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Two-dimensional nature of four-layer cuprate superconductors

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The magnetization of the four-layer superconductor $CuBa_2Ca_3Cu_4O_{12-\delta}$ with $T_c \simeq 117$ K is presented. The high-field magnetization around $T_c(H)$ follows the exact two-dimensional scaling function given by Tešanović and Andreev. This feature is contrary to the inference that the interlayer coupling becomes strong if the number of CuO_2 planes in a unit cell increases. Also, the fluctuation-induced susceptibility in the low-field region was analyzed by using the modified Lawrence-Doniach model. The effective number of independently fluctuating CuO_2 layers per unit cell, g_{eff}, turned out to be $\simeq 2$ rather than 4, which indicated that two among the four CuO_2 layers were in states far from their optimal doping levels. This result could explain why $CuBa_2Ca_3Cu_4O_{12-\delta}$ shows two-dimensional behavior.

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I. INTRODUCTION

Within a high-T_c homologous series, the T_c is expected to increase with the number of CuO_2 planes per unit cell, *n*, because an increase in *n* means an increase in the number of CuO_2 planes per unit volume and thereby increases in the charge-carrier density and the coupling between the conducting planes. In fact, the T_c increases with *n* within a high-T_c family. However, this tendency does not persist above a certain value of *n*. For example, within the $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ family, the T_c increases with *n* up to $n=3$, but for $n=4$ the value is lower by about 10 K in comparison with the value for $n=3$.

For compounds with $n \geqslant 3$, the unit cells contain two structurally different CuO_2 planes. In the case of $HgBa_2Ca_3Cu_4O_{10+\delta}$ (Hg-1234), among the four layers, two layers contain Cu with square-planar coordination (type-A), and the other two contain Cu with pyramidal coordination (type-B). Yamauchi and Karppinen[1] claimed from their bond-valence-sum (BVS) calculations that the charge carriers can be inhomogeneously distributed between type-A and type-B CuO_2 planes and that the holes may be concentrated mainly in the type-A CuO_2 planes.

As a consequence of the inequivalent hole distribution, the ''*microscopic*'' T_c's of the type-A and type-B planes will differ from each other.[2] The difference between the lower and the higher T_c's becomes severe as the degree of imbalance in the hole distribution increases. Thus, at temperatures around the higher T_c, one of the two different kinds of CuO_2 planes does not play the role of a superconducting layer by itself; hence the interlayer spacing in the system can be effectively quite large.

In our previous works,[3,4] we demonstrated that in high-field region, the thermal fluctuations of Hg-1234 show two-dimensional (2D) scaling behavior around $T_c(H)$. Furthermore, the strong anisotropic nature of this compound was observed through magnetic torque measurements by Zech *et al.*[5] They reported the anisotropy ratio, $\gamma = \lambda_c/\lambda_{ab}$, of Hg-1234 to be about 52. These results implying a weak interlayer coupling are consistent with our viewpoint that the inequivalent distribution of holes can effectively cause a large interlayer spacing.

The above studies prompted an examination of whether or not an inequivalent distribution of holes is a common feature in four-layer cuprates. With this aim, we measured the reversible and fluctuation-induced magnetization of another four-layer system $CuBa_2Ca_3Cu_4O_{12-\delta}$ (Refs. 6–10) (Cu-1234) with $T_c = 117$ K. The main difference between Cu-1234 and Hg-1234 lies in the structure of the charge reservoir block (CRB). While the CRB of Hg-1234 consists of a double rock-salt block $[BaO][HgO_\delta][BaO]$ $(\delta < 1)$, Cu-1234 contains a $CuO_{2-\delta}$ plane instead of a HgO_δ plane in the block. The *c*-axis parameter of Cu-1234 is shorter than that of Hg-1234 by about 1 Å due to the relatively thin CRB. The T_c, 117 K, of Cu-1234 is known not to vary even after post annealings under various conditions.[11]

In this paper, our intention is to elucidate the dimensional nature and the superconducting properties of Cu-1234. The measured magnetization data were analyzed using the high-field scaling theory proposed by Tešanović and Andreev,[12] the modified Lawrence-Doniach model,[13–15] and the Hao-Clem model.[16–20] From these analyses, we found that Cu-1234 had a strong 2D nature which was caused by an effective reduction of the number of CuO_2 planes due to an inequivalent hole distribution. Especially, the application of the Lawrence-Doniach model to our data gave a direct evidence for the inequivalent hole distribution.

