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Resistive transition curves in magnetic fields for $Tl_2Ba_2Ca_{n-1}Cu_nO_y$ ($n=1, 2, 4$) compounds: Dependence on the number of Cu-O layers

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A systematic measurement of the superconducting resistive transition curves in magnetic fields has been performed for $Tl_2Ba_2Ca_{n-1}Cu_nO_y$ ($n=1$, 2, 4) compounds. It is found that the broadening of the transition curves varies systematically with the number of Cu-O layers (i.e., the value n). The slope of the field-versus-temperature curves in fields parallel to the c plane increases with decreasing n, while the slope in perpendicular fields is almost independent of n. This result suggests that the upper critical fields and the coherence lengths of these compounds have a strong correlation with n. It is concluded that the coherence length along the c axis of $Tl_2Ba_2CuO_y$ is smaller than the thickness of the Tl-O-layer region. According to the Josephson-coupled layer model, $Tl_2Ba_2CuO_y$ is expected to be a two-dimensional superconductor.

Since the discovery of high-T_c oxide superconductors, the anisotropic nature of the resistivity[1,2] and upper[1,3-5] and lower[6] critical fields has been investigated for many high-T_c oxide superconductors. It is expected that the layer structure of high-T_c oxide superconductors contributes to their highly anisotropic properties. Concerning the upper critical field, a large anisotropy between fields perpendicular and parallel to the (001) basal plane has been reported for La-Sr-Cu-O,[1] $Ba_2YCu_3O_y$,[3] $Bi_2Sr_2CaCu_2O_y$,[4] and $Tl_2Ba_2Ca_3Cu_4O_y$.[5] All these compounds have Cu-O layers in their structures, and the layers are thought to be responsible for their superconductivity.

Among the high-T_c oxide superconductors the Tl-Ba-Ca-Cu-O system exhibits the highest T_c. In this system the superconducting compounds can be characterized by the chemical formula $Tl_mBa_2Ca_{n-1}Cu_nO_y$, where n is the number of Cu-O layers and m is the number of Tl-O layers ($m=1$ for a single Tl-O layer and $m=2$ for double Tl-O layers). In the case of compounds with double Tl-O layers, a range of T_c's has been reported[5,7-13] up to now: $0 \leqq T_c \leqq 85$ K for $n=1$, $90 \leqq T_c \leqq 108$ K for $n=2$, $114 \leqq T_c \leqq 125$ K for $n=3$, and $95 \leqq T_c \leqq 113$ K for $n=4$. The crystal structures of all these compounds with different n are comprised of Cu-O layers alternating with layers of Ba and double Tl-O layers stacked along the c direction. When $n \geq 2$, Ca layers are added between the Cu-O layers. If one neglects the modulated structure that occurs in these compounds, all the unit cells are tetragonal[9-13] (space group *I4/mmm*) with $a \sim 3.85$ Å and $c \sim 23.2$, 29.3, 35.9, and 41.9 Å for $n=1$, 2, 3, and 4, respectively. As mentioned above, $Tl_2Ba_2Ca_{n-1}Cu_nO_y$ superconductors have the same crystal structure and only the number of Cu-O and Ca layers differ. Therefore, this system is considered to be suitable to study the relationship between superconductivity and the number of Cu-O layers.

In this paper we report the superconducting resistive transition curves in magnetic fields of single crystals with $n=1$ and 2. The magnetic fields are applied parallel and perpendicular to the (001) basal plane. These transition curves are compared with the result for $n=4$ which was reported[5] previously. The degree of curve broadening and its relationship to the number of Cu-O layers (i.e., the value n) is discussed.

