Preparation, characterization, and superconducting properties of tetragonal $LaBaCaCu_3O_{7+\delta}$

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Samples of $LaBaCaCu_3O_{7+\delta}$ were prepared by standard solid-state reactions. X-ray-powder-diffraction data taken in the temperature range 6–300 K reveal no structural transition. Thermogravimetric analysis was used to determine the oxygen content δ. Both magnetization and resistivity measurements indicate sharp superconducting transitions ($\Delta T < 4$ K) at 78 K for samples with $\delta = 0 \pm 0.05$. Broad transitions were always observed for samples with $\delta < 0$, although the T_c onsets remained essentially constant. A sample with excess oxygen ($\delta > 0$) achieved by high-pressure oxygen annealing showed a broad transition, as well as a T_c which was depressed by 10 K. We consider these experimental results in the context of ordering of the cations La, Ba, and Ca as well as oxygen sublattice ordering. We estimate the electronic coefficient of specific heat γ and the Ginzburg-Landau parameters ξ_{GL}, λ_{GL}, and κ_{GL} from the measured temperature dependence of H_{c2} and the Pauli susceptibility.

INTRODUCTION

Since the first discovery of superconductors with transition temperatures (T_c) above 77 K,[1] much effort has been devoted to understanding the origin and mechanism of high-T_c superconductivity and to the search for new high-T_c materials. Detailed structural studies by x-ray[2] and neutron diffraction[3] have already established a unique structure as an oxygen-deficient layered perovskite $RBa_2Cu_3O_{7+\delta}$ (R is a rare-earth element). It is well known that the high-T_c superconducting oxides $RBa_2Cu_3O_{7+\delta}$ undergo an orthorhombic-to-tetragonal transition as a result of a variation in the oxygen content and oxygen sublattice distribution.[4] Oxygen content and oxygen distribution also dramatically affect the T_c values. When samples are heat treated at elevated temperature and/or in a reducing atmosphere, the oxygen content and T_c decrease. Many compounds in this series become tetragonal and semiconducting for $\delta < -0.5$. Tokura and co-workers[5] have demonstrated that the interrelated parameters of overall oxygen content, effective copper valence, and total charge associated with the noncopper cations all influence the superconducting transition temperature for $YBa_2Cu_3O_{7+\delta}$-like materials. We note that the orthorhombic structure is essential for achieving $T_c > 90$ K in this class of superconductors, although superconductivity near 70 K occurs in tetragonal structures for the systems $YBa_2(Cu_{0.96}Co_{0.04})_3O_{7+\delta}$,[6] $Y_{3-x}Ba_{3+x}Cu_6O_{14+\delta}$,[7] and $LaBa_2Cu_3O_{7+\delta}$.[8–10] In the system $LaBa_2Cu_3O_{7+\delta}$, both tetragonal and orthorhombic structures are found, with T_c around 60 and 90 K,[11] respectively; however, tetragonal $La_{1.5}Ba_{1.5}Cu_3O_{7+\delta}$ is not superconducting[12] although it has the same structure as tetragonal $LaBa_2Cu_3O_{7+\delta}$. Superconductivity above 70 K has been observed in $La_{3-x}Ba_{3+x}Cu_6O_{14+\delta}$ by varying the La/Ba ratio.[13] The structures of all of these superconducting and nonsuperconducting materials are closely related, which raises questions concerning the importance of crystal symmetry with respect to the origins of high-temperature superconductivity.

