Superconductivity and the Low-Temperature Orthorhombic to Tetragonal Phase Transition in La$_{2-x}$Ba$_x$CuO$_4$

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The relationship between the low-temperature orthorhombic-tetragonal (OT) phase transition in La$_{2-x}$Ba$_x$CuO$_4$ and the suppression of the superconducting state in samples with $x = 0.125$ has been investigated. Using high resolution synchrotron x-ray diffraction we show that the phase composition of a superconducting $x = 0.15$ sample varies with temperature identically to an $x = 0.125$ sample. This shows that the tetragonal structure does support bulk superconductivity in La$_{2-x}$Ba$_x$CuO$_4$ and the electronic transition which suppresses superconductivity at $x = 0.125$ is distinct from the OT structural transition.

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One of the striking features of all the high-$T_c$ cuprates is the close proximity of magnetic, electronic, and structural phase transitions. Understanding the competition between these states and the driving forces for the different instabilities is important for understanding high-$T_c$ superconductivity itself. The La$_{2-x}$A$_x$CuO$_4$ ($A=$Ba,Sr) (2:1:4) materials present the best opportunity for studying the delicate interplay between structure, magnetism, and superconductivity: they have a rich phase diagram yet have relatively simple crystal structures [1-3]. In the La$_{2-x}$Ba$_x$CuO$_4$ system, superconductivity is observed over the doping range $0.06 \lesssim x \lesssim 0.23$ [4] with a maximum $T_c$ onset around 27 K. However, at $x = 0.125 \pm 0.02$ and $T \approx 60$ K an electronic transition occurs which is evident in resistivity, thermopower, and Hall effect measurements [4, 5]. This results in a dramatic suppression of bulk superconductivity [4] even though the hole concentration $p$ is close to that required for optimal superconductivity. Only at $p = 1/8$ [6, 7] does the competing electronic ground state prevail over the superconductivity. Understanding how this occurs will give important information about the superconductivity itself. It is also in exactly this region of the $x$-$T$ phase diagram that the material undergoes the subtle structural phase transition from the low-temperature orthorhombic (LTO) to the low-temperature tetragonal (LTT) phase [8-10]. This is a first order transition and the phases coexist over a range of temperatures. Axe et al. noted a correlation between the fraction of LTT and the suppression of bulk superconductivity. These authors speculated that high-$T_c$ values of $25-30$ K occurred when the sample had the LTO structure while poor, or nonexistent, superconductivity occurred in the LTT phase. Following this observation, much theoretical effort has been applied to understand why the LTO phase should support bulk superconductivity while the LTT phase inhibits or destroys it [11-15]. We report results that make it clear that, contrary to this widely held view [5-8, 11-13, 15-17], the LTT phase in La$_{2-x}$Ba$_x$CuO$_4$ does support bulk superconductivity with high-$T_c$'s and the transition to the LTT structure itself is not sufficient to suppress bulk superconductivity. Neither is the LTT structure stabilized by the electronic transition as has been suggested by a number of authors [6, 7, 11].

We have carried out high resolution x-ray diffraction experiments, using synchrotron radiation, on samples with $x = 0.15$, which is a bulk superconductor, and $x = 0.125$, which is not, to compare the LTO-LTT (OT) transition in each sample. We have made a careful quantitative analysis of the phase composition of these samples and show for the first time that the bulk superconductivity in the $x = 0.15$ sample does not come from the residual LTO phase but originates in the LTT structure. The $x = 0.125$ sample has the same phase composition at any given temperature as the $x = 0.15$ sample.

Polycrystalline powders were carefully prepared by conventional solid state reaction. Mixtures of La$_2$O$_3$, BaCO$_3$, and CuO were calcined at various temperatures between 900 °C and 1050 °C with several intermediate grindings. The products were then sintered at 1000 °C for 100 h followed by an oxygen anneal at 800 °C for 100 h. Magnetic susceptibility measurements were carried out to characterize the superconducting state of the same powders that were used for the x-ray measurements by using a Quantum Design SQUID magnetometer. Results are shown in Fig. 1 where we have calculated the diamagnetism assuming a demagnetization factor appropriate for a sphere. The average particle size in both samples, observed in a scanning electron microscope, was $\approx 3 \mu m$. Since this value was comparable at both compositions, the comparison shown in Fig. 1 is expected to reflect accurately the relative superconducting fraction of each sample. We see that this fraction is approximately 10 times larger in the $x = 0.15$ sample than in the $x = 0.125$ material. Although a diamagnetic response appears in both samples at approximately 27 K, this re-
FIG. 1. Magnetic susceptibility curves for $x = 0.125$ (squares) and $x = 0.15$ (circles) samples. Measurements were made in a 10 Oe magnetic field after cooling to 5 K with no field (zero-field cooled) and with 10 Oe field (field cooled). In each case the lower curve comes from zero-field cooled data and the upper curve from field-cooled data. Data have been multiplied by 0.667 to account for demagnetization effects.

