

## Reversible magnetic properties of *c*-axis-oriented superconducting $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$

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Magnetization measurements on *c*-axis-oriented bulk superconducting  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  have been carried out with the magnetic field applied parallel to the *c* axis. Fitting the results to the variation model for magnetization suggested by Hao and Clem shows that the Ginzburg-Landau parameter  $\kappa$  is nearly constant for  $74 \leq T \leq 86$  K, with the value of 170 at 74 K, and slowly increases with temperature from  $\sim 86$  to  $\sim 100$  K.  $\kappa$  diverges in the vicinity of  $T_c$ . This unusual temperature dependence of  $\kappa(T)$  could come from extended fluctuation effects and a limitation of the Hao-Clem theory, which may fail to describe this extremely anisotropic Bi-based superconductor. By fitting the data with the value of  $\kappa$  equal to 170, the deduced values of some of the superconducting parameters are  $H_c(0) = 10600$  Oe,  $\xi(0)_{ab} = 10.5 \pm 0.6$  Å,  $\lambda(0)_{ab} = 1940 \pm 13$  Å,  $dH_{c2}/dT \approx -3.68$  T/K near  $T_c$ .

The basic properties of a superconductor, such as the thermodynamic critical field  $H_c$ , the Ginzburg-Landau parameter  $\kappa$ , and the magnetic field penetration depth  $\lambda$ , provide insight into the superconducting mechanism as well as useful information for understanding the flux-pinning mechanism. The difficulty in correctly determining these fundamental quantities in high- $T_c$  superconductors has been generally recognized<sup>1,2</sup> because of their large anisotropy and layered structures. The bismuth family,  $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$  [Bi(2:2:1:2)] and  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  [Bi(2:2:2:3)] is one of the most anisotropic of high- $T_c$  superconductors. There are experimental results<sup>3-7</sup> which have given widely varying estimates for the values of  $H_c$ ,  $H_{c1}$ ,  $H_{c2}$ , and  $\lambda$  in the bismuth family. Obtaining reliable values has proven to be an experimental challenge. This motivates the work reported here.

The most commonly used theory to describe the vortex structure in type II superconductors is the work by Abrikosov<sup>8</sup> based on the Ginzburg-Landau equation. However, for high- $T_c$  superconductors like  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (YBCO) and Bi(2:2:1:2, 2:2:2:3) which have high values of the Ginzburg-Landau parameter  $\kappa$  and large values of  $H_{c2}$ , Abrikosov's theory has been shown<sup>1,2</sup> to be valid only in a very small temperature region close to  $T_c$ , and is strongly affected by fluctuations.<sup>9-11</sup> Recently, a variation model has been proposed by Hao and Clem<sup>1,2</sup> to describe the reversible magnetization when  $H$  is parallel to one of the principal axes. A number of fundamental variables, for instance, the Ginzburg-Landau parameter  $\kappa$ , and the critical field, could be determined from direct application of this model to experimental data. Rather good agreement for YBCO single crystals and a grain-aligned polycrystalline sample have been reported by several groups.<sup>1,12,13</sup> In this paper, we present results of the application of this model to the reversible magnetization of a *c*-axis oriented

bulk superconducting Bi(2:2:2:3).