In an effort to probe the relationship between sublattice disorder and maximum T_c values, we first studied the system $La_{1.5}(Ba_{1-x}Ca_x)_{1.5}Cu_3O_{7+\delta}$. We found that, for $0 < x < 1.0$, all of the samples of $La_{1.5}(Ba_{1-x}Ca_x)_{1.5}Cu_3O_{7+\delta}$ display a tetragonal structure and show superconductivity above 70 K. However, all of the superconducting transitions were broad. In order to sharpen the transitions we tried varying the La/Ba/Ca ratios. Recently, Carim and co-workers[14] observed ordering phenomena in the tetragonal superconductor $LaCaBaCu_3O_{7+\delta}$, which prompted us to focus on the more homogenous $(LaBaCa)_3Cu_3O_{7\pm\delta}$ materials. In the series of tetragonal superconductors $La(Ba_{1-x}Ca_x)_2Cu_3O_{7+\delta}$, only one composition ($x = 0.5$) showed a sharp superconducting transition. In this paper, we report the synthesis, characterization, and superconducting properties of the tetragonal superconductor $LaBaCaCu_3O_{7+\delta}$ which has a sharp transition at 78.5 K, and does not undergo a tetragonal-to-orthorhombic transition.

EXPERIMENTAL RESULTS

Synthesis

Samples of $LaBaCaCu_3O_{7+\delta}$ were prepared by solid-state reaction from stoichiometric quantities of La_2O_3, BaO, $CaCO_3$, and CuO. The loose powders were thoroughly mixed and fired at 1050 °C in air for 12 h followed by a furnace cool to 975 °C. The samples were cooled to room temperature by air quenching. Then the powders were reground and heated at 975 °C in air for 10 h before furnace cooling to room temperature. After grinding a second time, the powders were pressed into loose pellets. These pellets were annealed at 575 °C in flowing O_2 for 24 h and were furnace cooled to room temperature.

X-ray diffraction

Powder-x-ray-diffraction data were taken for samples of $LaBaCaCu_3O_{7+\delta}$ using Cu $K\alpha$ radiation in the temperature range 6–300 K. Temperature control was maintained by a closed-cycle refrigerator mounted on the diffractometer. The lattice parameters were calculated from the diffraction peak positions by the least-squares method. The room-temperature x-ray-diffraction patterns indicated that samples of $LaBaCaCu_3O_{7+\delta}$ possess a single-phase tetragonal structure. The patterns are similar to those of $La_3Ba_3Cu_6O_{14+\delta}$ and showed no orthorhombic distortion within the limit of the x-ray method. The room-temperature lattice parameters determined by least-squares fitting[15] are $a = 0.3870(2)$ nm and $c = 1.161(2)$ nm, which are in good agreement with literature values.[14] With our technique, we do not observe supercell reflections.[14]

In order to determine the crystal symmetry in the superconducting state, low-temperature x-ray diffraction patterns were collected at various temperatures using a slow scanning speed to detect any line splittings. No detectable splitting from a lowering of the tetragonal symmetry can be observed down to 6 K. Within instrumental resolution, this ensures that there is no orthorhombic distortion above 0.3% in $\Delta a/a$.

The temperature dependence of the lattice parameters and unit-cell volume of $LaBaCaCu_3O_{7+\delta}$ are shown in Fig. 1. The solid line fits to the lattice parameters yield coefficients of linear expansion of $(3.9 \pm 0.4) \times 10^{-6}$/K in the a direction and $(2.9 \pm 0.2) \times 10^{-6}$/K in the c direction. Thus, the thermal expansion perpendicular to the c axis is larger than that along the c axis by about 33%. The corresponding coefficient of volume expansion is about $(1.6 \pm 0.2) \times 10^{-5}$/K. Within the resolution of this experiment, the lattice parameters vary smoothly with temperature through the superconducting transition temperature.

