PHYSICAL REVIEW B VOLUME 38, NUMBER 7 1 SEPTEMBER 1988

Superconducting properties of $La_{2-x}Ba_xCuO_4$

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(Received 29 April 1988)

We show that the superconducting transition temperature T_c of $La_{2-x}Ba_xCuO_4$ as a function of barium content ($0 \leq x \leq 0.25$, determined by mutual inductance measurements) has two maxima, both $T_c \approx 25$ K, near compositions $x = 0.09$ and $x = 0.15$. Between these two maxima is a local minimum (T_c about 5 K) for $x = 0.12$. dc magnetization data are also reported for six compositions. Anomalies in electrical resistance appear near $T = 50$–60 K at compositions $0.10 \leq x \leq 0.125$. Many samples clearly show a second resistive superconducting transition near 30 K in addition to the bulk transition most clearly observed magnetically. The variation of T_c with composition is discussed in relation to the occurrence of resistance anomalies. The tetragonal lattice parameters at room temperature are consistent with previous work, and show no obvious anomalies. The sample preparation procedures are discussed in detail.

I. INTRODUCTION

Two years ago Bednorz and Müller[1] discovered superconductivity near 30 K in the La-Ba-Cu-O system. Takagi *et al.*[2] then identified the room-temperature K_2NiF_4-type structure of the superconductor $La_{2-x}Ba_xCuO_4$. The substitution of Sr for Ba brought T_c's to near 40 K.[3] The replacement of La by Y led to the 90-K superconductors.[4,5] More recently, transition temperatures above 100 K have been observed in Bi- and Tl-containing compounds.[6–8]

One consequence of the fast pace of discoveries is that, in the $La_{2-x}Ba_xCuO_4$ system originally discovered by Bednorz and Müller, there have been few systematic studies of superconductivity as a function of composition. Conflicting results from many laboratories initially discouraged a complete study of this compound. Nevertheless, much remains to be learned from a careful study of the La_2CuO_4-based superconductors. The recent discovery of the Bi- and Tl-containing superconductors underscores the fact that these copper oxides are related members of a large family of perovskite-derived compounds containing CuO_2 planes. Thus, the detailed description of superconductivity in $La_{2-x}Ba_xCuO_4$ that we present in this paper is important for the development of an understanding of systematic trends in these superconductors.

An important facet of this work is the sample preparation procedure. It appears that small variations in the preparation method can result in remarkable changes in sample characteristics. Although the sample preparation for this $La_{2-x}Ba_xCuO_4$ system is similar to that of the analogous Sr-doped system, there are notable differences.

II. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURES

The method of preparation of our samples is based on the recipe of van Dover *et al.*[9] for the $La_{2-x}Sr_xCuO_4$ system. However, previous work[10] and our own inconsistent early results prompted us to fine tune our preparation process. In order to emphasize these important adjustments, we will compare some of the processing parameters used for the Ba-doped samples with those used in the preparation of $La_{2-x}Sr_xCuO_4$. The Sr-doped superconductor is initially heated as powder, being pelletized only once before the last high-temperature firing. We found that Ba-doped samples pelletized during all firings generally have larger ac susceptibility superconducting transitions and more reproducible T_c's than samples heated as powders in preliminary firings. Kishio *et al.*[10] studied the detrimental effect of water on superconductivity in the La-Sr-Cu-O system. They found that heating the sample to 900 °C in vacuum to remove water before attaining the final firing temperature resulted in samples with a larger ac susceptibility superconductivity signal. We found this procedure to be ineffective for the case of the Ba-containing superconductor. However, it was discovered that bringing samples from 700 to 750 °C in air for 3 to 4 h before higher temperature firings improved consistency. This procedure may be effective because water, incorporated into the samples during grinding in air, leaves the samples before significant reaction takes place.

Samples of nominal composition $La_{2-x}Ba_xCuO_4$ ($0 \leq x \leq 0.25$) were prepared from dried La_2O_3, reagent $BaCO_3$, and fully oxidized CuO powders. Components in stoichiometric proportions were mixed and ground in air in an agate mortar (about 1 h for a 7-g sample) in order to promote homogeneity before the first firing. The powder mixture was pressed with 5000 pounds force into pellets having a 1 cm diameter.

