Structural Phase Transformations and Superconductivity in $La_{2-x}Ba_xCuO_4$

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(Received 14 April 1989)

$La_{2-x}Ba_xCuO_4$ has been found to undergo the following sequence of transformations upon cooling: tetr.($I4/mmm$) → ortho.($Bmab$) → tetr.($P4_2/ncm$), over a range of composition $0.05 < x < 0.20$. The newly discovered low-temperature tetragonal phase can be thought of as a *coherent* superposition of the twin-related *Bmab* structures. The system can be modeled as an *XY*-spin system with temperature-dependent quartic anisotropy, $v(T)$. Slight differences between orthorhombic and tetragonal structures appear to have large effects upon the superconductivity.

PACS numbers: 74.70.Vy, 61.60.+m, 64.70.Kb

The role of structural phase transformations in the La_2CuO_4 high-T_c superconductors has been extensively studied and discussed since their discovery by Bednorz and Müller.[1] Structural studies[2-4] reveal both high-temperature-tetragonal (HTT) and low-temperature-orthorhombic (LTO) modifications, which interconvert via a continuous phase transformation. Inelastic neutron scattering measurements have identified a soft-mode phonon instability which drives the transformation.[5,6] Reports of anomalies in the thermal,[7] elastic,[8,9] optical,[10] and transport[11,12] properties of both doped and undoped La_2CuO_4 suggest the possibility of additional phase transformations at low temperatures. Here we report a study of the $La_{2-x}Ba_xCuO_4$ system, identify a new structural modification, determine the (x,T) phase diagram, and develop a Landau theory for its stability that involves novel features. The relationship of this structural transformation to the unusual superconducting properties of these materials is briefly discussed.

The polycrystalline ceramic samples were prepared from La_2O_3, $BaCO_3$, and CuO powders by a systematic process of multiple firings in air and oxygen which has been described previously and shown to yield a series of $La_{2-x}Ba_xCuO_4$ samples with consistent and reproducible properties.[11] Figure 1 shows the temperature dependence of the (110) HTT reflection of $La_{2-x}Ba_xCuO_4$ ($x=0.125$) resulting from a synchrotron x-ray powder-diffraction study carried out at the X22B and C beam lines at the National Synchrotron Light Source. 2Θ scans were performed using 1.6–1.7-Å x rays from a perfect Ge(111) monochromator in a vertical scattering geometry on samples placed in a closed-cycle He refrigerator. Grain averaging was accomplished by simultaneous oscillation of the sample (1°). From room temperature to 210 K there is a single peak, which splits progressively as the temperature is lowered further, indicating the continuous HTT-LTO transformation. Below about 80 K a central component appears between the split components, and the three features coexist to the lowest temperatures, suggesting the reemergence of a tetragonal phase. Above 80 K the Lorentzian line shapes of the individual components are consistent with instrumental resolution, possibly slightly broadened by grain-size effects. Below this temperature the still Lorentzian lines are noticeably broadened, which may be explained by a reduction in crystallite grain size to about 2000 Å. The results are qualitatively similar to those derived from a preliminary lower-resolution study of $La_{2-x}Ba_xCuO_4$ ($x=0.10$) using a conventional x-ray

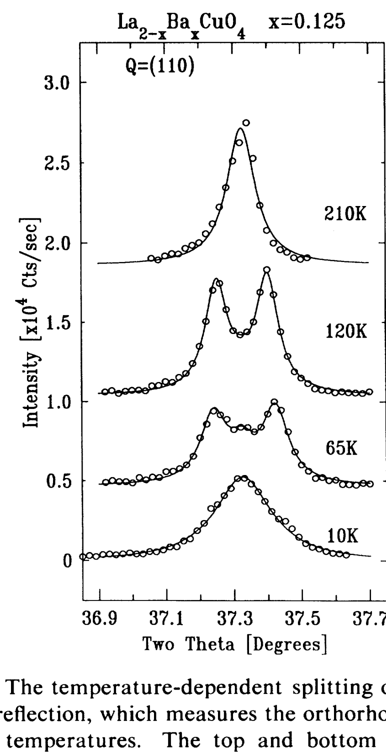

FIG. 1. The temperature-dependent splitting of the tetragonal (110) reflection, which measures the orthorhombic splitting at several temperatures. The top and bottom data sets are fitted with a single Lorentzian line shape. The intermediate data sets are fitted assuming two and three components, respectively. Note that the 10-K peak is wider than the 210-K data, and still shows unresolved orthorhombic components.

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source, which is published elsewhere.[13] The HTT-LTO transformation temperature and the maximum saturation value of $\eta(T)$ both decrease with increasing x. Above $x=0.15$, indicated by the dashed lines in Fig. 2, the orthorhombic splitting falls below the instrumental resolution of the present experiment.