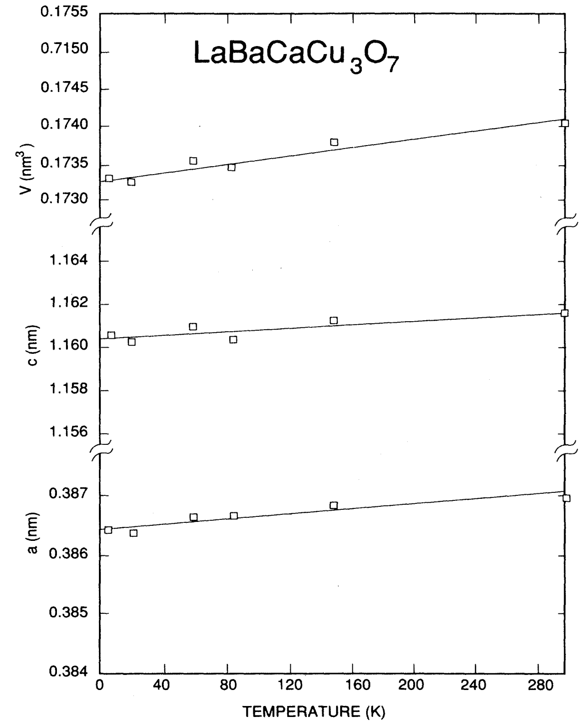

FIG. 1. The temperature dependence of the lattice parameters a, and c, and unit-cell volume of $LaBaCaCu_3O_7$.

Thermogravimetry

Thermogravimetric analysis (TGA), using a Dupont 951 TGA system, was used to determine oxygen content of samples. The typical starting sample mass was approximately 50 mg, with a balance resolution of 2 μg. A typical scan involved flowing forming gas (6% H_2, 94% N_2) through the sample chamber and ramping the temperature to 1000 °C at 10 °C/min. Oxygen loss was observed as early as 200 °C with mass loss saturating by 800 °C.

Reduction of $LaBaCaCu_3O_{7+\delta}$ by H_2 occurs according to the following chemical reaction,

$$2LaBaCaCu_3O_{7+\delta} + (7+2\delta)H_2 = La_2O_3 + 6Cu + 2CaO + 2BaO + (7+2\delta)H_2O\,.$$

The La_2O_3, CaO, BaO, and metallic Cu formed in this reaction are identified by x-ray diffraction. By monitoring the weight change of $LaBaCaCu_3O_{7+\delta}$ in the reducing atmosphere, the absolute value of δ can be obtained.

A TGA scan showing the sample weight change with temperature to 1000 °C is shown in Fig. 2. The value $\delta = -0.02$ is obtained. The oxygen content of our samples showing sharp superconducting transitions were always 7.00 ± 0.05. Samples were also made with oxygen content lower than 7.0; however, the superconducting transition was always broad, indicating the existence of

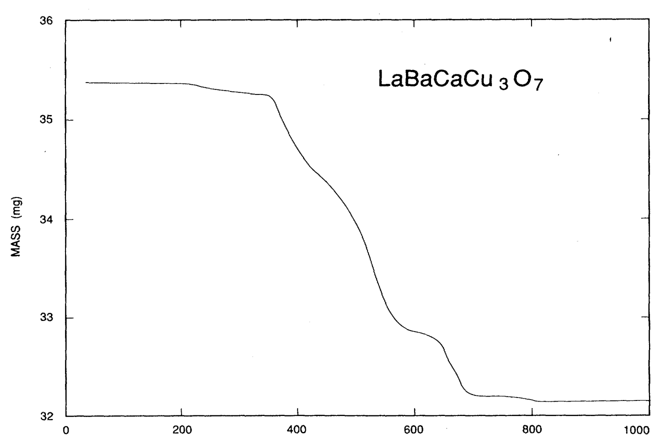

FIG. 2. A thermogravimetric analysis showing the sample mass change as temperature is increased from 20 to 1000 °C in flowing forming gas (6% H_2, 94% N_2) at a rate of 10 °C/min.

sublattice inhomogeneity associated with oxygen nonstoichiometry in some regions of the sample. In order to increase the oxygen content beyond 7.0, we annealed one sample in a high-pressure oxygen furnace at 575 °C and 3 kbar for 72 h. This was followed by a slow cool of 1 °C/min to room temperature. After superoxygenation the oxygen content of the samples determined from TGA was 7.42 ± 0.05. In addition, the sample mass was carefully determined before and after the high-pressure oxygen treatment. This measurement gave a consistent value of 7.34 ± 0.05 for the final oxygen content. For this superoxygenated sample, the magnetization measurements showed that the T_c shifted downward by 10 K, and the superconducting transition became very broad. No structural change was observed in the x-ray-powder-diffraction patterns of this high-oxygen-content sample.

