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Temperature and composition dependence of the tetragonal-orthorhombic distortion in $La_{2-x}Sr_xCuO_{4-\delta}$

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We have mapped the temperature and composition dependence of the tetragonal-orthorhombic phase-transition temperature T_d in the high-temperature superconductor $La_{2-x}Sr_xCuO_{4-\delta}$ using high-resolution powder x-ray diffraction and measurements of the thermal expansion. The maximum volume fraction of ideal diamagnetism occurs in the composition range where T_d is approaching the superconducting transition. In the composition range x > 0.20, where no orthorhombic distortion is observed above 12 K, no bulk superconductivity is observed in $La_{2-x}Sr_xCuO_{4-\delta}$.

High-temperature superconductivity has been reported in a number of solid solutions with the composition $La_{2-x}Sr_xCuO_{4-\delta}$ and $La_{2-x}Ba_xCuO_{4-\delta}$.¹⁻⁹ The exact transition temperature and the volume fraction of the superconductivity is a function of the sample preparation and the subsequent annealing; however, bulk superconductivity, as indicated by ideal diamagnetism from a substantial fraction of the sample, has been reported at temperatures as high as 40 K in $La_{2-x}Sr_xCuO_{4-\delta}$ with x=0.15-0.20.^{4,7-9} Above x=0.2, the volume fraction of the superconducting material falls off rapidly, although broad resistive transitions have been measured with the Sr content as high as x=0.5.⁸

The superconducting phase of $La_{2-x}Ba_{x}CuO_{4-\delta}$ and $La_{2-x}Sr_{x}CuO_{4-\delta}$ has been identified as having the tetragonal K₂NiF₄ structure, ^{2,10} a structure type that has been extensively studied in metal oxides.¹¹⁻¹³ The tetragonal K₂NiF₄ structure can be thought of as alternation along the c axis of layers of perovskite (CuO₃) and rocksalt (La or Sr-O) structure types. The perovskite layers, which are perpendicular to c_0 , consist of corner-sharing CuO_6 "octahedra" that are slightly elongated along the c_0 axis. The elongation results because the Cu is actually fourfold coordinated and bonded more strongly to the inplane oxygens than to the oxygens in the neighboring La or Sr-O layers. Each perovskite layer is shifted relative to the next so that the copper sites in one CuO₃ layer are aligned with the oxygens in the next CuO₃ layer. Metal oxides with the K₂NiF₄ structure are known to be susceptible to changes in the oxygen ion positions and distortions of the tetragonal structure as one changes the metal constituents.¹¹⁻¹³ For example, in undoped La₂CuO₄, a material with no bulk superconductivity, a small orthorhombic distortion from the K₂NiF₄ structure occurs at 533 K.¹³ There has been some controversy in the literature concerning the correct space group of the orthorhombic distortion in La₂CuO₄; however, it is thought that the distortion primarily consists of a tilting of the CuO₆ octahedra to form corrugated perovskite layers.¹¹⁻¹³ The partial substitution of Sr or Ba for La in La₂CuO₄ stabilizes the tetragonal K₂NiF₄ structure at room temperature.

In this Rapid Communication we examine the temperature and composition dependence of the tetragonal-orthorhombic distortion temperature T_d in $La_{2-x}Sr_{x}CuO_{4-\delta}$. We show that T_{d} does not reach the superconducting temperature T_c until $x \approx 0.20$, indicating that in most samples superconductivity occurs in the distorted K₂NiF₄ phase. It has been suggested that an enhanced superconducting transition may be obtained coupling into phonon modes initially associated with a separate structural phase transition. For example, La_2CuO_4 is predicted to be susceptible to a Peierls instability.¹⁴ In this model, in-plane Cu-O breathing modes induce an orthorhombic distortion and an opening of a Peierls gap at low temperatures. (This is thought to be a separate distortion from the tilting of the octahedra discussed above.) The role of the Sr or Ba is to spoil the Fermi-surface nesting and the Peierls instability but leave states near the Fermi energy with large deformation potentials which can provide strong electron-phonon coupling.

 $La_{2-x}Sr_{x}CuO_{4-\delta}$ Sintered pellets of and $La_{2-x}Ba_{x}CuO_{4-\delta}$ were obtained as described previously.⁴ Powder diffraction samples were obtained by mixing the ground pellets with ethanol and allowing the resulting slurry to evaporate on a Pt substrate. The sample and substrate were sealed in a helium-filled chamber and mounted in a closed-cycle helium refrigerator. Cu Ka x rays, obtained from a rotating anode generator, were monochromated and collimated by scattering from Ge (111) plates before and after the sample. In this configuration, the instrumental resolution measured on a single crystal is about 7.5×10^{-4} Å⁻¹ full-width at half maximum (FWHM). For the powders used in this experiment, the strongest powder line, the (103) tetragonal peak [(113) in the orthorhombic phase], had a width of about 0.055° FWHM at a 2θ of 31.21° , corresponding to a ΔQ of about 4×10^{-3} Å⁻¹. Broadening of the powder line can result from particle size or strain broadening as well as microscopic inhomogeneities in the composition. The observation of powder lines which are not resolution limited implies that the x-ray scattering will be sensitive to changes in ordering length scales as a function of temperature; however, it is likely that in these solid solutions the length scales are dominated by chemical inhomogeneity.

