significant thermally activated fluxoid motion for the field in the c-axis direction. This behavior was reported by Watanabe *et al.*[14] in a $YBa_2Cu_3O_{7-\delta}$ film, Kumakura *et al.*[15] in textured $Bi_2Sr_2CaCu_2O_x$ tapes, and Nishizaki *et al.*[16] in single-crystalline thin films of $YBa_2Cu_3O_{7-\delta}$. The remarkable feature of Fig. 6 is that ΔM declines gradually with increasing applied magnetic field; there is no abrupt drop of ΔM in the low-field range (<0.1 T). It is well known that the $\Delta M(H)$ behavior of a sample consisting of a weak-link network shows an abrupt $\Delta M(H)$ drop in the low-field region.[17,18] Therefore, it is concluded that no sign of weak links exists in the $\Delta M(H)$ behavior in the present study.

The anisotropic ratio of the magnetic-flux irreversibility is defined by $\Delta M_{\|c}(H)/\Delta M_{\perp c}(H)$. These values decrease rapidly with increasing applied magnetic field up to 0.5 T at all temperatures but decrease slowly in the high-field region at a low temperature, as shown in Fig. 7. Our results indicate that the more significant activation of the fluxoid in the c direction reduces ΔM rapidly in a low field and/or in a high temperature. Ultimately, these values decrease below 1 with increasing applied magnetic field at a temperature above 30 K, where $\Delta M_{\|c}(H)/\Delta M_{\perp c}(H)=1$ does not mean that J_c is independent of sample orientation because of the shape of the grains. Recently, Lewis *et al.*[5] reported that J_c at 0.8 T and 20 K was independent of $HgBa_2CuO_{4+\delta}$ sample orientation. But we have no evidence that J_c for Hg-1223 is independent of sample orientation in our study.

The temperature dependence of $\Delta M_{\|c}$ and $\Delta M_{\perp c}$ for various applied magnetic fields is shown in Figs. 8 and 9, respectively. Linear behavior in the low-temperature region below 30 K indicates that the dependence can be

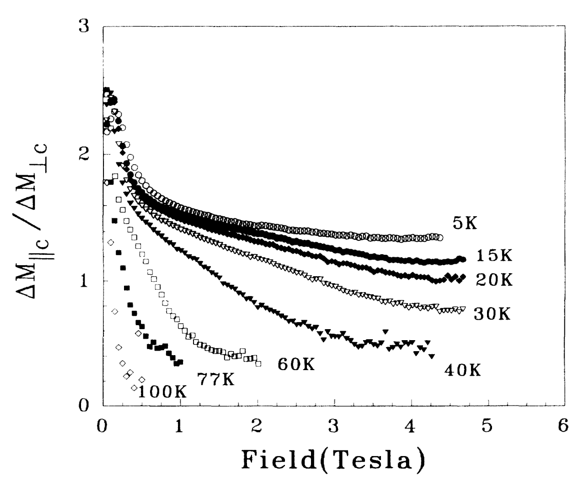

FIG. 7. Anisotropic ratio of the magnetic-flux irreversibility $\Delta M_{\|c}/\Delta M_{\perp c}$ as a function of applied magnetic field at 5, 15, 20, 30, 40, 60, 77, and 100 K.

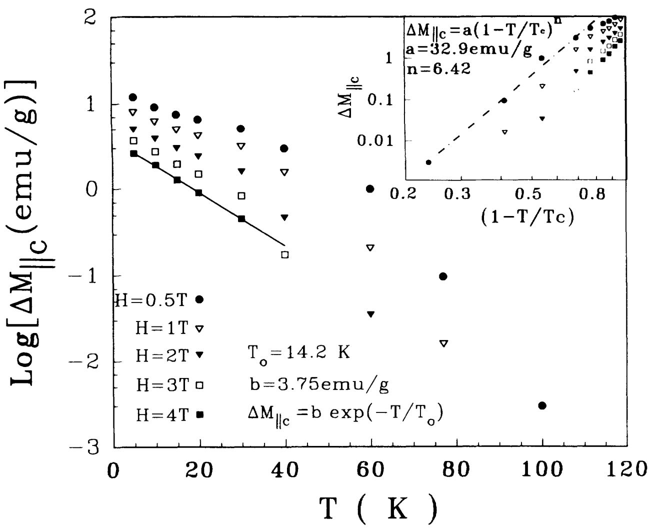

FIG. 8. Temperature dependence of the magnetic-flux irreversibility $\Delta M_{\parallel c}(T)$ at 0.5, 1, 2, 3, and 4 T. Exponential dependence of $\Delta M_{\parallel c}(T)$ below 30 K was observed. [The inset displays the logarithmic plots of $\Delta M_{\parallel c}(T)$ versus $(1-T/T_c)$ at the fields mentioned above.]

fitted by the exponential function

$$\Delta M(T)=a\exp(-T/T_0)\ ,$$

with $T_0=14.2$ K, $a=3.75$ emu/g for $H\|c$, and $T_0=18.2$ K, $a=2.50$ emu/g for $H\perp c$ at 4 T; the fitting parameter T_0 increases with decreasing applied magnetic field for both directions. A remarkable fact is that T_0 for $H\|c$ is smaller than that for $H\perp c$.