Single crystals were grown by the CuO flux method using high-purity powders of Tl_2O_3, CaO, CuO, and $BaCuO_2$ compounds. In the case of $Tl_2Ba_2CuO_y$, no CaO powder was included in the starting material. These powders were mixed to produce the needed compositions (i.e., $n=1$ and 2 compounds) and then sealed in alumina crucibles with alumina caps to inhibit Tl volatilization. The samples were heat treated between 930 ~950 °C for 1 h, the temperature depending on the nominal composition, and then cooled to 800 °C at a rate of 5 °C/h. The typical crystal size was about $0.3 \times 0.6 \times 0.025$ mm^3. More complete details of the sample preparation procedure are being published separately.[9] Composition and structure analyses of the single crystals by electron microprobe and x-ray diffraction confirmed the formation of the $Tl_2Ba_2CuO_y$ ($n=1$) and $Tl_2Ba_2CaCu_2O_y$ ($n=2$) compounds. To make low-resistance contacts Au was deposited on four separate regions of the crystal and a 25-μm-diam gold wire was bonded to each region using Ag epoxy. Resistivity-versus-temperature curves were measured in magnetic fields up to 12 T. The temperature was measured with a carbon-glass resistor. The magnetic field was applied both perpendicular and parallel to the (001) basal plane, but always perpendicular to the probing current (0.1 mA) direction.

Figure 1 shows the temperature dependence of the resistivity of $Tl_2Ba_2CuO_y$ and $Tl_2Ba_2CaCu_2O_y$ single crystals. The magnetic field is parallel to the c plane for Figs. 1(a) and 1(c), and perpendicular to it for Figs. 1(b) and 1(d). In zero magnetic field the zero-resistivity temperatures are 86 and 97 K for these $Tl_2Ba_2CuO_y$ and $Tl_2Ba_2CaCu_2O_y$ single crystals. A field-broadened transi-