Transport

Electrical resistivity data were obtained by the standard four-probe technique using silver paste electric contacts and a constant current (10 mA) source. The voltage drop was measured using a digital nanovoltmeter. Measurements were performed in the temperature range of 10–300 K.

Figure 3 shows the relative resistivity as a function of temperature for a $LaBaCaCu_3O_{7+\delta}$ sample. The sample exhibits the onset of superconductivity at 78.5 K and zero resistance at 74.2 K. The high value of the room-temperature resistivity (57 mΩ cm) most likely is due to the porous nature of the powder specimen. The sample was pressed into a loose pellet in the final annealing, to promote uniform oxygen diffusion. The normal-state resistivity is approximately linear in temperature above 90 K, with a distinct change in the slope of the resistivity data occurring near 220 K. This behavior correlates with an anomaly in the magnetic-susceptibility data described below.

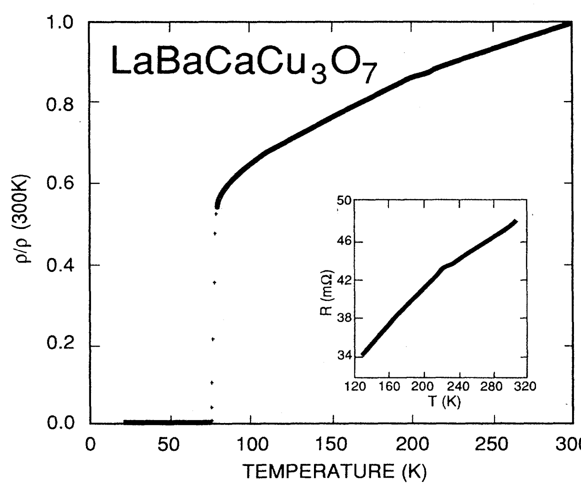

FIG. 3. Relative resistivity vs temperature for the tetragonal superconductor $LaBaCaCu_3O_7$. The zero-resistance transition point occurs at 74.2 K. The inset focuses on the break in slope at 220 K.

Magnetic susceptibility

Meissner effect, diamagnetic shielding, and normal-state magnetic-susceptibility measurements were obtained between 5 and 300 K using a Quantum Design SQUID magnetometer. Meissner effect and shielding measurements were collected in an applied field of 10 Oe. Normal-state properties were measured using fields ranging from 2 to 50 kOe.

Figure 4 shows the Meissner effect and diamagnetic shielding in $LaBaCaCu_3O_{7+\delta}$ between 5 and 120 K. These data clearly show that superconductivity is a bulk property of the sample. The Meissner effect is approximately 10% of that expected for a full diamagnetic signal. The diamagnetic shielding effect is nine times larger than the Meissner shielding, as is common in the superconducting oxides.

The normal-state magnetic susceptibility of $LaBaCaCu_3O_{7+\delta}$ was examined up to 300 K. The susceptibility is positive and can be fitted by a Curie-Weiss law of the form $\chi=\chi_0+C/(T-\Theta)$ in the temperature ranges 80–180 K, where χ_0 is the temperature-independent susceptibility, C is the Curie constant, and Θ is the Curie-Weiss temperature. Figure 5 plots $1/(\chi-\chi_0)$ vs T for the $LaBaCaCu_3O_{7+\delta}$ sample. Values of χ_0, C, and Θ obtained by a least-squares fit are 2.63×10^{-4} emu/mol, 7.54×10^{-2} emu K/mol, and 0.4 K, respectively. A straight line through the lower temperature data in Fig. 5 indicates the quality of this fit. At about 180 K, the inverse magnetic susceptibility deviates downward from this fit. This smooth change in slope in $1/(\chi-\chi_0)$ vs T continues from approximately 180 to 220 K defining a changeover region of width 40 K. For temperatures above 220 K, the data resume a Curie-Weiss behavior with the values of χ_0, C, and Θ being 3.13×10^{-4} emu/mol, 7.22×10^{-2} emu K/mol, and -11.4 K. The 220-K onset of the changeover region corresponds to a distinct change in slope of the resistivity data shown in Fig. 3. Since powder-x-ray-diffraction experiments reveal no overt modification in lattice symmetry, we hypothesize these correlated features in the magnetic susceptibility and electrical resistivity origi-