The *c*-axis oriented Bi(2:2:2:3) tape samples used for this study were made by a method reported previously.<sup>14,15</sup> A precalcined and sintered mixture from  $\text{Bi}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{CuO}$  powders with high purity was put into the silver tubes and formed into a thin tape through a combination of drawing and rolling. The tape was sintered twice with intermediate pressing. The composition of the superconducting core as determined by various chemical analysis is  $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{2.2}\text{Cu}_3\text{O}_y$ . Transmission electron microscopy (TEM) studies<sup>15,16</sup> confirmed the highly textured nature of the entire superconducting tape in which *c* axes of Bi(2:2:2:3) grains are aligned perpendicular to the tape surface and individual grains connect together smoothly with a very small angle boundary typically around  $6^\circ$  or less. Optical microscopy revealed only small amounts of  $(\text{CaSr})_2\text{CuO}_3$ , and  $(\text{CaSr})_2\text{PbO}_3$  ( $\leq 5\%$ ) segregated as precipitates. Such highly textured Bi(2:2:2:3) tapes were shown to carry more than  $47000$  A/cm<sup>2</sup> supercurrent<sup>17</sup> at 77 K at zero field demonstrating the excellent quality of the grain-aligned bulk Bi(2:2:2:3) material. The critical current density of the tape used for our study was  $\sim 30000$  A/cm<sup>2</sup> at 77 K and zero field. For the magnetization measurement, a  $40 \times 3 \times 0.1$  mm<sup>3</sup> tape was cut into ten pieces, stacked along the *c* axis and held by a GE varnish. The superconducting Bi(2:2:2:3) core had a volume of 3.81 mm<sup>3</sup>. All the magnetization measurements were carried out in a magnetic field applied parallel to the *c* axis by using a quantum design superconducting quantum interference device (SQUID) magnetometer with a 2 cm scan length, where the field inhomogeneity is estimated to be no greater than 0.01%.

The shielding data taken for a magnetic field of 2 Oe for the Bi(2:2:2:3) sample shows a very sharp transition.

The value of  $4\pi M$  at 10 K is  $-26.7$  G which leads to the fraction of ideal shielding volume close to 100% after taking account the correction for the demagnetization factor<sup>18</sup> along the  $c$  direction. A linear extrapolation of  $4\pi M(T)$  data to the zero moment line defined as  $T_c(H=0 \text{ T})=107.5$  K, and that to the horizontal  $4\pi M = -26.7$  G line gives the transition width of 2.6 K, demonstrating that our sample is rather uniform in a quite large scale (a 4-cm-long tape). The irreversible temperature,  $T_r$ , for the magnetic field applied parallel to the  $c$  axis was measured first in order to determine the reversible magnetization region within which Hao and Clem's theory applies. It was found that  $T_r$  equals approximately 70 K at  $H=4000$  Oe, 60 K at  $H=10000$  Oe, and 40 K at  $H=50000$  Oe. Due to the large fluctuation near  $T_c$  for the bismuth family superconductors, the correct subtraction of the background signal is extremely important for ensuring a reliable experimental data set, especially at high fields. What we have done was to measure the magnetization versus temperature for the sample at various fixed magnetic fields from  $T_r$  up to 250 K. A 15-min delay was introduced after each temperature change to stabilize the system so that the system temperature was always within  $\pm 0.02$  K of the target temperature prior to measurement. An accuracy of better than  $2 \times 10^{-6}$  emu (equivalent to  $6 \times 10^{-3}$  G for the value of  $4\pi M$ ) for magnetic moments was obtained for all the measurements.  $M(T)$  vs  $T$  data at temperatures between 170 and 250 K, where the contribution from fluctuation effect could be neglected, was fitted to a constant diamagnetic term contributed by the Ag sheath, and to a positive term slowly decreasing with increasing temperature attributed to the impurities, mostly from Cu oxide. The positive term was fitted by means of Curie-Weiss law. Thus, by subtracting this constant diamagnetization plus the extrapolation of Curie-Weiss type magnetization to  $T_r$ , we obtained the whole set of reversible  $4\pi M(T)$  vs  $T$  data for the superconducting Bi(2:2:2:3) free of background in fields ranging from 1000 to 50000 Oe. Shown in Fig. 1 are the plots of  $4\pi M$  vs  $T$  after subtracting the background for selected fields, 1000, 7000, 15000, 30000, and 50000 Oe. The large field-induced diamagnetism in the vicinity of  $T_c$  is well illustrated by the crossover of these  $M(T)$  curves. Particularly for magnetic fields above 20000 Oe, a field-