The HTT-LTO transformation is accompanied by the appearance of weak superlattice reflections which are associated with an enlargement of the unit cell.[6] These superlattice reflections are readily seen with neutron powder diffraction (albeit, at lower resolution), and we have established that these reflections persist in the new low-temperature form,[13] even though $\eta(T)$ vanishes or greatly diminishes. Thus the transformation involves a truly new phase, not simply the restabilization of the HTT phase. Yet the similarities in the diffraction patterns suggest that all three phases are closely related. To discover the relationship, it is helpful to review the HTT-LTO transformation.

The HTT phase of La_2CuO_4 has the body-centered tetragonal K_2NiF_4 structure ($I4/mmm$), in which the characteristic structural units are staggered planes of CuO_6 octahedra. There are two variants (twin modifications) of the LTO phase. In one variant these corner-shared CuO_6 octahedra rotate about the HTT $(1\,-10)$ axis (with alternate rows rotating in opposite directions as dictated by the corner sharing). The resulting B face-centered orthorhombic cell has its a-b axes along the HTT [110] directions, and belongs to the space group $Bmab$. The other LTO invariant differs only in

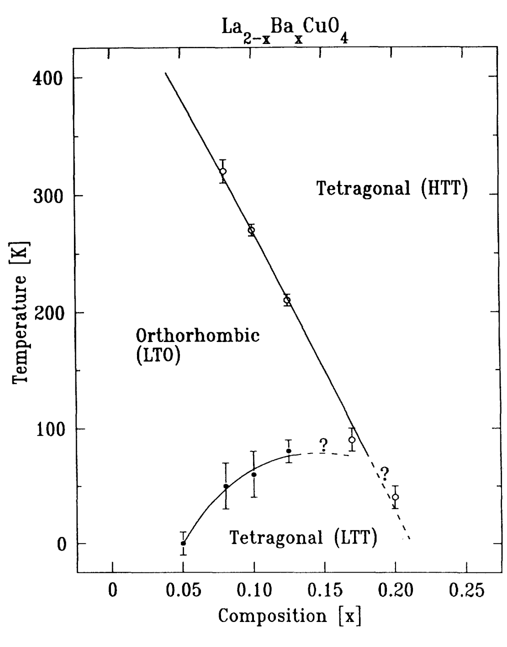

FIG. 2. Experimental phase diagram. For $x>0.15$ the small orthorhombicity increasingly blurs the distinction between orthorhombic and tetragonal.

that the octahedra rotate about (110), and the orthorhombic a-b axes are interchanged. These displacement patterns (the above description is somewhat oversimplified) generate an irreducible representation of the group of $I4/mmm$, with wave vectors $\mathbf{q}_1=\frac{1}{2}(110)$ and $\mathbf{q}_2=\frac{1}{2}(1\,-10)$, and also describe a degenerate pair of soft phonons with amplitudes (Q_1,Q_2).[6]

To provide a framework within which to discuss phase transformations in this system, we have constructed a Landau-Ginzburg free-energy function by considering symmetry-invariant combinations of the degenerate primary order parameters, $\mathbf{Q}=(Q_1,Q_1)$, and the secondary order parameter, η, representing the orthorhombic strain $(a-b)/(a+b)$:

$$F=\tfrac{1}{2}a(T-T_0)(Q_1^2+Q_2^2) + u(Q_1^2+Q_2^2)^2+v(Q_1^4+Q_2^4)+\cdots + \tfrac{1}{2}c\eta^2+d(Q_1^2-Q_2^2)\eta+\cdots . \quad (1)$$

The $Q^2\eta$ coupling provides orthorhombic strain proportional to $Q_1^2-Q_2^2$, as has been observed,[5,6] and renormalizes T_0, but can otherwise be ignored in a qualitative discussion. The first line of Eq. (1) is familiar in magnetism as the Landau representation of the XY model.[14] The instability induced by the quadratic terms for $T<T_0$ is resolved in two different ways depending upon the relative values of the isotropic and anisotropic quartic terms, u and v. If $v<0$ (and $u+v>0$), Q_1 or Q_2 is separately nonzero, corresponding to the two twin modifications of the observed LTO structure. However, if $v>0$ (and $2u+v>0$), a *coherent* superposition of the two LTO twins, where $|Q_1|=|Q_2|$, is the stable form. The coherently superimposed structure is tetragonal, $\eta=0$, since $Q_1^2-Q_2^2=0$.