II. EXPERIMENTS

The details on the sample preparation under a high-pressure condition ($\sim$4 Gpa) are given elsewhere.[21] The lattice parameters, $a=b=3.858$ Å and $c=17.98$ Å, were obtained from x-ray diffraction. To obtain a *c*-axis aligned sample, we employed the Farrell method.[22] First, we passed the powder of the sample through a 20-μm sieve to filter out

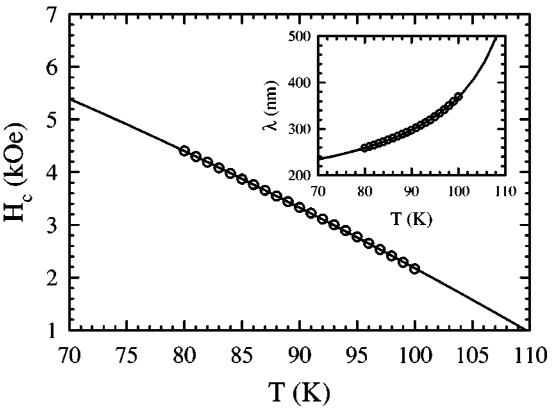

FIG. 1. Temperature dependence of the thermodynamic critical field $H_c(T)$ extracted by using the Hao-Clem model. The solid line represents the BCS temperature dependence of $H_c(T)$. The inset shows the temperature dependence of the penetration depth $\lambda_{ab}(T)$, and the theoretical curve (solid line) assumes the BCS clean limit.

grains with multidomains. This fine powder was aligned in commercial epoxy (Hardman, Inc.) under an external magnetic field of 7 T. The dimension of the permanently aligned sample was approximately 9.5 mm in length and 3 mm in diameter. From the x-ray rocking-curve measurement, the full width at half maximum (FWHM) of the (006) reflection was found to be less than 2°. The temperature dependence of the magnetization was measured in the magnetic field range of $0.05\ \mathrm{T} \leqslant H \leqslant 5\ \mathrm{T}$ by using a SQUID magnetometer (MPMS, Quantum Design).

For high fields, quite weak background contribution originated from the diamagnetic epoxy and the paramagnetic impurities were appropriately subtracted from the observed values by fitting the magnetization curve at the high temperature region of $200\ \mathrm{K} \leqslant T \leqslant 300\ \mathrm{K}$ by $C_1/T + C_2$, where C_1 and C_2 are the constants which linearly depend on external field. For $H=5$ T, the value of C_2 is about -0.8 G. The Curie-type signal was significantly small in comparison with the diamagnetic constant background.

III. RESULTS AND DISCUSSION

Various thermodynamic parameters characterizing Cu-1234 were evaluated by applying the Hao-Clem model to the reversible magnetization measured in the field range $1\ \mathrm{T} \leqslant H \leqslant 5$ T parallel to the c axis of the sample. Figure 1 shows the temperature dependence of the thermodynamic critical field $H_c(T)$ obtained from the above analysis. In this figure, the solid line represents the BCS temperature dependence of H_c.[23] This model yields $H_c(0)=0.9$ T and $T_c = 117$ K, which corresponds to a slope of $dH_c/dT = -129$ Oe/K near T_c. Using the relationship $H_{c2}(T) = \sqrt{2}\kappa H_c(T)$ and employing $\kappa=127$, which was deduced from the Hao-Clem model analysis, we estimated the upper critical field slope as $(dH_{c2}/dT)_{T_c} = -2.3$ T/K. This slope can be used to calculate the upper critical field at zero temperature by using the Werthamer-Helfand-Hohenberg formula,[24] and $H_{c2}(0)$ was estimated to be 196 T [$\xi_{ab}(0) = 12.8$ Å] in the clean limit. The penetration depth $\lambda(T)$ was evaluated by using the relationship $\lambda = \kappa(\phi_0/2\pi H_{c2})^{1/2}$, as shown in inset of Fig. 1. The solid line in the inset represents the penetration depth $\lambda_{ab}(T)$ in the clean limit with $\lambda_{ab}(0)=198$ nm. In Table I, all these parameters are summarized along with those of Hg-1234[3] for comparison. With this preliminary information, we now proceed to study other superconducting properties of Cu-1234.