Details of the firing schedule are as follows (note that all firings in air are immediately preceded by the 3 to 4 h heat treatment at 700 to 750 °C). The pellets were set onto alumina and fired in air at 1000 °C for a minimum of 12 h. A regrinding and repelletizing was followed by an identical heat treatment. A final regrinding and pellitizing was followed by a heat treatment of 1100 °C in air for at least 12 h. Finally, the samples were heated in oxygen at 900 °C for 12 h, then furnace cooled over a period of 4 h. Sample compositions in all cases are nominal compositions. Proportions for the metal elements are the starting values. Oxygen content was not determined.

Samples prepared in the above manner proved to be hard and well sintered, with consistent superconducting properties. However, some variations in sample characteristics are evident in T_c and resistivity measurements. These will be discussed as results are presented. T_c measurements were performed using an ac susceptibility apparatus operating at 200 Hz. The temperatures in this apparatus are reproducible to better than 0.5 K. The resistivity samples were cut from sintered pellets. The electrical leads were indium soldered onto gold strips, which had been sputtered onto the polished sample. Thermometer accuracy for resistivity measurements is ± 1 K. In some cases resistivity measurements show small irreversible jumps on the order of 1%. We speculate that these are due to stress-induced cracks. Magnetization data (shielding at 100 G) between 6 and 200 K for six samples were obtained using a fully automated superconducting quantum interference device magnetometer.[11]

Room-temperature x-ray powder diffraction was performed using Cu $K\alpha$ radiation with a diffracted beam monochromator. The Si powder was mixed with powdered samples to provide an internal standard. In all cases the major $La_{2-x}Ba_xCuO_4$ phase was observed, tetragonal for $x \geq 0.065$ and orthorhombic for $x \leq 0.05$. Impurity phases did not appear in diffraction patterns above the 2% level of detection, except in the case of one sample with Ba composition $x=0.10$.

III. RESULTS

A. ac susceptibility and dc magnetization

Superconducting transitions at various Ba contents, determined using ac susceptibility, have a characteristic shape shown in Fig. 1. In most samples there is a slight onset, usually near 25–30 K, involving a few percent of the sample. A subjective estimate of the highest temperature that the signal deviates from the normal-state value we call the "highest onset." We identify the "bulk onset" as the point at which the extrapolation of the normal-state susceptibility signal intercepts the extrapolated steepest slope of the transition. The superconducting transition temperature T_c is defined to be a specific normalized susceptibility signal, 200 μV/(g sample), which is 30% of the full transition in the sample exhibiting the largest transition (Fig. 1). Finally, there is a gradual drop in susceptibility to the lowest temperatures measured (about 4.2 K).

T_c's, bulk onsets, and highest onsets are plotted in Fig. 2. T_c as a function of Ba composition x has two maxima, near $x=0.10$ and near $x=0.15$. A local minimum $T_c=5$ K appears near $x=0.125$. There is some scatter in T_c, especially in the regions where T_c is varying strongly with composition. Note that we have included on this plot *all* samples prepared according to the method described above; we have not eliminated samples for any reason.

In addition, dc magnetization data between 6 and 200 K were obtained for samples at six compositions. Figure 3 displays magnetization data below 40 K for these six samples. (The sample with $x=0.10$ is that having $T_c=12.5$ K in Fig. 2.) The magnetization data above T_c in all cases show no anomalies. There is always a slight diamagnetic signal below 30 K. The bulk superconducting transitions are in reasonable agreement with the ac susceptibility results. An interesting trend is apparent in the magnetization data that is not clearly observable in the ac susceptibility results. The shielding appears to be reduced in samples with reduced T_c's. This behavior is reminiscent of that observed in $La_{2-x}Sr_xCuO_4$ by van Dover and coworkers.[9]

The overall behavior of T_c as a function of composition is clear. The minimum in T_c near $x=0.12$ is especially

