Disappearance of Superconductivity in Overdoped $La_{2-x}Sr_xCuO_4$ at a Structural Phase Boundary

H. Takagi, R. J. Cava, M. Marezio,[a] B. Batlogg, J. J. Krajewski, and W. F. Peck, Jr.
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

P. Bordet
Laboratoire de Cristallographie, CNRS-UJF, BP 166, 38042 Grenoble CEDEX 09, France

D. E. Cox
Brookhaven National Laboratory, Upton, New York 11973

(Received 6 January 1992)

The electronic and structural phase diagram of heavily doped $La_{2-x}Sr_xCuO_4$ ($0.15 \le x \le 0.3$) is reexamined. We demonstrate that the disappearance of superconductivity in "overdoped" $La_{2-x}Sr_xCuO_4$ is associated with an orthorhombic to tetragonal structural phase transition near $x=0.2$, implying a relationship between superconductivity and subtle structural change. The bulk superconducting phase is thus confined to a much narrower composition range than believed. A complete solid solution of La and Sr is observed in the composition range investigated.

PACS numbers: 74.70.Vy, 74.65.+n

Superconducting cuprates have layered structures, with electronically active CuO_2 planes alternating with "charge reservoir" layers [1]. Through chemical modifications of the charge reservoirs, charge can be introduced into the CuO_2 layers, and the compounds can be changed from insulating antiferromagnets to metals with high superconducting transition temperatures. It is commonly assumed that the charge carrier concentration n_h in the CuO_2 layer can be changed continuously and homogeneously over a certain range, and that T_c is a smooth function of n_h. Here we reexamine the superconducting behavior of $La_{2-x}Sr_xCuO_4$, conceptually one of the simplest cuprate superconductors, in the composition range where superconductivity disappears on "overdoping" [2-4], i.e., for $0.15 \le x \le 0.3$. Combining high-resolution x-ray diffraction and magnetic measurements on a series of samples annealed for one month, we find that the disappearance of superconductivity coincides with a change of structure near $x=0.20$. These results not only indicate a much narrower range for bulk superconductivity than previously suggested [2-4], but also point to the close relationship between the occurrence of superconductivity in the overdoped region and subtle structural modifications, analogous to the observed disappearance of superconductivity in $La_{2-x}Ba_xCuO_4$ near $x=\frac{1}{8}$ [5]. In the process of reexamining the phase diagram, we have also addressed the issue of chemical phase purity in the heavily doped region. We show that the solid solution of La and Sr can be formed at least up to $x=0.3$, in contrast to the recent report of chemical phase separation above $x=0.2$ [6].

A series of sintered pellets of $La_{2-x}Sr_xCuO_4$ ($0.15 \le x \le 0.3$) was prepared by conventional ceramic processing techniques from mixtures of freshly dried La_2O_3, $SrCO_3$, and CuO. The reaction and sintering were performed at 1050-1080 °C for 100 h with several intermediate grindings, followed by oxygen annealing at 800 °C and slow cooling to room temperature.

In order to examine the possibility of thermodynamic instability with respect to phase separation, it is *not* sufficient to check the phase purity of the materials prepared under the usual synthetic conditions. Our approach to the issue of chemical phase purity was to anneal the series of samples for a prolonged period. If a two-phase region exists in thermal equilibrium, then prolonged annealing will enhance the tendency towards phase separation. Thus, we have divided our samples into two sets and have annealed these for one month (720 h), which is 1 to 2 orders of magnitude longer than the time scale for sintering and annealing in the usual sample preparation procedure. The two sets of samples were annealed at 850 and 1000 °C, respectively, low enough to allow for the formation of a chemical miscibility gap, if one is to occur, and high enough to allow for interdiffusion of the cations. After the annealing, the samples were cooled to room temperature at the rate of 10 °C/h to allow for maximum oxygen uptake. The oxygen content determined by the hydrogen reduction technique was kept within 3.99 ± 0.02 for the whole series of samples.

We employed two experimental probes to investigate the crystallographic and superconducting properties of the materials: synchrotron x-ray powder diffraction, which was performed at Brookhaven National Laboratory, and Meissner-effect measurements performed in a SHE SQUID magnetometer. While the former gives us information on a length scale a few hundreds of Å or longer, the latter may be able to probe electronic properties on much smaller length scales, since the superconducting coherence length is estimated to be as short as a few tens of Å ($\xi_{ab} \sim 30$ Å).