Response is clearly due to a small fraction ($\approx 1\%$) of the sample for $x = 0.125$.

Diffraction data were collected using the 6-circle Huber diffractometer on beam line 7-2 at the Stanford Synchrotron Radiation Laboratory. The finely ground samples were spread onto a flat copper plate which was attached to the second stage of a closed cycle helium refrigerator. Sample temperatures were monitored and controlled with a calibrated Si diode, mounted approximately 0.5 cm from the sample, and a temperature controller. A beryllium radiation shield, attached to the first stage of the refrigerator and held at ca. 40 K, surrounded the sample and was mounted inside a Be windowed vacuum shield. The entire assembly was mounted on the $\theta$ arm of the diffractometer. An intrinsic Ge detector, with windows set to collect the elastic scattering, was mounted on the $2\theta$ arm of the diffractometer. The Si(220) double crystal monochromator was set to a wavelength of 1.800 Å. The orthorhombic (400) and (040) peaks, with the indices referring to the $Abma$ space group, were measured in $\theta-2\theta$ scans. The choice of wavelength places the peaks close to $2\theta = 84.6^\circ$ yielding a good dispersion without compromising intensity. Averaging over grains was improved by rocking the sample for one cycle of $\pm 1.0^\circ$ about $\theta$, which resulted in a collection time of approximately 7.5 s/point.

Diffraction data from selected temperatures are shown in Figs. 2 and 3 for the $x = 0.125$ and $x = 0.15$ samples, respectively. From these data we wished to find out the temperature at which the transition began and ended, the degree to which each sample transformed, and also to establish that both samples were undergoing a first order transition to the LTT phase rather than the possible second order transition to the $Pcnn$ phase. Such a transition has been observed in $La_{2-x}Sr_xNd_yCu_4O_8$ samples over a limited Sr concentration range [18, 19] though there is no evidence that it occurs in the $La_{2-x}Ba_xCuO_4$ system [8]. We analyzed the data both by peak fitting and by taking differences between data collected at different temperatures. The peak fitting gives quantitative estimates of the phase compositions of the samples as a function of temperature. The difference plots give a model independent determination of how the transformation is evolving with temperature.

Because of the small orthorhombic splitting in the $x = 0.15$ sample, peak fitting had to be carried out

FIG. 2. Powder diffraction data from the (400)/(040) peaks of the $x = 0.125$ sample at various temperatures. Data are shown as closed circles. The smooth curves are from the Lorentzian fits described in the text. The data sets above 10 K are offset for clarity.

FIG. 3. Powder diffraction data from the (400)/(040) peaks of the $x = 0.15$ sample at various temperatures. Data are shown as closed circles. The smooth curves are from the Lorentzian fits described in the text. The data sets above 10 K are offset for clarity.
carefully and will be described in some detail. Pure Lorentzian line shapes were used throughout. The experimental peak shapes contain a small Gaussian component due to the instrument response. This is more evident in narrower peaks which are closer to, but still broader than, the instrument resolution. However, it was desired to keep the number of variables in the fits to a minimum and the Gaussian part was ignored. The refined values for peak positions, widths, and intensities varied smoothly with temperature and yielded realistic values which indicates that this approximation does not significantly bias the results. Single-peak, two-peak (2P), and three-peak (3P) fits were made to data throughout the entire temperature range. The “best” fits were selected based on $\chi^2$ for the fits and on information obtained from the difference plots. These were 3P fits for temperatures up to 70 K and 2P fits for higher temperatures. In single-peak fits position, width, intensity, and a constant background were varied. In the two-peak fits the relative weights of the two components ([400] and [040]) of the orthorhombic doublet (LTOD) were constrained to be the same. The error this introduces, because of the slight reduction of the (040) component by the tilting of the CuO$_6$ octahedra, is very small. Two regimes were used in the 3P fitting. In each regime the peak parameters from the majority phase were varied, the position and width of the minority peak, or peaks, were fixed, and the intensities in both the orthorhombic and tetragonal components were varied.

The nature of the OT transition in the $x = 0.125$ can be seen clearly in Fig. 2. As the temperature falls, the intensity in the LTO peaks diminishes while a central LTT peak grows. This behavior can also be seen in the difference plots in Fig. 4(a): in this figure, the dashed lines give the positions of the LTOD peaks at 80 K obtained from the peak fitting. The OT transition begins at $T_{d2} = 70$ K and the central peak is clearly established by 65 K. Examination of Fig. 4(b) shows that below 30 K there is no further transformation. This behavior clearly indicates that this sample is undergoing a first order transition from LTO to LTT, as expected [8,10]. Although the transformation has ended by 30 K, it is clear that some residual LTO remains. The 10 K data in Fig. 2 are shown fitted with a single Lorentzian. Some residual intensity from the LTO peak at 1.3328 Å is evident as a small shoulder. The 3P fit to these data indicates that 5% of the sample remains untransformed (Fig. 5).