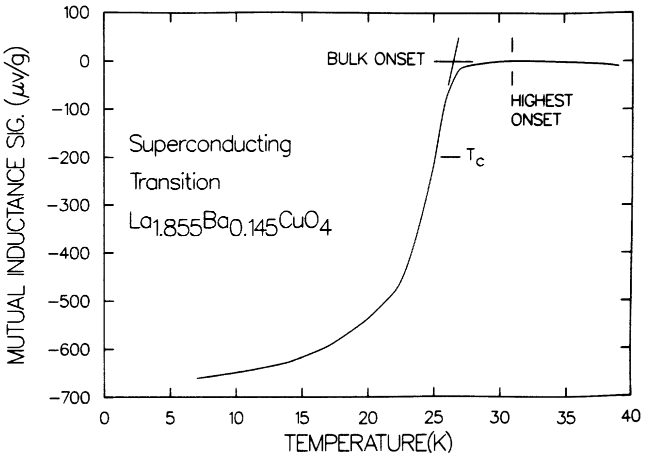

FIG. 1. Mutual inductance superconducting transition for $La_{1.855}Ba_{0.145}CuO_4$ normalized to sample mass. The "highest onset" is an estimate of the temperature at which the susceptibility signal deviates from the nonsuperconducting value. The "bulk onset" and T_c, illustrated, are defined in the text.

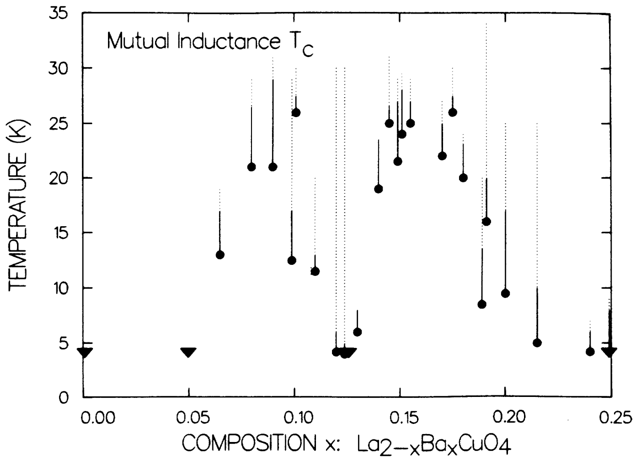

FIG. 2. Mutual inductance T_c vs composition for $La_{2-x}Ba_xCuO_4$. Solid circles represent T_c. Triangles represent samples whose T_c's are not above 4.2 K. Solid lines are drawn between T_c and the "bulk onset;" dotted lines are drawn between bulk onset and highest onset. T_c, bulk onset, and highest onset are illustrated in Fig. 1 and defined in the text.

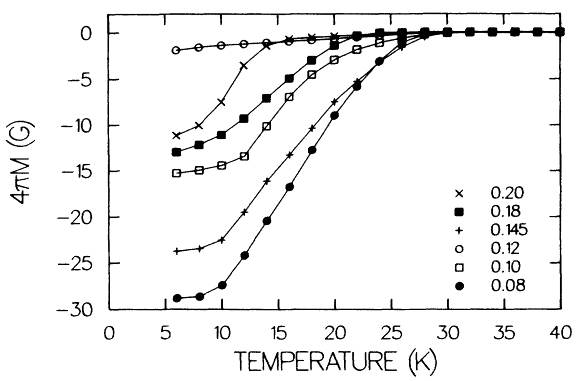

FIG. 3. dc magnetization at 100 G at low temperature for six compositions of $La_{2-x}Ba_xCuO_4$, illustrating the diamagnetic shielding. Values of x are associated with the appropriate symbol in the lower-right-hand corner.

well defined. These abrupt variations in T_c have not been reported by other workers.[12] Nevertheless, the result is reproducible in our laboratory. There are three factors which we believe may have allowed this effect to go unnoticed. First, the density of data points in previous research is low, with very little data for x near 0.12. Second, sample preparation procedures may have resulted in samples which had inhomogeneities that smeared out the sharp composition dependence we observe. Finally, earlier measurements were often made using electrical resistance, a method which may measure filamentary superconductivity. A small quantity of superconductivity does occur in many of our samples up to 30 K.