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As the temperature is lowered through the tetragonalorthorhombic transition, certain lines in the x-ray powder pattern will split into doublets. The temperature dependence of one of the lines which splits, the (110) tetragonal peak, is shown in Fig. 1 for an $La_{2-x}Sr_{x}CuO_{4-\delta}$ sample with x = 0.15. As the temperature is lowered, the (110) line moves to larger values of 2θ , and at 190 K it splits to form the (020)-(200) doublet of the distorted, orthorhombic phase. (The orthorhombic cell is indexed on a cell which is rotated 45° with respect to the tetragonal cell with $a_0 \approx b_0 \approx \sqrt{2}a_T$ and $c_0 \approx c_T$.) The transition is second order with the magnitude of the splitting increasing as the temperature is decreased. The inset to Fig. 1 shows the temperature dependence of the (020)-(200)splitting for x = 0.15. For all samples measured, an asymmetry was seen in the widths of the (020) and (200) peaks of the orthorhombic phase. For example, in the x = 0.15sample shown in Fig. 1, a least-squares fit of a Lorentzian line shape to the (020) peak has a FWHM of 0.15°, while the (200) peak has a width of 0.075° . An x = 0.15 sample that was annealed for less time than the one shown in Fig. 1 showed a (020)-(200) doublet with widths of 0.238° and 0.083°. A sample of $La_{2-x}Ba_xCuO_{4-\delta}$ with x = 0.15and a short annealing time showed only a single line which broadens at T_d , reaching a width of 0.47° at 12 K. The asymmetric widths of the (020)-(200) doublet result because b_0 is a stronger function of composition than a_0 . This effect is illustrated in Fig. 2 where we show the position of the (020) and the (200) peak at 12 K as a function



FIG. 1. θ -2 θ scans through the (110) tetragonal line at room temperature and the (020)-(200) orthorhombic doublet at 49 K for La_{2-x}Sr_xCuO_{4- δ}, x=0.15. The lines are Lorentzian fits. The inset shows the temperature dependence of the (020)-(200) splitting.



FIG. 2. The peak positions of the (020) and the (200) lines of the orthorhombic phase of $La_{2-x}Sr_xCuO_{4-\delta}$ as a function of composition at 12 K. For compositions with $x \ge 0.20$, no orthorhombic splitting was observed above 12 K.

of composition. One can use the asymmetry in the widths of the (020)-(200) doublet to monitor the quality and the homogeneity of the sample. The excess width of the (020) line of the best x = 0.15 sample indicated an approximate composition spread of $x = 0.15 \pm 0.01$.

The tetragonal-orthorhombic transition can also be seen in thermal expansion data. We measured the temperature-dependent length change of a sample of $La_{2-x}Sr_xCuO_{4-\delta}$ with x=0.15 with respect to a copper reference. Commercial strain gauges were attached with epoxy and formed the arms of a resistance bridge. The unbalanced voltage of the bridge is proportional to the difference of the sample and the reference length. These oxides are harder than copper, and the linear thermal expansion coefficient of this ceramic is $\approx 12 \times 10^{-6} \text{ K}^{-1}$ around room temperature. As the temperature is lowered, a change of slope that we associate with a change of the thermal lattice properties occurs at 197 ± 3 K. Indeed, our x-ray diffraction studies reveal a structural change at this temperature as shown in the inset to Fig. 1.

Our studies establish that for all compositions of $La_{2-x}Sr_xCuO_{4-\delta}$ with x less than about 1.9, the superconducting phase is the distorted orthorhombic phase. We showed in Fig. 2 that the magnitude of the orthorhombic distortion measured at 12 K decreases as x increases, reaching zero for x = 0.20. Figure 3 shows the composition dependence of T_d along with a plot of the fraction of ideal diamagnetism at 4.2 K from Ref. 8. The slope of the T_d as a function of concentration increases as $x \rightarrow 0.20$ becoming steep in the concentration range x = 0.15 - 0.20. The concentration at which the $T_d \approx T_c$ can be estimated from Fig. 3 to be about x = 0.19. Most samples measured thus far have T_d well above T_c , but since the volume fraction of the ideal diamagnetism is



FIG. 3. The composition dependence of the tetragonalorthorhombic transition temperature T_d and the composition dependence of the fraction of ideal diamagnetism at 4.2 K (from Ref. 8). The lines are guides to the eye.