The results of the high resolution x-ray diffraction studies are summarized in Fig. 1. In the lower part of the figure and the inset, the systematic variation of peak positions with composition shows that the solid solution exists at least up to $x=0.3$ in $La_{2-x}Sr_xCuO_4$. To check further for any hidden information on phase instability, we

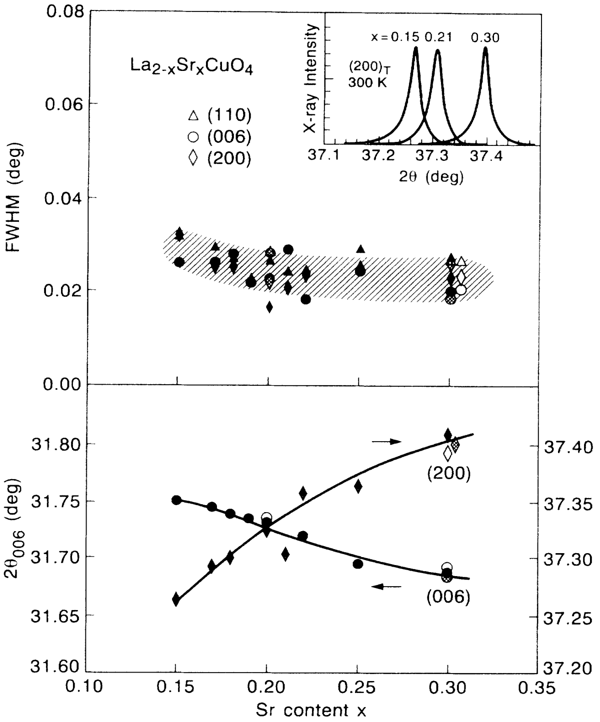

FIG. 1. The results of synchrotron x-ray powder diffraction measurements ($\lambda \simeq 1.2$ Å) as a function Sr content x. The full width at half maximum (top) and the peak position (bottom) of the $(110)_T$ (triangle), $(006)_T$ (circle), and $(200)_T$ (diamond) peaks obtained by least-squares fits at 300 K [18]. Symbols: open, as-prepared; closed, annealed at 850 °C for one month; shaded, annealed at 1000 °C for one month. Inset: Raw diffraction data for the $(200)_T$ reflection for samples annealed at 850 °C for one month.

plot the composition dependence of the linewidths of several diffraction peaks obtained by fitting a pseudo Voigt function. The linewidths (0.025-0.03 deg) are only slightly larger than the instrumental resolution measured with a highly crystalline Si standard (0.015-0.02 deg) and tend to *decrease* upon Sr doping. Considering this decrease of the linewidth, and the saturation in the lattice constants, i.e., the peak positions, upon Sr doping, we conclude that most of the observed line broadening originates from a compositional distribution $\pm\Delta x$ ($\Delta x \simeq 0.01$) about the average composition x. This compositional distribution is due to the imperfect mixing inherent in chemical solid solutions, not due to an instability against phase separation. If the latter were the case, the lines would broaden in the phase-separation composition region on extended annealing. We do not, however, observe any such line broadening after annealing over the whole composition range investigated.

The highly sensitive Meissner measurements shown in Fig. 2 provide insights into electronic homogeneity on a shorter length scale than x-ray diffraction. On a linear scale, shown in the upper panel, what appears to be a well-defined "T_c onset" systematically shifts to lower temperatures with increasing Sr content. However, if the same data are plotted on a logarithmic scale (lower panel), the T_c onset is actually quite ambiguous for $x > 0.15$, with a low magnetization "tail" starting from 36 to 39 K in all samples. Since 39 K corresponds to the optimized T_c for $x = 0.15$ in this system, this is evidence for compositional distribution leading to short-scale electronic properties similar to the ones at $x \simeq 0.15$. Focus now on this tail structure. If there is a tendency for phase separation, long-time annealing would *enhance* the tail structure associated with the optimal T_c. However, comparing the as-prepared samples and the annealed samples in the lower panel of Fig. 2, it is clear that the annealing process *suppresses* the tail structure. This means that the solid solution becomes more homogeneous with time, even on a microscopic scale. There is no evidence for chemical phase separation.