B. Resistivity

Electrical resistivity measurements were performed on many samples ($0.08 \le x \le 0.20$). The character of resistivity is metallic (resistance falls as temperature is reduced), without apparent anomalies, between room temperature and 100 K. The values of resistivity at room temperature vary nonsystematically by an order of magnitude. Perhaps these variations are due to cracks in the samples. This explanation is consistent with our suggestions that the irreversible jumps in resistivity on the order of 1%, which are often detected in our measurements, may be due to strain-induced cracks. Resistivities for six compositions for temperatures below 100 K are displayed in Figs. 4 and 5. (The sample with $x = 0.10$ in Fig. 4 is the sample with $T_c = 12.5$ K in Fig. 2 whose magnetization data are shown in Fig. 3.) For $x = 0.10$ and $x = 0.12$ (shown in Fig. 4) and $x = 0.125$ (not shown) there is a local minimum in resistance. The minimum appears near $T = 48$ K at $x = 0.10$ and $T = 58$ K at $x = 0.12$ and $x = 0.125$. The resistance appears nonmetallic (resistance rises as temperature is reduced) below the minimum to the superconducting transition. The resistivities for compositions $x = 0.08$ and $0.145 \le x \le 0.20$ show no such well-defined minimum. The superconducting transitions observed resistively are notable also. The samples with low transition temperatures ($x = 0.12$ and $x = 0.20$) show clearly two superconducting transitions, one with an onset near 30 K, which we associate with the highest onset in ac susceptibility, and another which corresponds well with the bulk onset. The higher temperature transition (10%–20% of resistivity) appears to be associated with a susceptibility transition on the order of 2%–3% of the total susceptibility transition (see Fig. 3). It is often the case (as observed here) that a small volume of "filamentary" superconductivity is observed as a large resistive transition, while the magnitude of the magnetically measured transition more closely corresponds to the volume which is actually superconducting. These double transitions suggest that, at least at low temperatures, these samples may contain two superconducting phases. The majority has T_c, which corresponds to the superconducting bulk transitions. A trace of a second phase occurs which has T_c near 30 K.

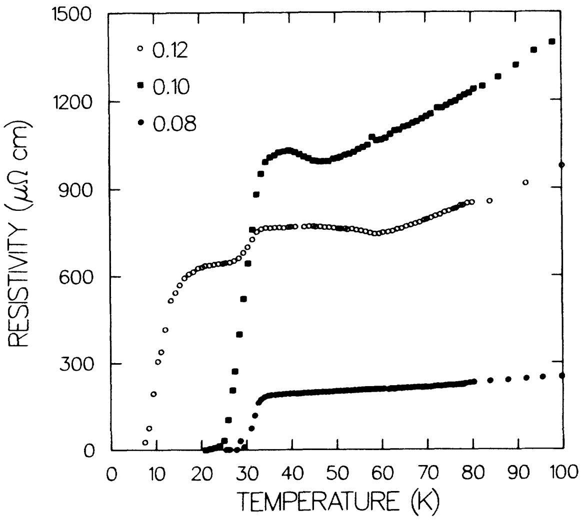

FIG. 4. Electrical resistivity at low temperatures for $La_{2-x}Ba_xCuO_4$, $x = 0.08$, 0.10, and 0.12.

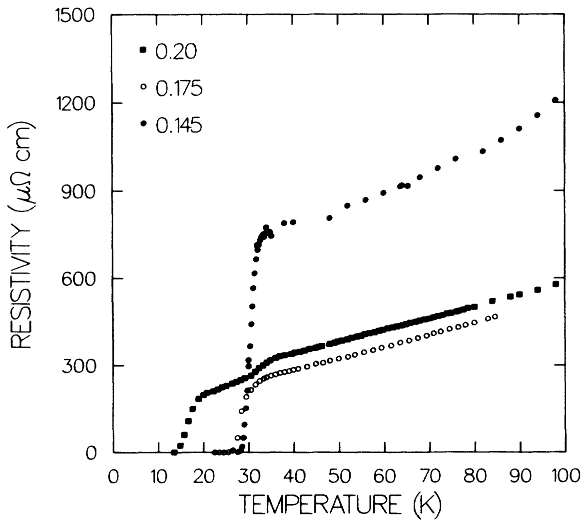

FIG. 5. Electrical resistivity at low temperatures for $La_{2-x}Ba_xCuO_4$, $x = 0.145$, 0.175, and 0.20.