high for both x=0.15 and x=0.20, superconductivity may also occur in the tetragonal phase. (Neither $La_{2-x}Sr_xCuO_{4-\delta}$ or $La_{2-x}Ba_xCuO_{4-\delta}$ with x=0.20showed any measurable orthorhombic splitting at 12 K; however, since the splitting increases slowly as the temperature is decreased, it is possible that either of these samples could have a T_d as high as T_c .) If superconductivity exits in the tetragonal phase, it is apparently limited to a narrow composition region near x=0.20 because once x is increased to 0.30, bulk superconductivity is no longer observed.⁸

The stabilization of the tetragonal phase for x > 0.20can be correlated with several other physical properties of $La_{2-x}Sr_{x}CuO_{4-\delta}$. The most striking correlation is the disappearance of bulk superconductivity by x = 0.30, suggesting that a sharp superconducting phase boundary may exist near x = 0.20. This can be contrasted with the slower increase in the volume fraction of the superconductivity as $x \rightarrow 0.15$ from the low-concentration side. A similar asymmetry can be observed in the resistive superconducting transitions,⁸ although the trends are less obvious since a minute superconducting volume can produce a resistive transition. For 0.1 < x < 0.2, the resistive superconducting transitions are relatively narrow and T_c (as measured at the midpoint of the transition) increases from about 30 to 37 K. For x > 0.2 the temperature of the midpoint of the transition decreases slightly, but width of the resistive transition broadens dramatically. There are also room-temperature structural changes which occur near x = 0.20. 6,7,15 As the Sr content is increased from x=0, c/a initially increases. An increase in the c/a ratio, which is associated with the distortion of the CuO_6 octahedra discussed above, means that the compound is

becoming more two dimensional. At about x = 0.28, the slope of c_0 versus composition changes sign and begins to decrease with composition. At the same composition a_0 begins to vary more slowly with composition.

If the superconducting transition and the tetragonalorthorhombic transition are strongly coupled, one might expect that the evidence of the superconducting transition would be present in structural information associated with the orthorhombic distortion; however, we have seen no structural evidence of this type. No extra peaks were observed in the powder patterns as the temperature was varied through the superconducting transition, and no broadening or large change in the intensity of lines other than those associated with the tetragonal-orthorhombic phase transition were observed. Lattice parameters obtained from least-squares fits to the powder patterns show no significant anomaly at T_c . The magnitude of the orthorhombic splitting is not affected by changing the temperature through the superconducting transition.

Since the optimum composition for superconductivity is reached when T_d is in the vicinity of T_c and bulk superconductivity disappears at concentrations where there is no orthorhombic transition, it is interesting to consider whether or not both phase transitions have a common origin. A detailed analysis is difficult because we do not yet know the space group of the distorted phase in the range x = 0.6 to x = 0.20. Since T_d falls much faster for x < 0.05 than x > 0.5, one might question whether or not the orthorhombic distortion in the superconducting compounds is the same as that seen for x=0. Lack of knowledge about the space group also prevents a definitive statement of whether or not the observed orthorhombic distortion is the predicted distortion resulting from a Peierls instability.¹⁴ This distortion is expected to involve Cu-O breathing modes, e.g., in-plane distortions of the CuO_6 octahedra. In the present case, an argument against this type of mechanism is the lack of strong electronic effects at T_d . The tetragonal-orthorhombic distortion does not strongly affect electronic properties such as the resistance and the magnetic susceptibility, ¹⁶ suggesting that T_d is not associated with a Peierls distortion. Nevertheless, the coincidence of the maximum superconducting volume in the same composition range where the structural phase transition is marginally stable is intriguing.

In this experiment we have investigated the temperature dependence of the tetragonal-orthorhombic distortion in $La_{2-x}Sr_xCuO_{4-\delta}$. In the range of composition considered optimum for superconductivity, the distortion temperature T_d , which is varying rapidly with composition, occurs in the same temperature range as T_c . Several changes in the physical properties of $La_{2-x}Sr_xCuO_{4-\delta}$ are associated with an increase in the Sr content above x = 0.20. For x > 0.20, the tetragonal phase is stable above 12 K and the fractional volume showing of ideal diamagnetism rapidly decreases.⁸ The resistive transitions become much broader⁸ and at room temperature, a change in the sign of slope of c_0 versus composition has been observed.^{6,7,15} The data clearly indicate that superconductivity occurs in the distorted orthorhombic phase of $La_{2-x}Sr_xCuO_{4-\delta}$. It is less clear whether or not superconductivity also occurs in the undistorted, tetragonal phase; however, data from the x = 0.20 sample indicate that bulk superconductivity exists in the tetragonal phase as well. If bulk superconductivity does occur in the tetragonal phase, it is apparently limited to a narrow composition range near x = 0.20.

Note added in proof. In Ref. 17 a relation between the

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orthorhombic-tetragonal phase boundary at room temperature and the maximum in T_c have been described.

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