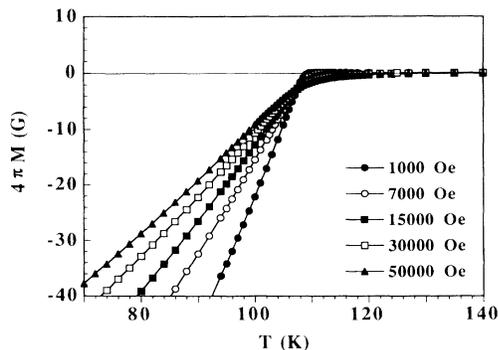


FIG. 1. Temperature dependence of background-signal-free magnetization of Bi(2:2:2:3) in various fields applied parallel to the  $c$  axis.

induced diamagnetism was observed at temperatures up to 160 K as limited by the accuracy of the magnetometer. Therefore, it is worthwhile to note that these thermal fluctuations may extend to temperatures well below  $T_c$  just as above  $T_c$ . A central issue in data fitting here is to decide the temperature at which fluctuations make the use of the Hao-Clem theory invalid. A discussion on the observed large fluctuation in the specimen will be given elsewhere.

With the fitting of  $M(H)$  vs  $H$  at each fixed temperature to Eq. (20) of Ref. 1, together with  $-4\pi M = H - B$ ,  $\kappa_c$ ,  $H_c(T)$ , and  $H_{c2}(T)$  can be derived. The subscript  $c$  for  $\kappa$  indicates the value of  $\kappa$  with the applied field along the  $c$  axis. The fitting procedure suggested by Hao *et al.*<sup>1</sup> starts by assuming a trial value of  $\kappa_c$ . Then the value, which makes the best fit of whole data set, gives an experimental value of  $\kappa_c$ . The procedure implies that  $\kappa$  is temperature independent. A constant  $\kappa$  value for superconductors should not be taken for granted, if the data values of  $M(H)$  used are taken over a significant temperature region of the superconducting state. For Bi(2:2:2:3), the data we used for fitting start from 74 K up to  $T_c$  (107.5 K). Thus, we do not assume  $\kappa$  is a constant initially, but rather a fitting parameter just as  $H_c$ . The result of  $\kappa_c$  values obtained by fitting  $M(H)$  data in the region 74–104 K is plotted in the inset of Fig. 2. As shown in the figure,  $\kappa_c$  is nearly constant in the lower temperature region with a value of 170 at 74 K, then it slowly increases at temperatures above 86 K, and finally diverges around 104 K. This unusual temperature dependence of  $\kappa_c$  (increasing as temperature increases) near  $T_c$  is opposite to what we might expect for a conventional type II superconductor.<sup>19</sup> This behavior could come from either the extended fluctuation below  $T_c$ , or perhaps the quasi-two-dimensional (2D) nature of the bismuth-based oxide superconductor. It should be pointed out that the Hao-Clem model is based on a 3D anisotropic mean-field theory which does not include the characteristic nature of a quasi-2D superconductor.

By using the average value of  $\kappa_c$  (170.4) in between 74 and 80 K,  $H_c(T)$  could be derived directly as a fitting result, which was plotted as solid circles in Fig. 2, where a

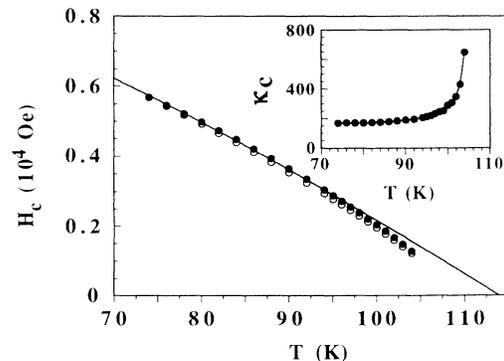


FIG. 2. Temperature dependence of  $H_c$  for a Bi(2:2:2:3) superconductor determined by using the Hao-Clem fitting method, where solid and open symbols correspond to the values derived with a constant  $\kappa_c$  (170.4) and linearly varying  $\kappa_c$ , respectively. The solid line shows a BCS fit to the  $H_c(T)$  data with a constant  $\kappa_c$ . The inset shows the temperature dependence of  $\kappa_c$ .