TABLE I. Thermodynamic parameters of $CuBa_2Ca_3Cu_4O_{12-\delta}$ and $HgBa_2Ca_3Cu_4O_{10+\delta}$ superconductors deduced from the reversible magnetization.

	$CuBa_2Ca_3Cu_4O_{12-\delta}$	$HgBa_2Ca_3Cu_4O_{10+\delta}$
T_c(K)	117	125
κ	127	102
$-(dH_{c2}/dT)_{T_c}$ (T/K)	2.3	2.2
$H_c(0)$(T)	0.9	1.1
$H_{c2}(0)$(T)	196	205
$\xi_{ab}(0)$(Å)	12.8	12.7
$\lambda_{ab}(0)$(nm)	198	157

Figure 2 shows the irreversibility line of Cu-1234 (open circles) obtained from the dc magnetization curves $4\pi M(T)$ for $0.1\ \mathrm{T} \leqslant H \leqslant 5$ T. To obtain the line, the irreversible temperature $T_{\mathrm{irr}}(H)$ was defined as a temperature where a simple criterion $M_{\mathrm{fc}}/M_{\mathrm{zfc}} = 0.99$ holds, where M_{fc} and M_{zfc} are the field-cooled and the zero-field-cooled magnetization, respectively. The open squares in the figure denote the data for Hg-1234. We note that the irreversibility line of Cu-1234 is shifted to higher temperature in comparison with that of Hg-1234. This implies that the vortex pinning in Cu-1234 is more effective. It is generally accepted that a strong interlayer coupling gives rise to a strong flux pinning.[25] As mentioned in the Introduction, the interlayer spacing of Cu-1234 is smaller than that of Hg-1234. We conjecture that this causes an enhanced interlayer coupling.

Because the interlayer coupling of Cu-1234 is rather strong, one can expect a more enhanced superconductivity. However, the transition temperature of Cu-1234 is lower than the value of 125 K for Hg-1234 by 8 K. Not only the interlayer coupling strength[26–29] but also the carrier concen-

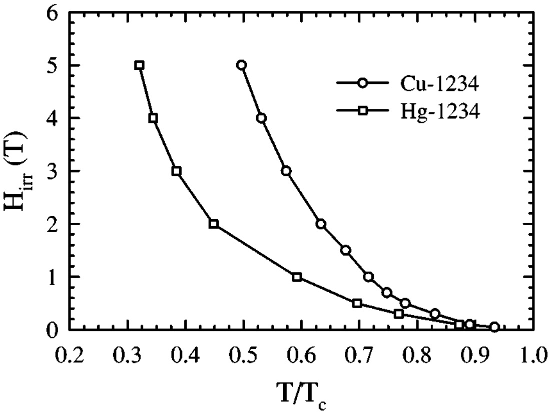

FIG. 2. Irreversibility lines of $CuBa_2Ca_3Cu_4O_{12-\delta}$ and $HgBa_2Ca_3Cu_4O_{10+\delta}$.

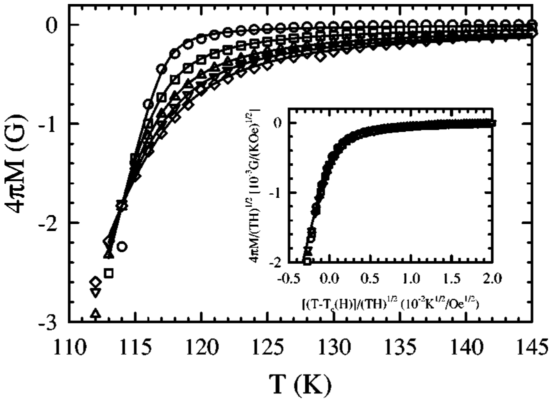

FIG. 3. Temperature dependence of the magnetization $4\pi M(T)$ around T_c. The solid lines represent theoretical curves obtained by using the exact scaling function proposed by Tešanović and Andreev [○ (1 T), □ (2 T), △ (3 T), ∇ (4 T), and ◇ (5 T)]. The inset shows 2D scaling of the fluctuation-induced magnetization $4\pi M(T,H)$.