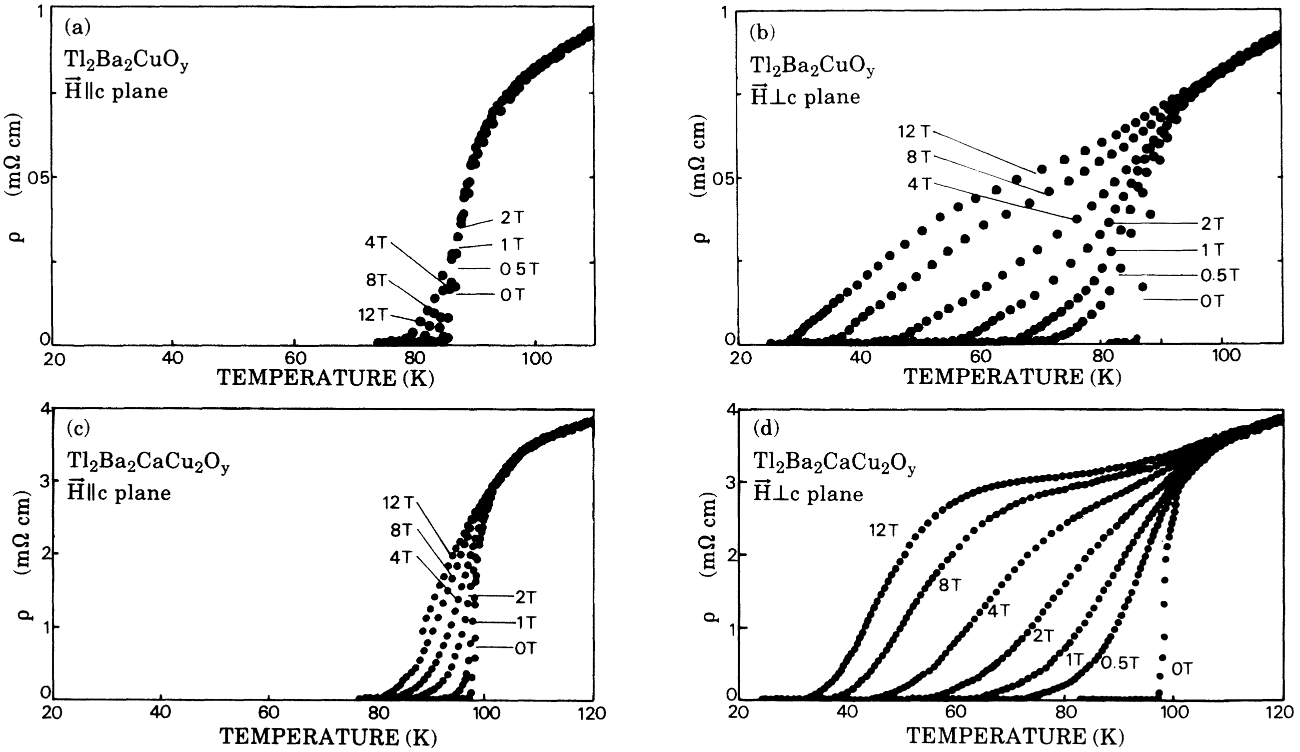

FIG. 1. Temperature dependence of resistivity of $Tl_2Ba_2CuO_y$ and $Tl_2Ba_2CaCu_2O_y$ single crystals. Magnetic fields are applied parallel to the c plane in (a) and (c), and perpendicular to the c plane in (b) and (d). The transition curves for $Tl_2Ba_2CuO_y$ are not as broad as those of $Tl_2Ba_2CaCu_2O_y$.

tion is observed when the field is perpendicular to the c plane, Figs. 1(b) and 1(d). On the other hand, transition curves are less sensitive in parallel fields. These broad transitions in fields perpendicular to the c plane are a common feature in the high-T_c oxide superconductors. Compared with those for a $Tl_2Ba_2CaCu_2O_y$ single crystal, the transition curves for a $Tl_2Ba_2CuO_y$ single crystal are less broad, especially for fields parallel to the c plane. Only the low-resistivity region, the end of the transition, has a tail to low temperature for fields greater than 2 T. In the case of $Tl_2Ba_2Ca_3Cu_4O_y$ (our previous work[5]), the degree of curve broadening is greater than that of $Tl_2Ba_2CaCu_2O_y$.

In addition to the curve broadening, a deviation from a linear temperature dependence in high magnetic fields perpendicular to the c plane and a large normal-state resistivity are observed for the $Tl_2Ba_2CaCu_2O_y$ single crystal, as compared to the $Tl_2Ba_2CuO_y$ single crystal. A much larger deviation is observed for the $Tl_2Ba_2Ca_3Cu_4O_y$ single crystal (Ref. 5). If this large deviation is caused by the strong disorder in these specimens, the normal-state resistivity of the $Tl_2Ba_2Ca_3Cu_4O_y$ specimen should be larger than that of the $Tl_2Ba_2CaCu_2O_y$ specimen. The normal-state resistivity of the $Tl_2Ba_2Ca_3Cu_4O_y$ (0.8 mΩ cm at 105 K, taken from Ref. 5) is smaller than that of the $Tl_2Ba_2CaCu_2O_y$ specimen (2.5 mΩ cm at 100 K, taken from Fig. 1). Therefore we estimate that this deviation is not caused by the disorder in these specimens, though the large normal-state resistivity of the $Tl_2Ba_2CaCu_2O_y$ specimen is probably due to the macroscopic disorder (not microscopic, since the T_c is not depressed).

The observed field-broadened curves reflect not only the anisotropic nature of the upper critical field in these materials but also the flux-creep and flux-flow resistivities.[14] As Welp *et al.* pointed out,[15] H_{c2}'s estimated from the field-broadened transition curves would be considerably underestimated, especially when H_{c2} is defined at the zero resistance point.

Figure 2 shows the midpoint-temperature (T_m) dependence of the field-broadened transition curves of $Tl_2Ba_2CuO_y$, $Tl_2Ba_2CaCu_2O_y$, and $Tl_2Ba_2Ca_3Cu_4O_y$ single crystals for fields parallel and perpendicular to the c plane. Here, the temperature is represented in the reduced form (T_m/T_c). It should be noted that a factor of $1/T_c$ must be included to obtain the slope $-dH/dT_m$. The values of $-dH/dT_m$ in a parallel field ($-dH^{\parallel}/dT_m$) are observed to increase as the number of Cu-O layers decrease, while the values of $-dH/dT_m$ in a perpendicular field ($-dH^{\perp}/dT_m$) are small and almost independent of the number of Cu-O layers. For $Tl_2Ba_2CuO_y$ the value of $-dH^{\parallel}/dT_m$ is much larger than 5 T/K, while that of $Tl_2Ba_2CaCu_2O_y$ is 1.8 T/K.