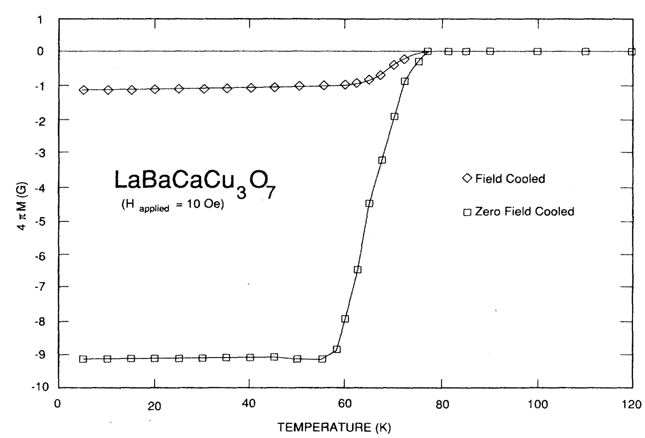

FIG. 4. Meissner effect (field cooled) and diamagnetic shielding curve (zero field cooled) as measured at $H=10.0$ Oe for $LaBaCaCu_3O_7$.

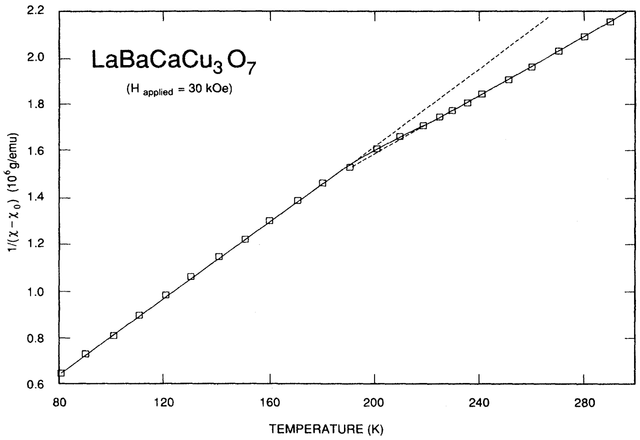

FIG. 5. Inverse susceptibility vs temperature for $LaBaCaCu_3O_7$. Two straight lines represent least-squares fits to the data as described in the text.

nate from a more subtle sublattice ordering.

We analyze the susceptibility data by writing the total temperature-independent part of the susceptibility as

$$\chi_0=\chi^{\text{core}}+\chi^{\text{Pauli}}+\chi^{\text{Landau}} , \tag{1}$$

where χ^{core} is the core diamagnetism term, χ^{Pauli} is the Pauli paramagnetism due to the conduction electrons, and χ^{Landau} is the diamagnetic orbital contribution due to the conduction electrons. The core diamagnetism may be estimated from tabulated values[16] [La^{3+}: −20; Ba^{2+}: −32; Ca^{2+}: −8; Cu^{2+}: −11; O^{2-}: −12 (all in units of 10^{-6} emu/mol)] which yield a value of $\chi^{\text{core}}=-1.77\times10^{-4}$ emu/mol. Representing the conduction-electron band effects by an effective mass, m^*, permits one to relate χ^{Pauli} to χ^{Landau} (Ref. 17)

$$\chi^{\text{Landau}}=-\frac{1}{3}\left[\frac{m}{m^*}\right]^2\chi^{\text{Pauli}} . \tag{2}$$