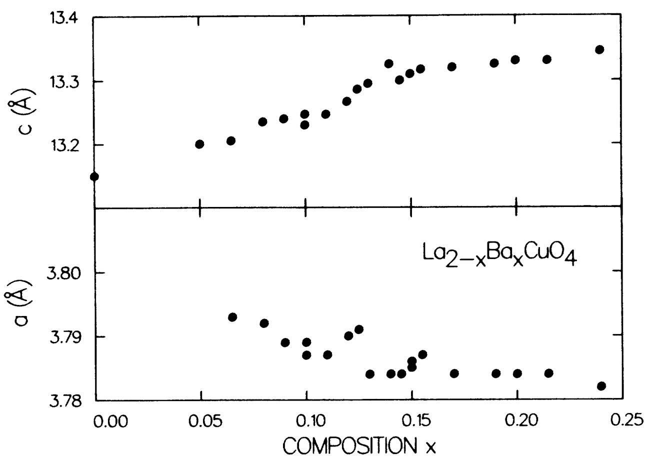

FIG. 6. Lattice parameters at room temperature of K_2NiF_4-type tetragonal $La_{2-x}Ba_xCuO_4$. Also shown, for $x=0$ and $x=0.05$, are c lattice parameters for the orthorhombic structure. Uncertainty in a is about ±0.003 Å; in c, ±0.01 Å.

C. X-ray diffraction

Tetragonal lattice parameters at room temperature are shown in Fig. 6. Also shown is c for two orthorhombic samples with $x \leq 0.05$. These are consistent with other published data[12,13] and show no obvious anomalies which might be correlated with the variation of T_c with composition.

IV. DISCUSSION

The superconducting transition temperature in $La_{2-x}Ba_xCuO_4$ is a sensitive function of composition and of preparation method. A local minimum in T_c of 5 K near $x=0.125$ occurs in a composition range where resistivity anomalies occur near 60 K. These anomalies indicate the existence of an electronic transition (distinct from the tetragonal-to-orthorhombic transition occurring at higher temperatures) whose crystallographic manifestation is presently being studied with low-temperature x-ray diffraction and neutron diffraction measurements.

Published studies of low-temperature phase transitions using x-ray and neutron diffraction are not entirely consistent.[14-16] Sample-to-sample variation is a likely cause of some difficulties. Paul *et al.*[15] found, in an $x=0.15$ sample, the tetragonal-to-orthorhombic phase transition temperature T_{TO} to be 180 K. No obvious change in character of electrical resistance is observed near T_{TO}, either in their work or in ours. Near 60 K, they observed an abrupt change in the orthorhombic distortion that was accompanied by an upturn in resistance. We observe similar behavior in resistance, but only for Ba contents of 0.10, 0.12, and 0.125, and not for $x=0.145$ or $x=0.15$. Low-temperature powder x-ray and neutron diffraction experiments designed to map out the complex phase diagram are underway.

Two superconducting transitions commonly occur in these samples. A small volume which becomes superconducting near 30 K may be related to superconductivity observed in pure La_2CuO_4.[17,18] However, we see no ac susceptibility transition at all in our $x=0.0$ and $x=0.05$ samples. The volume of material involved is small enough to be inconspicuous in x-ray diffraction data, even if it were a distinct crystallographic phase. Perhaps the low-temperature crystallographic transitions are incomplete. Thus only at low temperature may two phases be present. It is known that at room temperature, high-resolution x-ray diffraction reveals the presence, in at least some specimens, of two similar but distinct $La_{2-x}Ba_xCuO_4$ phases.[14]

The superconducting behavior of $La_{2-x}Ba_xCuO_4$ is surprisingly complex. The analogous $La_{2-x}Sr_xCuO_4$ system appears to have a simpler dependence of T_c on composition, with a single peak in T_c near $x=0.15$.[9] The Ca-substituted system has been incompletely studied.[19] In the $La_{2-x}Na_xCuO_4$ system, studied by Markert *et al.*,[20] T_c rises slowly with increasing Na content. Superconductivity in $La_{2-x}Ba_xCuO_4$ varies from 25 K to below 5 K and back to near 25 K with a change in x of 0.05 (from 0.10 to 0.15). Apparently, subtle changes in crystal structure and electronic state drastically affect superconductivity. Such changes are extremely unlikely to be accounted for well in theoretical treatments of these complex compounds. Thus we must rely heavily on careful experimental observations in our exploration of high-temperature superconductivity.