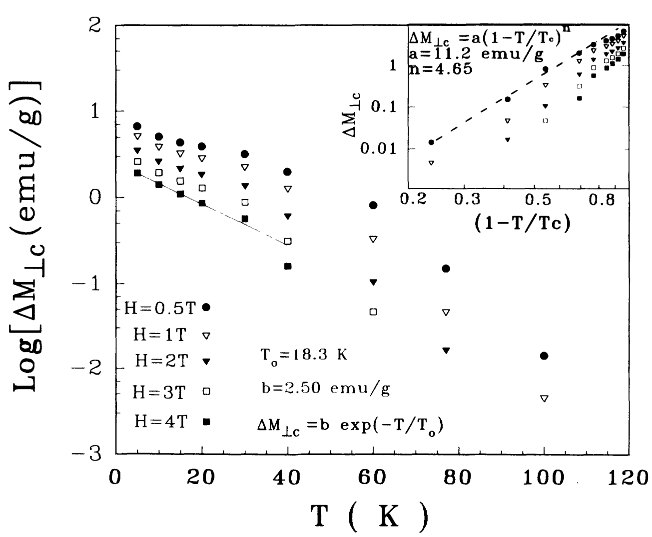

FIG. 9. Temperature dependence of the magnetic-flux irreversibility $\Delta M_{\perp c}(T)$ at 0.5, 1, 2, 3, and 4 T. Exponential dependence of $\Delta M_{\perp c}(T)$ below 30 K was observed. [The inset displays the logarithmic plots of $\Delta M_{\perp c}(T)$ versus $(1-T/T_c)$ at the fields mentioned above.]

In the high-temperature region above 30 K, no simple exponential function can be found. However, the temperature dependence of $\Delta M_{\parallel c}$ and $\Delta M_{\perp c}$ can be determined using the logarithmic plot for various applied magnetic fields as shown in the inset of Figs. 8 and 9. We can fit the dependence by the simple power law

$$\Delta M(T)=b(1-T/T_c)^n\ ,$$

with $n=6.42$, $b=32.9$ emu/g for $H\|c$ and $n=4.65$, $b=11.2$ emu/g for $H\perp c$ at 0.5 T; the power value n increases with increasing applied magnetic field for both directions. This description of the temperature dependence of the current density was obtained in an analysis based on thermally activated flux creep with collective pinning.

The temperature dependence of J_c is still rather controversial; the controversial feature, pointed out by Senoussi *et al.*[19] and verified by others,[20–24] is that the magnetic J_c decreases linearly and rapidly with increasing temperature, developing a long tail approaching T_c. The data in some cases approximately fit an exponential form $J_c\propto\exp(-T/T_0)$.[25–27] In epitaxial films near T_c, a power law of the form $J_c(T)\propto(1-T/T_c)^n$ with $n=\frac{3}{2}$ or 2 was reported.[28–30] The proper form is far from clear at this time and may differ from sample to sample, depending on material quality. Furthermore, the origin of the temperature dependence of $J_c(T)$ has not been made clear yet and further studies are needed.

IV. CONCLUSIONS

The anisotropic ratio of the susceptibility $\chi_{\parallel c}/\chi_{\perp c}$ in the superconducting state exhibits weakly temperature-dependent behavior and strongly magnetic-field-dependent behavior in the low-field region. The magnetic-flux irreversibility ΔM decays exponentially with increasing magnetic field, and the critical current density for the magnetic field parallel to the c axis was estimated to be approximately $\sim 10^7$ A/cm^2 using the Bean model at 0.5 T and 5 K. The anisotropic ratios of the magnetic flux irreversibility decrease dramatically with increasing magnetic field up to 0.5 T at all temperatures, but decrease slowly in the field region higher than 0.5 T at a low temperature. This result indicates that more significant activation of fluxoid in the c direction reduces ΔM rapidly. Surprisingly, $\Delta M_{\parallel c}(H)/\Delta M_{\perp c}(H)$ decreases below 1 with increasing applied magnetic field at temperatures above 30 K. The data $\Delta M_{\parallel c}$ and $\Delta M_{\perp c}$ in the low-temperature region below 30 K can be fitted by the exponential function $\Delta M(T)=a\exp(-T/T_0)$ with $T_0=14.2$ K, $a=3.75$ emu/g for $H\|c$ and $T_0=18.2$ K, $a=2.50$ emu/g for $H\perp c$ at 4 T, and in the high-temperature region above 30 K, a simple power law $\Delta M(T)=b(1-T/T_c)^n$ was observed with $n=6.42$, $b=32.9$ emu/g for $H\|c$ and $n=4.65$, $b=11.2$ emu/g for $H\perp c$ at 0.5 T.

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