solid line shows a fit of  $H_c(T)$  data at temperatures between 74 and 86 K to the BCS temperature dependent  $H_c(T)$  formula given by Clem,<sup>20</sup>

$$\frac{H_c(T)}{H_c(0)} = 1.7367 \left[ 1 - \frac{T}{T_c} \right] \times \left[ 1 - 0.2730 \left[ 1 - \frac{T}{T_c} \right] - 0.0949 \left[ 1 - \frac{T}{T_c} \right]^2 \right] \quad (1)$$

which yields  $H_c(0) = (1.06 \pm 0.01) \times 10^4$  Oe with  $T_c = 114$  K for  $H$  parallel to the  $c$  direction. The fit itself is rather good for temperatures up to 96 K. It is easy to see, for temperatures above 100 K, some discrepancy between the experimental data and the BCS fit. This was attributed to the large fluctuation effect involved and hence only  $H_c(T)$  data below 86 K was used in the fit. The  $T_c$  value derived here is higher than the superconducting onset temperature measured in low-field (2 Oe)  $M$  vs  $T$  data. A similar behavior was also reported by Hao *et al.*<sup>1</sup> giving a result 2° higher for  $T_c$  from BCS fit of  $H_c(T)$  to their YBCO single-crystal data, where a fixed  $\kappa$  value was used. It is well known that  $\kappa$  for conventional type II superconductors decreases as temperature increases.<sup>19</sup> For the purpose of comparison, we did one more Hao-Clem fitting to our  $M(H)$  data by assuming  $\kappa$  to be a linearly varying function of temperature, whose value at  $T_c$  is 25% less than the value at zero degree, and equal to 170 at 74 K. Such derived values of  $H_c(T)$  are shown as open circles in Fig. 2. Then,  $H_c(0)$  and  $T_c$  were obtained via Eq. (1) to be  $1.07 \times 10^4$  Oe and 112.9 K, respectively. It is easy to see that the assumption of a slowly decreasing value of  $\kappa$  only changes  $H_c(T)$  slightly. If a temperature dependence of  $1 - (T/T_c)^2$  for  $H_c(T)$  was assumed,  $H_c(0)$  and  $T_c$  would be  $(1.00 \pm 0.03) \times 10^4$  Oe and  $112.7 \pm 1.0$  K, respectively. Nevertheless, the value of  $H_c(0)$  for Bi(2:2:2:3) is around  $1.05 \times 10^4$  Oe, which is comparable to the value for YBCO of  $1.1 \times 10^4$  Oe reported by Hao *et al.*<sup>1</sup>

$H_{c2}(T)$  can be calculated from the equation

$$H_{c2} = \kappa_c \sqrt{2} H_c(T). \quad (2)$$

The results are plotted in Fig. 3, where solid circles correspond to the values obtained by using a constant value of  $\kappa_c$  (170.4), and open circles to the values by assuming  $\kappa_c$  being a linearly decreasing function of temperature just as in the case for  $H_c(T)$ . Relatively larger difference for derived  $H_{c2}(T)$  values between fixed  $\kappa_c$  and variable  $\kappa_c$  comes from the fact that  $H_{c2}$  is directly proportional to  $\kappa$ . The slope,  $dH_{c2}(T)/dT$ , can be obtained from the BCS fit of  $H_c(T)$  which yields  $dH_{c2}/dT \approx -3.68$  T/K near  $T_c$ , where a fixed  $\kappa_c = 170.4$  is used. It is about a factor of 2 higher than the corresponding value of YBCO.<sup>1</sup> The  $H_{c2}(0)$  is estimated from the equation<sup>19</sup>

$$H_{c2} = 0.5758 \left[ \frac{\kappa_1(0)}{\kappa} \right] T_c \left| \frac{dH_{c2}}{dT} \right|_{T_c}, \quad (3)$$

where  $\kappa_1(0)/\kappa$  equals 1.20 in the dirty limit,<sup>21</sup> and 1.26 in