One can estimate the value of the electronic specific-heat coefficient, γ, from the measured Pauli susceptibility using the free-electron conversion $\gamma=\frac{1}{3}\ (\pi k_B/\mu_B)^2\chi^{\text{Pauli}}$. This estimate does not take into account various enhancements to the susceptibility or specific heat which do not apply to each equally. Therefore, this formula is only a very rough approximation; however, it is still important to get estimates of these critical parameters. By neglecting various enhancements, we approximate the effective mass m^* by the free-electron mass m, so that $\chi^{\text{Landau}}=-\frac{1}{3}\chi^{\text{Pauli}}$. Then, Eq. (1) is reduced to

$$\chi^{\text{Pauli}}=\tfrac{3}{2}\,(\chi_0-\chi^{\text{core}}) . \tag{3}$$

Using these approximations yields an estimate for χ^{Pauli} of 6.60×10^{-4} emu/mol. This gives an estimate of γ to be 48.1 mJ/K^{2}mol (16.0 mJ/K^{2}mol Cu). For $LaBaCaCu_3O_{7+\delta}$, there are no reported values of γ from specific-heat measurements to compare with our value derived from the magnetic susceptibility. However, there are reported values on $YBa_2Cu_3O_{7-\delta}$ and $(La_{2-x}Sr_x)CuO_4$. For example, Nevitt, Crabtree, and Klippert[18] obtained 54 mJ/K^{2}mol [18 mJ/K^2 (mol Cu)] and 20 mJ/K^2 (mol Cu) for $YBa_2Cu_3O_{7-\delta}$ and $La_{1.85}Sr_{0.15}CuO_4$, respectively, from heat capacity measurements, which are consistent with our results.

The upper critical field $H_{c2}(T)$ up to 50 kOe was measured magnetically with the SQUID magnetometer for temperatures near T_c. In our experiments we observe no evidence of flux lattice melting as reported in some single-crystal studies.[19] The temperature dependence of H_{c2} is shown in Fig. 6. The slope of the upper critical-field curve near T_c, in conjunction with the electronic heat-capacity coefficient estimated from the measured Pauli susceptibility, provides an estimate of certain normal-state and superconducting parameters. Values of the Ginzburg-Landau (GL) parameters[20] are derived using the BCS Gorkov equations[21] near T_c in the dirty limit. The GL parameters ξ_{GL}, λ_{GL}, and κ_{GL} depend only on quantities such as T_c, γ, and the residual resistivity ρ. The intrinsically short coherence length of the superconducting oxides (~20 Å) is not unlike the small coherence length (~100 Å) of many traditional supercondcutors in the dirty limit. Therefore, while direct applicability of the GL equations to the high-T_c materials has not been substantiated, the short coherence length makes this approach reasonable. We note that parameters derived in this manner are consistent with experimental results.

Table I contains the values of the experimentally determined quantities, as well as the parameters derived from them. The value of T_c was determined from the onset of zero-resistance. The value of $(dH_{c2}/dT)_{T=T_c}$ is taken from Fig. 6 and is shown in Table I, along with the Maki parameter[21,22]

$$\alpha=5.2758\times10^{-2}\left[-\frac{dH_{c2}(\text{kOe})}{dT}\right]_{T=T_c} .$$

The residual resistivity ρ is determined from

$$\rho=42.56\alpha/\gamma , \tag{4}$$

in units of $\mu\Omega$ cm. The values of the GL parameters are

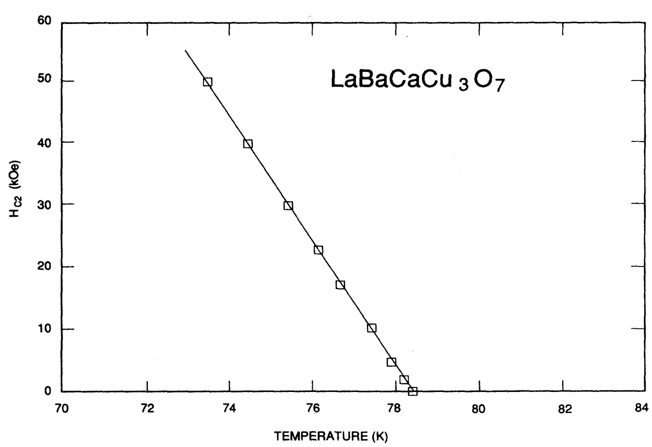

FIG. 6. Temperature dependence of upper critical field H_{c2} for $LaBaCaCu_3O_7$.