This behavior can be compared to that of the $x = 0.15$ sample. First, from the difference plots in Figs. 4(c) and 4(d) it is clear that the transformation onset temperature is the same for both samples and that, in both cases, the transformation has finished by 30 K. Figure 4(c) indicates that the $x = 0.15$ sample is also showing first order behavior and is transforming to the LTT, rather than the $P_{cco}$ phase, in the same way as the $x = 0.125$ sample. Because the splitting of the LTOD is less in this case, it is not possible to see the behavior directly from the qualitative peak shape in Fig. 3 and the changes are less pronounced in the difference plots (Fig. 4). However, the peak fitting, carried out in exactly the same way as for the $x = 0.125$ sample, indicates that the phase fractions of the two samples are evolving identically with temperature (Fig. 5). The 3P fit to the 10 K data indicates that there is 5% of residual LTO; furthermore, it is clear

![Graph](image)

**FIG. 4.** Difference in measured intensity $I$ between diffraction data collected at various temperatures. The difference function is defined in each panel. Data are offset from one another for clarity. The dashed lines indicate the peak positions of the orthorhombic peaks at 80 K (90 K) in the $x = 0.125$ ($x = 0.15$) samples obtained from peak fitting.

![Graph](image)

**FIG. 5.** Fraction of LTT phase in the sample as a function of temperature. The squares are from the $x = 0.125$ sample; the circles are from the $x = 0.15$ sample; the line is a guide to the eye.
from Fig. 3 that the LTT peak at 10 K is considerably narrower than the 50 K compound peak and is well fitted with a single Lorentzian. This is strong evidence that, just as in the $x = 0.125$ sample, the fraction of LTO in the $x = 0.15$ sample at low temperature is small and is $\lesssim 5\%$.

It is clear from these analyses that the transformation behavior of the good superconductor ($x = 0.15$) and the poor superconductor ($x = 0.125$) is identical and the differing electrical properties cannot be attributed to the presence of residual LTO in the former phase. The fraction of LTO is too small to account for the observed bulk superconductivity in the $x = 0.15$ sample, and at least as much LTO phase is present in the $x = 0.125$ sample at low temperatures. Thus, it is clear that within the LTT phase the electronic ground state can be either metallic and superconducting with a $T_c$ up to 27 K in the La$_{2-x}$Ba$_x$CuO$_4$ system, or show suppressed superconductivity. The electronic transition which occurs at $T \approx 60$ K and $x = 0.125$ is distinct from the OT transition which occurs over a wider range of temperatures and compositions. Nonetheless, some coupling of the electrons to this transition is implied by the fact that the same electronic anomalies are not observed in the absence of LTT [20].

It has been observed in La$_{2-x}$Sr$_x$Nd$_y$CuO$_4$ that the LTT structure supports superconductivity [18, 19]. In this case samples with the LTT structure had a lower $T_c$ than samples with the same hole content but with the LTO structure. This could be explained simply by the prediction of LDA calculations [13] that there is a smaller density of states at the Fermi level in LTT than LTO. This would also explain why La$_{2-x}$Ba$_x$CuO$_4$ has a lower maximum $T_c$ (27 K) than La$_{2-x}$Sr$_x$CuO$_4$ (37 K) [1, 2] which remains in the higher symmetry LTO structure at low temperature. However, it cannot explain the superconducting anomaly at $x = 0.125$ in La$_{2-x}$Ba$_x$CuO$_4$.

The electronic transition occurs over a very narrow range of hole concentration close to $p = 1/8$. This rational number suggests that maybe an insulating charge [11] or spin [12] density wave ground state is stabilized for commensurate wave vectors. No long range spin or charge ordering has been observed experimentally although some evidence exists for local magnetic order in nonsuperconducting LTT material [21, 22]. Whatever the origin of the electronic anomaly, it is clear from the present work that it is not responsible for stabilizing the LTT phase as has been suggested [11].

The effect of structural instabilities on superconductivity has long been of interest [23] and there is evidence that in the 2:1:4 materials the structure does affect the superconductivity [3]. However, we have shown that, in La$_{2-x}$Ba$_x$CuO$_4$, the LTT structure does support superconductivity with high $T_c$’s and the electronic transition which suppresses superconductivity at $x = 0.125$ is distinct from the OT transition.

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[20] In the systems La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) and La$_{2-x}$Sr$_x$Nd$_y$CuO$_4$ a small dip is seen in $T_c$ at a value of $x = 0.125$, though the samples are bulk superconductors. This behavior has been explained as being due to incipient LTT formation as evidenced by the continued softness of the mode responsible for the LTT transition in LSCO.