The superconducting phase boundary in the overdoped region has been previously believed to be near $x = 0.3$, since a "continuous" decrease in the T_c onset is observed up to this composition range [2-4]. This can be misleading, however, because T_c can be modified by the proximity effect if the sample consists of a microscopic mixture of a metal and a superconductor, manifesting itself, e.g., in a significantly reduced superconducting volume fraction.

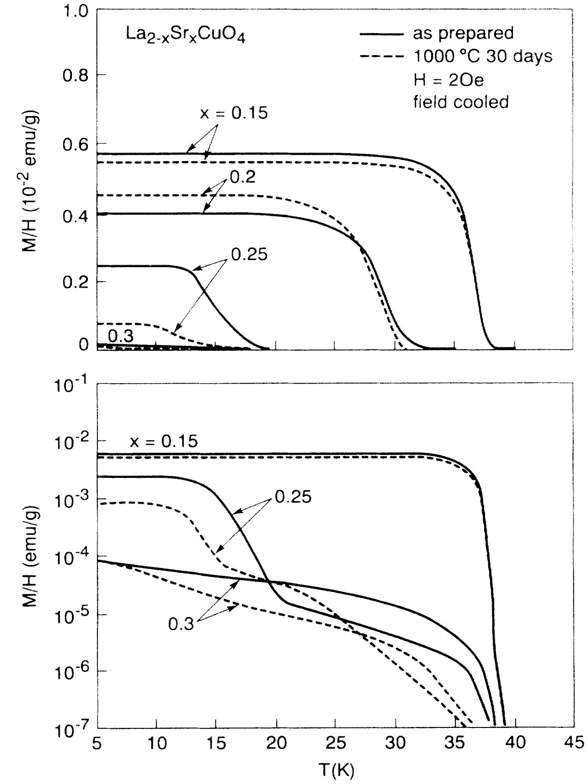

FIG. 2. Temperature dependence of the Meissner signal (field cooled, $H = 2$ Oe) for samples as-prepared (solid line) and annealed at 1000 °C (broken line) for one month.

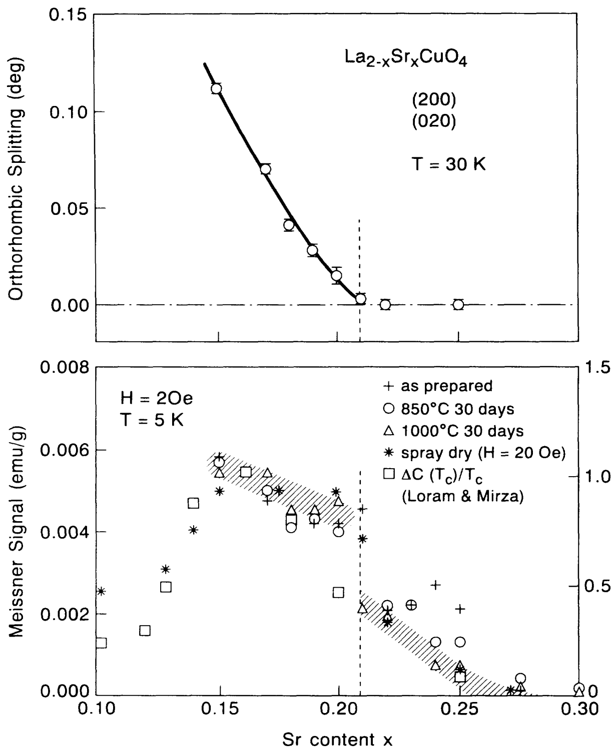

FIG. 3. Relationship between orthorhombicity and superconductivity. The orthorhombic splitting $\Delta\theta$ between $(200)_O$ and $(020)_O$ at 30 K obtained by synchrotron x-ray diffraction (top) and the Meissner signal at 5 K in a field of $H=2$ Oe (bottom). The Meissner data from Ref. [3] and the specific heat jump at T_c, $\Delta C(T_c)/T_c$, from Ref. [8] are included in the bottom panel for comparison. The hatching connects the data for the samples annealed at 1000 °C for 30 days.