According to the Werthamer-Helfand-Hohenberg (WHH) theory,[16] the upper critical field H_{c2}'s at 0 K can be calculated from dH_{c2}/dT. As mentioned above, $-dH_{c2}/dT$ obtained from resistivity transition curves leads to an underestimation of the intrinsic H_{c2}. Nevertheless, the monotonic increase of $-dH^{\parallel}/dT_m$ with decreasing n reflects the relationship between $H_{c2}^{\parallel}(0)$ and the number of Cu-O layers, namely, $H_{c2}^{\parallel}(0)$ increases as the number of Cu-O layers decreases.

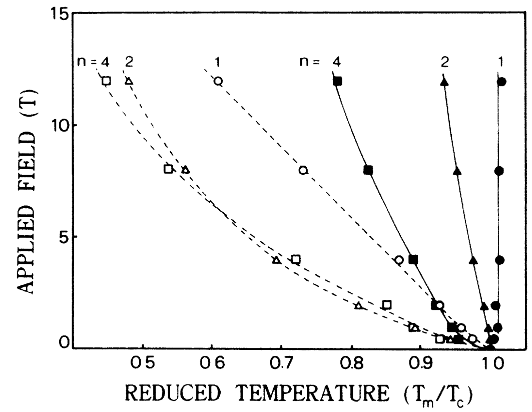

FIG. 2. Applied magnetic field vs midpoint temperature (T_m) of resistive transition curves for $Tl_2Ba_2Ca_{n-1}Cu_nO_y$ single crystals ($n=1$, 2, 4). Temperature is plotted in the reduced form (T_m/T_c). Magnetic fields are applied both parallel (solid) and perpendicular (open) to the c plane. For fields parallel to the c plane the value of $-dH/dT_m$ increases as the number of Cu-O layers decreases.

Here, instead of the number of Cu-O layers, we define the "effective layer thickness" ($t_{\rm eff}$), i.e., the region of the unit cell that contains the Cu-O layers. This thickness is defined as the distance separating the two Ba-O layers that sandwich the Cu-O region. The effective layer thicknesses are 3.86 Å for $Tl_2Ba_2CuO_y$, 7.14 Å for $Tl_2Ba_2CaCu_2O_y$, and 13.36 Å for $Tl_2Ba_2Ca_3Cu_4O_y$. These values are calculated from Ref. 13. If the Tl-O layers and adjacent regions are assumed to be sufficiently insulating, a crossover from a three dimensional to a two-dimensional (3D to 2D) superconducting state could occur when tunneling between adjacent superconducting regions becomes very small. If one defines the width of this insulating region S as the thickness of the Ba-Tl-Tl-Ba layers, then this parameter is the separation between neighboring superconducting regions. The thicknesses of the insulating regions are 7.76 Å for $Tl_2Ba_2CuO_y$, 7.52 Å for $Tl_2Ba_2CaCu_2O_y$, and 7.61 Å for $Tl_2Ba_2Ca_3Cu_4O_y$, which are also calculated from Ref. 13. With this definition the sum of $t_{\rm eff}$ and S is equal to $c/2$, half of the c lattice parameter. According to the Josephson-coupled layer model[17] a 3D-to-2D crossover is expected when the coherence length is less than $S/\sqrt{2}$. From the relations $H_{c2}^{\perp}(0)=\Phi_0/2\pi\xi_{ab}^2$, $H_{c2}^{\parallel}(0)=\Phi_0/2\pi\xi_{ab}\xi_c$, and the WHH formula,[16] the c-axis coherence length of $Tl_2Ba_2CuO_y$ is estimated to be less than 3 Å (using the values $-dH^{\parallel}/dT_m>5$ T/K and $-dH^{\perp}/dT_m=0.36$ T/K obtained from the curves in Fig. 2). This c-axis coherence length is smaller than $S/\sqrt{2}$ (i.e., 5.5 Å) while ξ_c of $Tl_2Ba_2CaCu_2O_y$, 6.8 Å ($-dH^{\parallel}/dTm=1.8$ T/K and $-dH^{\perp}/dTm=0.4$ T/K) and $Tl_2Ba_2Ca_3Cu_4O_y$, 10 Å ($-dH^{\parallel}/dTm=1.1$ T/K and $-dH^{\perp}/dTm=0.25$ T/K) are larger than $S/\sqrt{2}$. Consequently, a crossover is expected when n decreases from 2 to 1 for the $Tl_2Ba_2Ca_{n-1}Cu_nO_y$ compounds. The coherence lengths obtained here are only approximate because of the flux motion resistivity. However, when this is taken into consideration, the intrinsic coherence lengths are expected to be shorter than the values obtained above. In this case, the c-axis coherence length of $Tl_2Ba_2CuO_y$ is possibly much smaller than the criterion $S/\sqrt{2}$. Thus $Tl_2Ba_2CuO_y$ is expected to show strong 2D properties.