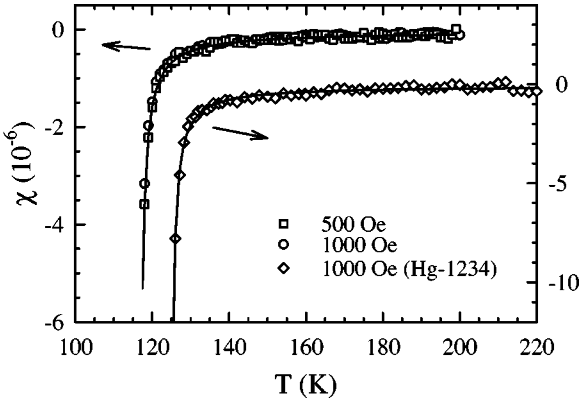

FIG. 4. Temperature dependence of the fluctuation-induced susceptibility $\chi(T)$ for Cu-1234 and Hg-1234. The solid lines represent the modified Lawrence-Doniach model for a 2D system.

tration is known to be responsible for determining the transition temperature of layered superconductors.[30] Thus, it is plausible that the relatively low T_c of Cu-1234 compared to that of Hg-1234 is due to a low carrier density within the conducting planes. The longer penetration depth of Cu-1234, $\lambda_{ab}(0)=198$ nm, than that of Hg-1234 might support this postulation.

Previously, we reported that Hg-1234 is a strong 2D superconductor.[3,4] The direct evidence for this was based on a scaling analysis of the fluctuation-induced magnetization in the high-field region. The same analysis using the high-field scaling function was applied to Cu-1234. In the high-field limit, according to Tešanović and Andreev,[12] the exact scaling function for a 2D system is given by

$$\frac{M(H,T)}{\sqrt{HT}}\,\frac{\phi_0 H'_{c2} d}{A}=x-\sqrt{x^2+2}, \tag{1}$$

where A is a constant, $x=A[T-T_c(H)]/(TH)^{1/2}$, $H'_{c2}=(dH_{c2}/dT)_{T_c}$, and d is the effective interlayer spacing. To compare the theory with our data, we used a modified form of Eq. (1):

$$\frac{M}{M^*}=\frac{1}{2}\{1-\tau-h+\sqrt{(1-\tau-h)^2+4h}\}, \tag{2}$$

where M^* is the field-independent magnetization[3,4,31–34] which is observed at a certain temperature $T^*(<T_c)$, $\tau=(T-T^*)/(T_c-T^*)$, and $h=H/H_{c2}(T^*)$. Figure 3 shows our attempt to fit the fluctuation-induced magnetization data by using Eq. (2) with the experimental values of $4\pi M^*=-1.8$ G and $T^*=114$ K. The scaled magnetization curves for various values of the field are shown in the inset of Fig. 3. The solid lines represent the theoretical curves. This analysis gives $T_c=117$ K and $(dH_{c2}/dT)_{T_c}=-2.27$ T/K, which are fairly consistent with the results from the Hao-Clem model analysis. On the other hand, the fit using the 3D version of the scaling function proposed by Ullah and Dorsey[35] was less satisfactory. As stated before, the interlayer coupling of Cu-1234 is enhanced compared with that of Hg-1234. However, the above scaling result indicates that in spite of the smaller interlayer distance, the coupling strength of Cu-1234 is still weaker than those of 3D superconductors such as $YBa_2Cu_3O_y$ and $YBa_2Cu_4O_y$.