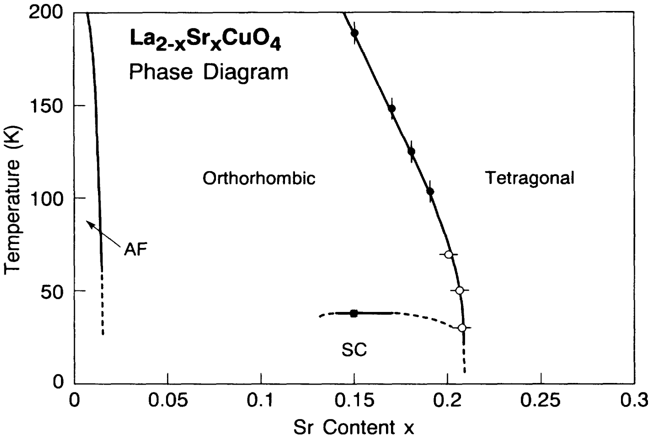

FIG. 4. The revised electronic and structural phase diagram for $La_{2-x}Sr_xCuO_4$. The superconducting transition temperature T_c has been defined by the onset of the Meissner curve on a linear scale. As discussed in the text, the meaning of "T_c" for the samples away from the optimized composition is somewhat ambiguous due to the broadening of the transition and the reduction of the volume fraction. The structural phase boundary was determined from the splitting of the orthorhombic (200) and (020) reflections either as a function of T for a fixed x (closed circles) or as a function of x for a fixed T (open circles). The $x=0.22$ and $x=0.25$ samples do not show any trace of the orthorhombic distortion within our resolution down to 10 K.

To locate the superconducting phase boundary, we summarize the magnetization data for our series of samples in Fig. 3. The Meissner (field cooled in 2 Oe) signal decreases remarkably near $x=0.2$, although the T_c onset decreases smoothly through $x=0.2$ [7]. Furthermore, as a consequence of the homogenization on annealing, this drop in the Meissner signal is more pronounced in the long-time annealed samples (hatched bands). We therefore conclude that the bulk superconducting phase is confined to a very narrow composition range with a maximum x of 0.2. The observation of only minor amounts of superconductivity above $x=0.2$ by a specific heat measurement [8] (shown in Fig. 3 for comparison) and a muon spin rotation measurement [9] further confirms the present result. One of the consequences of this conclusion is that quantitative arguments concerning T_c as a function of doping are not meaningful, as "T_c" in the nonoptimal composition range away from $x=0.15$ is an ambiguous quantity due to the chemical inhomogeneity inherent to a solid-solution system.

The other key result of this study relates the disappearance of superconductivity near $x=0.2$ to a structural phase boundary. The structural phase boundary from high-temperature tetragonal (HTT) to low-temperature orthorhombic (LTO) structure had been reported to be just above $x=0.15$, and is thus believed to have little to do with the superconducting phase boundary [10]. (However, one of the earliest studies suggested a correlation between the two phase boundaries [11].) We have investigated the LTO-HTT structural phase transformation in detail by high resolution x-ray diffraction. The correlation between superconducting and structural phase boundaries becomes evident in Fig. 3. The peak splitting at low temperatures ($T=30$ K in Fig. 3) due to the orthorhombic distortion can be seen up to $x=0.2$ and it disappears above $x=0.22$. The LTO-HTT phase boundary is located just above $x=0.2$, which is the same composition at which the Meissner signal shows a significant drop.

Even after the annealing, there still remains a small Meissner signal for $x>0.2$ (Fig. 3), indicating the presence of the superconducting "patches" in the samples. This can be ascribed either to short-range compositional distribution or to short-range orthorhombic fluctuations which cannot be detected by the x rays, because they probe the sample statically over more than a few hundred Å. The presence of dynamic fluctuations can be expected as a result of low thermal excitation energies of a few meV for the corresponding soft lattice mode [12].

A revised phase diagram is shown in Fig. 4. The combined structural and magnetic studies we have presented here clearly indicate that the disappearance of superconductivity on overdoping, which occurs *near* $x = 0.2$, is associated with a structural phase transformation. The disappearance of superconductivity has heretofore been believed to be purely the consequence of electronic overdoping, which induces a modification of the electronic states [3,4]. The present observation shows that not only hole concentration, but also a delicate structural distortion is very likely to play a role in the disappearance of the superconductivity in heavily doped $La_{2-x}Sr_xCuO_4$ [13].