TABLE I. Values of the experimentally determined quantities and the parameters derived from them.

T_c (K)	74.2
γ (mJ/K^{2}mol)	48
$-\left(\frac{dH_{c2}}{dT}\right)_{T=T_c}$ (kOe/K)	10.7
α	0.565
ρ ($\mu\Omega$cm)	74
κ_{GL}	32
$\xi_{\mathrm{GL}}(0)$ (Å)	20
$\lambda_{\mathrm{GL}}(0)$ (Å)	640

then determined from the following equations:[23]

$$\xi_{\mathrm{GL}}(T)=[8.57\times10^2/(\rho T_c\gamma)^{1/2}]\left(1-\frac{T}{T_c}\right)^{-1/2}, \quad (5)$$

$$\lambda_{\mathrm{GL}}(T)=[6.42\times10^2(\rho/T_c)^{1/2}]\left(1-\frac{T}{T_c}\right)^{-1/2}, \quad (6)$$

in units of Å, and

$$\kappa=0.749[\gamma]^{1/2}\rho\,, \quad (7)$$

where all lengths are in units of Å, and γ is in units of mJ/K^{2}cm^3. The value of ξ_{GL} indicates that the $LaBaCaCu_3O_{7+\delta}$ superconductor has very low coherence length compared with traditional low-temperature superconductors. The κ value shows that the $LaBaCaCu_3O_{7+\delta}$ compound is an extreme type-II superconductor.

DISCUSSION AND CONCLUSION

The material examined, $LaBaCaCu_3O_{7+\delta}$, in the present study has equiatomic concentrations of La, Ba, and Ca, which give rise to a sharp superconducting transition. In contrast, samples with different concentrations in the system $La_{1.5}(Ba_{1-x}Ca_x)_{1.5}Cu_3O_{7+\delta}$, have broad superconducting transitions under a wide variety of preparation conditions. It is natural to explain the observed phenomenon by considering the ordering of the cations La, Ba, and Ca. The high-resolution electron microscopy combined with image simulation by Carim, de Jong, and Leeuw[14] indicates that ordering of the cations La, Ba, and Ca as well as oxygen ordering exists in the tetragonal superconductor $LaBaCaCu_3O_{7+\delta}$. There may be a correlation between ordering and the superconducting transition in $LaBaCaCu_3O_{7+\delta}$ compounds with varying La/Ba/Ca ratios. The basic structure is very similar to $YBa_2Cu_3O_{7+\delta}$, with Ca on the Y sites and La on Ba and probably Y sites.[14] X-ray diffraction experiments showed that the $LaBaCaCu_3O_{7+\delta}$ compounds remain tetragonal down to 6 K. One interesting aspect of this data is the distinct change in the slope of the norml-state resistivity and inverse magnetic-susceptibility data near 220 K. This provides evidence of a more subtle type of transition, which may be associated with sublattice disorder.

By combining the magnetization data and thermogravimetric analysis, we observe that samples with lower oxygen content result in broader superconducting transitions, although the T_c onset remained roughly constant at 74 K. An excess oxygen content of 7.42 obtained by high-pressure annealing showed a broadened superconducting transition with a T_c suppressed by 10 K. Of the samples examined, those with oxygen content near 7.0 showed the sharpest superconducting transitions ($\Delta T_c < 4$ K).

The high-T_c superconductors are particularly sensitive to the type of sublattice disorder discussed above. Since the coherence length is small ($\sim$20 Å), sample inhomogeneity, even over length scales of only a few unit cells, could lead to a mixture of superconducting and nonsuperconducting regions, with the volume fraction of superconducting material and transition width depending sensitively on oxygen content and ordering.

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