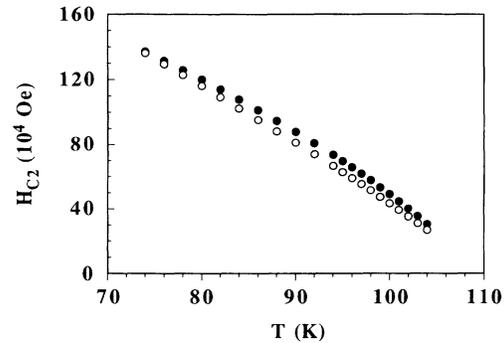


FIG. 3. Temperature dependence of  $H_{c2}$  for Bi(2:2:2:3), where solid and open symbols correspond to the values derived with a constant  $\kappa_c$  (170.4) and linearly varying  $\kappa_c$ , respectively.

the clean limit.<sup>19</sup> Thus,  $H_{c2}(0)$  is  $(297 \pm 27) \times 10^4$  Oe. From the relation  $H_{c2,||c}(0) = \phi_0 / \pi \xi_{ab}^2(0)$  ( $\phi_0$  is one flux quantum, equal to  $2.07 \times 10^{-7}$  Gcm<sup>2</sup>), we obtained  $\xi_{ab}(0) = 10.5 \pm 0.6$  Å. Obviously, the large separation between the Cu-O planes in the Bi-based superconductor makes a smaller coherence length than that in YBCO [ $\xi_{ab}(0) = 17.5$  Å].<sup>1</sup> The penetration depth  $\lambda$  can be obtained through the relation  $\sqrt{2}H_c = \kappa \phi_0 / 2\pi \lambda^2$ , which results in  $\lambda_{ab}(0) = 1940 \pm 13$  Å. Interestingly, the use of the London approximation<sup>7</sup> also leads to a value of  $\lambda_{ab}(0)$  only 8% higher than the value reported here. For a Bi(2:2:1:2) single crystal, there are several measurements of the penetration depth  $\lambda_{ab}(0)$ . Using a similar magnetization measurement method, Mitra *et al.*<sup>3</sup> obtained  $\lambda_{ab}(0) = 3000$  Å. Recently, the measurement by means of muon-spin-relaxation technique<sup>22</sup> estimated the intrinsic value of  $\lambda_{ab}(0)$  to be around 3100 Å. This factor of  $\lambda_{ab}(0)$ ,  $\frac{1}{3}$  smaller in Bi(2:2:2:3) than in Bi(2:2:1:2), may be related to their structural difference. The zero-temperature London penetration depth  $\lambda_{ab}(0)$  is proportional to  $(m_{ab}^*/n)^{1/2}$ , where  $m_{ab}^*$  is the effective mass in the  $a$ - $b$  plane,  $n$  is the carrier concentration. Bi(2:2:2:3) has three Cu-O planes in a unit cell instead of two as in Bi(2:2:1:2), which presumably gives either a higher carrier concentration or a smaller effective mass, or both. Also, a higher  $T_c$  for Bi(2:2:2:3) [approximately 30° higher than Bi(2:2:1:2)] might give a smaller value of  $(m_{ab}^*/n)^{1/2}$  than Bi(2:2:1:2), for  $T_c \propto \omega_p \propto (m^*/n)^{-1/2}$  based on the framework of BCS theory.

In conclusion, the reversible magnetization of  $c$ -axis oriented superconducting Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> has been studied with an applied field along the  $c$  direction. By applying Hao-Clem theory to our experimental data, we have established a set of fundamental variables for this family regarding to its thermodynamic properties. The large fluctuation in the vicinity of  $T_c$  has been observed which results in the diverging behavior of  $\kappa_c$  value. The fact that  $\kappa_c$  increases as temperature increases clearly shows the limitation of Hao-Clem theory in describing the reversible magnetization behavior of Bi(2:2:2:3) superconductors.

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