One may argue that a specific structural environment is indispensable for the occurrence of high-T_c superconductivity. Although most high-T_c cuprates have an orthorhombic structure at low temperatures, a simple correlation between orthorhombic symmetry and superconductivity obviously does not hold true. We know of apparent exceptions, e.g., $La_{2-x}Sr_xCaCu_2O_6$ [14] and $Tl_2Ba_2Ca_2Cu_3O_{10}$ [15], which are tetragonal below T_c. However, since the local structure can be different from the average structure observed by conventional diffraction techniques, detailed studies to clarify a possible interplay between local symmetry (i.e., on the length scale of the superconducting coherence length) and superconductivity are interesting [16,17].

In summary, an intriguing relationship has been revealed between a subtle lattice symmetry change and the disappearance of superconductivity, in $La_{2-x}Sr_xCuO_4$, one of the simplest cuprate superconductors. The superconducting phase boundary and the low-temperature orthorhombic to high-temperature tetragonal structural phase boundary coincide near $x = 0.2$. The bulk superconducting phase is therefore confined to a narrow composition region only up to $x \simeq 0.2$, which is much lower than believed so far.

We would like to thank S-W. Cheong, J. Kwo, J. C. Phillips, J. Jorgensen, Y. Tokura, and J. B. Torrance for useful discussions. The work of D.E.C. was supported by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

---

[a] Also at Laboratoire de Cristallographie, CNRS-UJF, BP166, 38042 Grenoble CEDEX 09, France.

[1] R. J. Cava, Science **247**, 656 (1990).

[2] J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, and S. S. P. Parkin, Phys. Rev. Lett. **61**, 1127 (1988).

[3] H. Takagi *et al.*, Phys. Rev. B **40**, 2254 (1989).

[4] J. B. Torrance *et al.*, Phys. Rev. B **40**, 8872 (1989).

[5] A. R. Moudenbaugh, Y. Xu, M. Suenaga, T. J. Folkerts, and R. N. Shelton, Phys. Rev. B **38**, 4596 (1988); J. D. Axe *et al.*, Phys. Rev. Lett. **62**, 2751 (1989).

[6] J. D. Jorgensen, P. Lightfoot, S. Pei, B. Drabrowski, D. R. Richards, and D. G. Hinks, in *Advances in Superconductivity III*, edited by K. Kajimura and H. Hayakawa (Springer-Verlag, Berlin, 1990), p. 337. In earlier papers, however, the presence of the chemical phase separation has not been reported. See, e.g., N. Nguen *et al.*, J. Phys. Chem. Solids **44**, 389 (1983); Ref. [2], and references therein.

[7] The shielding (zero-field-cooled) signal showed complete shielding for $x < 0.25$, followed by rapid decrease at $x \cong 0.25$.

[8] J. W. Loram and K. A. Mirza, in *Electronic Properties of High-T_c Superconductors and Related Compounds*, edited by H. Kuzmany, M. Mehring, and J. Fink (Springer-Verlag, Berlin, 1990), p. 92.

[9] D. Harshman *et al.*, Phys. Rev. Lett. **63**, 1187 (1989).

[10] For example, Ref. [4].

[11] R. M. Fleming, B. Batlogg, R. J. Cava, and E. A. Rietman, Phys. Rev. B **35**, 7191 (1987).

[12] T. R. Thurston *et al.*, Phys. Rev. B **39**, 4327 (1989).

[13] The disappearance of bulk superconductivity on the lower doping side ($x \lesssim 0.14$) is also very pronounced (see Fig. 3). It is most likely associated with the subtle structural change into the low-temperature tetragonal phase (see Ref. [5]).

[14] R. J. Cava *et al.*, Physica (Amsterdam) **172C**, 138 (1990).

[15] D. E. Cox, C. C. Torardi, M. A. Subramanian, J. Gopalakrishnan, and A. W. Sleight, Phys. Rev. B **38**, 6624 (1988).

[16] B. H. Toby, T. Egami, J. D. Jorgensen, and M. A. Subramanian, Phys. Rev. Lett. **64**, 2414 (1990).

[17] X. Jiang, P. Wochner, S. C. Moss, and P. Zscack, Phys. Rev. Lett. **67**, 2167 (1991).

[18] Since the measurements were performed in two independent runs with slightly different x-ray wavelengths, the two groups of peak positions were adjusted to fit each other.