In conclusion, the superconducting resistive transition curves of single crystals of $Tl_2Ba_2CuO_y$ and $Tl_2Ba_2CaCu_2O_y$ in magnetic fields were measured and compared with those of a single crystal of $Tl_2Ba_2Ca_3Cu_4O_y$. It is suggested that the c-axis coherence length ξ_c decreases as the number of Cu-O layers decreases. A 3D-to-2D superconducting crossover is expected between $Tl_2Ba_2CaCu_2O_y$ and $Tl_2Ba_2CuO_y$ since ξ_c tends to become less than $S/\sqrt{2}$ (i.e., Tl-O insulating region thickness/$\sqrt{2}$).

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[1] Y. Hidaka, Y. Enomoto, M. Suzuki, M. Oda, and T. Murakami, Jpn. J. Appl. Phys. **26**, L377 (1987).

[2] S. Martin, A. T. Fiory, R. M. Fleming, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. Lett. **60**, 2194 (1988).

[3] Y. Iye, T. Tamegai, H. Takeya, and H. Takei, Jpn. J. Appl. Phys. **26**, L1057 (1987).

[4] Y. Koike, T. Nakanomyo, and T. Fukase, Jpn. J. Appl. Phys. **27**, L841 (1988).

[5] K. Togano, H. Kumakura, H. Mukaida, K. Kawaguchi, and M. Nakao, Jpn. J. Appl. Phys. **28**, L907 (1989).

[6] T. R. Dinger, T. K. Worthington, W. J. Gallagher, and R. L. Sandstrom, Phys. Rev. Lett. **58**, 2687 (1987).

[7] Z. Z. Sheng and A. M. Hermann, Nature (London) **332**, 55 (1988); **332**, 138 (1988).

[8] S. S. P. Parkin, V. Y. Lee, A. I. Nazzal, R. Savoy, T. C. Huang, G. Gorman, and R. Beyers, Phys. Rev. B **38**, 6531 (1988).

[9] K. Kawaguchi and M. Nakao, in *Proceedings of the Ninth International Conference on Crystal Growth, Sendai, 1989*, (North-Holland, Amsterdam, to be published).

[10] C. C. Torardi, M. A. Subramanian, J. C. Calabrese, J. Gopalakrishnan, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdhry, and A. W. Sleight, Science **240**, 631 (1988).

[11] M. A. Subramanian, J. C. Calabrese, C. C. Torardi, J. Gopalakrishnan, T. R. Askew, R. B. Flippen, K. J. Morrissey, U. Chowdhry, and A. W. Sleight, Nature (London) **332**, 420 (1988).

[12] C. C. Torardi, M. A. Subramanian, J. C. Calabrese, J. Gopalakrishnan, E. M. McCarron, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdhry, and A. W. Sleight, Phys. Rev. B **38**, 225 (1988).

[13] R. V. Kasowski and W. Y. Hsu, Phys. Rev. B **38**, 6470 (1988).

[14] T. T. M. Palstra, B. Batlogg, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. Lett. **61**, 1662 (1988).

[15] U. Welp, W. K. Kwok, G. W. Crabtree, K. G. Vandervoort, and J. Z. Liu, Phys. Rev. Lett. **62**, 1908 (1989).

[16] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. **147**, 295 (1966).

[17] R. A. Klemm, A. Luther, and M. R. Beasley, Phys. Rev. B **12**, 877 (1975).