Finally, we measured the temperature dependence of the fluctuation-induced magnetic susceptibility at fields of 500 and 1000 Oe, as shown in Fig. 4. In the modified Lawrence-Doniach model, the fluctuation-induced diamagnetic susceptibility in a 2D system is given by

$$\chi_c^{2\mathrm{D}}(T)=-g_{\mathrm{eff}}\frac{\pi k_B T\xi_{ab}^2(0)}{3\phi_0^2 s}\left(\frac{T_c}{T-T_c}\right), \tag{3}$$

where s is the c-axis repeat distance and g_{eff} is the effective number of independently fluctuating CuO_2 layers per unit cell.

The solid lines of Fig. 4 represent least-squares fits of Eq. (3) in the temperature range of $T>T_c$. From this analysis, we obtain $g_{\mathrm{eff}}\pi T_c k_B \xi_{ab}^2/3\phi_0^2 s=4.7\times10^{-8}$ and $T_c=116.4$ K. If we employ $s=17.9$ Å and $g_{\mathrm{eff}}=4$, then the coherence length $\xi_{ab}(0)$ is estimated to be 7.3 Å. However, this value is significantly smaller than the value of $\xi_{ab}(0)=12.8$ Å obtained from the Hao-Clem model and the high-field scaling analyses. This discrepancy strongly implies that the value of g_{eff} is less than four. For comparison, we reexamined the temperature dependence of the fluctuation-induced magnetic susceptibility of Hg-1234, which is also shown in Fig. 4. The $\xi_{ab}(0)$ for Hg-1234 is estimated to be 9.6 Å based on the modified Lawrence-Doniach model. This value is also smaller than the value of $\xi_{ab}(0)=12.7$ Å presented in Table I.

A possible scenario to explain these experimental results is as follows: For Cu-1234 and Hg-1234, among the four conduction layers, two CuO_2 layers are bridged to the charge reservoir block by apical oxygen. However, the other two layers have an infinite-layer structure without apical oxygen. This structural feature might cause the imbalance in the charge-carrier concentration between the two different kinds of CuO_2 planes, as suggested by the BVS calculation.[1] If one of the two kinds of CuO_2 layers is in a strongly overdoped (or underdoped) state, the superconductivity in the layers could be highly suppressed. In this context, one can assume $g_{\text{eff}}=2$ rather than 4. Assuming $g_{\text{eff}}=2$, we recalculated the $\xi_{ab}(0)$'s and obtained 10.3 Å and 12.1 Å for Cu-1234 and Hg-1234, respectively. Compared with the values obtained assuming $g_{\text{eff}}=4$, these values are close to the values obtained from the Hao-Clem model analysis.

In a high-T_c homologous series, the transition temperature increases until a certain value of n and then slowly decreases for higher values of n. The Cu-based homologous series shows the same feature. As in the Hg-based series, the compound with $n=3$ has the maximum T_c.[11,36] From the above analysis of the magnetic susceptibility, we can infer that such a decrease in T_c with n for high-T_c compounds of $n\geqslant 4$ might be due to the CuO_2 planes that do not play roles as superconducting layers.

IV. SUMMARY

In summary, the magnetization $4\pi M(T)$ of c-axis oriented Cu-1234 was measured in the field range of 0.05 T $\leqslant H \leqslant 5$ T. In comparison with Hg-1234, the irreversible region in the H-T phase diagram is more broader, which originates from enhanced interlayer coupling due to the relatively short c-axis parameter. However, from the high-field scaling analysis of the magnetization around $T_c(H)$, the dimensionality of Cu-1234 is found to be still two dimensional. Our experimental results for the magnetic susceptibilities of four-layer compounds (Cu-1234 and Hg-1234) suggest that two among the four CuO_2 layers do not contribute to the superconductivity due to an inequivalent hole distribution between the two different CuO_2 planes. This could explain the origin of the weak interlayer coupling in four-layer superconductors and provide the reason for the T_c of compounds with $n\geqslant 4$ decreasing with n. In other words, if the optimum number of holes is doped into all the CuO_2 planes equivalently, stronger interlayer coupling, and thereby a higher T_c can be achieved.

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