ACKNOWLEDGMENTS

This work was initiated as a collaboration with J. D. Axe and K. Mohanty, who are currently studying these materials using high-resolution x-ray diffraction. D. E. Cox is participating in neutron diffraction studies. Research at Brookhaven National Laboratory is supported by the U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

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[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L123 (1987).

[3] R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Reitman, Phys. Rev. Lett. **58**, 408 (1987).

[4] Z. X. Zhao, L. Q. Chen, Q. S. Yang, Y. Z. Huang, G. H. Chen, R. M. Tang, G. R. Lin, C. G. Cui, L. Chen, L. Z. Wang, R. Q. Guo, F. L. Li, and J. Q. Bi, Kexue Tongbao **32**, 412 (1987).

[5] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[6] C. Michel, H. Hervieu, M. M. Borel, A. Grandin, F. Deslandes, J. Provost, and B. Raveau, Z. Phys. B **68**, 421 (1987).

[7] H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. **27**, L209 (1988).

[8] Z. Z. Sheng, A. M. Hermann, A. El Ali, C. Almasan, J. Estrada, T. Datta, and R. J. Matson, Phys. Rev. Lett. **60**, 937 (1988).

[9] R. B. van Dover, R. J. Cava, B. Batlogg, and E. A. Rietman,

Phys. Rev. B **35**, 5337 (1987).

[10] K. Kishio, N. Sugii, K. Kitazawa, and K. Fueki, Jpn. J. Appl. Phys. **26**, L466 (1987).

[11] Quantum Design, Inc., San Diego, CA.

[12] T. Fujita, Y. Aoki, Y. Maeno, J. Sakurai, H. Fukuba, and H. Fujii, Jpn. J. Appl. Phys. **26**, L368 (1987).

[13] K. Oh-ishi, M. Kikuchi, Y. Syono, K. Hiraga, and Y. Morioka, Jpn. J. Appl. Phys. **26**, L484 (1987).

[14] S. C. Moss, K. Forster, J. D. Axe, H. You, D. Hohlwein, D. E. Cox, P. H. Hor, R. L. Meng, and C. W. Chu, Phys. Rev. B **35**, 7195 (1987).

[15] D. McK. Paul, G. Balakrishnan, N. R. Bernhoeft, W. I. F. David, and W. T. A. Harrison, Phys. Rev. Lett. **58**, 1976 (1987).

[16] J. D. Jorgensen, H.-B. Schuttler, D. G. Hinks, D. W. Capone II, K. Zhang, M. B. Brodsky, and D. J. Scalapino, Phys. Rev. Lett. **58**, 1024 (1987).

[17] J. Beille, R. Cabanel, C. Chaillout, B. Chevallier, G. Demazeau, F. Deslandes, J. Etourneau, P. Lejay, C. Michel, J. Provost, B. Raveau, A. Sulpice, J. Tholence, and R. Tournier, C.R. Acad. Sci. Ser. 2 **304**, 1097 (1987).

[18] P. M. Grant, S. S. P. Parkin, V. Y. Lee, E. M. Engler, M. L. Ramirez, J. E. Vasquez, G. Lim, and R. D. Jacowitz, Phys. Rev. Lett. **58**, 2482 (1987).

[19] J. G. Bednorz, K. A. Müller, and M. Takashige, Science **236**, 73 (1987).

[20] J. T. Markert, C. L. Seaman, H. Zhou, and M. B. Maple, Bull. Am. Phys. Soc. **33**, 556 (1988); Solid State Commun. **66**, 387 (1988).