Thus an extremely plausible suggestion for a low-temperature tetragonal (LTT) structure, one that bears the requisite close relationship of the HTT and LTO structures, is this $|Q_1|=|Q_2|$ phase. Under this postulate, the LTT space group is ($P4_2/ncm$), which has the same rotated and enlarged unit cell as the LTO phase but is primitive rather than base centered and, of course, $a=b$. (In terms of *primitive* unit cells, there is an enlargement in passing from LTO to LTT, corresponding to further loss of translational symmetry. The primitive HTT, LTO, and LTT cells contain, respectively, one, two, and four formula units.) If one neglects the small orthorhombic splitting, in practice it is difficult to distinguish between the diffraction patterns of the LTO and LTT phases. The intensities of the HTT-allowed reflections are independent of $\mathbf{Q}=(Q_1,Q_2)$ to lowest order. As for superlattice reflections, half of them present in the LTT phase are missing in an untwinned LTO crystal, but these are precisely the reflections supplied by the other twin. Excluding face-centered extinctions, one can show that LTO and LTT phases have identical superlattice intensities when averaged over unbiased twin distributions, assuming both phases have equal displacement amplitudes, $Q=(Q_1^2+Q_2^2)^{1/2}$.

We have performed a neutron powder-diffraction study of the LTT phase of $La_{2-x}Ba_xCuO_4$ ($x=0.10$), and find the data to be in agreement with the proposed $P4_2/ncm$ structure.[13] The *lack* of substantial changes in either the primary or allowed superlattice intensities in the vicinity of the LTO-LTT phase boundary indicates that Q does not change appreciably in passing from LTO to LTT.

A direct demonstration of the temperature-dependent reversal of the sign of $v(T)$, which can be inferred from the behavior of the soft phonons in the LTO phase, would constitute the ultimate proof of the correctness of the above picture.[15] Although single crystals of $La_{2-x}Ba_xCuO_4$ suitable for inelastic neutron scattering are not presently available, we have carried out such measurements on La_2CuO_4 and find that $v(T)$ does soften significantly with decreasing temperature, indicating an incipient LTO-LTT transformation even in the undoped material.[15]

Equation (1) makes an LTO-LTT transformation plausible resulting from the vanishing with temperature of the quartic anisotropy, $v(T)=0$, but is inadequate to discuss this case, as it omits higher-order anisotropy terms which become important as $v(T)\to 0$. This leads us to investigate the following free-energy function:

$$F=A(Q_1^2+Q_2^2)+u(Q_1^2+Q_2^2)^2+v(Q_1^4+Q_2^4)+w(Q_1^8+Q_2^8)\,. \tag{2}$$

Substituting $Q_1=Q\cos\theta$ and $Q_2=Q\sin\theta$, Eq. (2) can be rewritten as

$$F(Q,\theta)=f(Q)+\alpha\cos4\theta+\beta\cos8\theta\,, \tag{3}$$

where $\alpha=v(T)Q^4=\frac{1}{4}vQ^4+\frac{7}{16}wQ^8$ and $\beta=\frac{1}{64}wQ^8$. The phase diagram resulting from minimizing F with respect to θ has been discussed previously in a different context.[16] If β (i.e., w) <0, the LTO-LTT transformation is discontinuous (first order) and occurs at a temperature T_1 given by $v(T_1)=0$. If, on the other hand, $\beta>0$, the LTO-LTT phase boundary is split by the appearance of a new phase. This new phase is intermediate between LTO and LTT in the sense that it interpolates smoothly between, for example, the ($|Q_1|\neq0, |Q_2|=0$) LTO phase and the ($|Q_1|=|Q_2|\neq0$) LTT phase by a continuous growth of $|Q_2|$. The orthorhombic strain, although smaller than for LTO, is still present since $Q_1^2-Q_2^2\neq0$. The space group is *Pccn*, which is a subgroup of *Bmab* and $P4_2/ncm$. The *Pccn* phase is stable over a limited range of v (i.e., temperature), given by $w<4v(T)Q^{-4}<-w$, and both the LTO-*Pccn* and the *Pccn*-LTT transformations are continuous.

The abrupt reappearance of the unsplit tetragonal reflections with decreasing temperature suggests to us that in $La_{2-x}Ba_xCuO_4$ the LTO-LTT transformation proceeds discontinuously ($w<0$). However, the issue is somewhat clouded by the pronounced residual broadening of the LTT peaks, and by the persistence of the LTO phase at low temperature. Our neutron powder-diffraction data are equally consistent with either a LTT or a *Pccn* structure with appropriate small η.[13] (An LTO diffraction pattern differs from *Pccn* by systematic missing reflections. Such qualitative differences do not exist between LTT and *Pccn*.) Other neutron scattering studies of both Ba (Ref. 17) and Sr-doped La_2CuO_4 (Ref. 18) possibly consistent with an LTO-*Pccn* transformation have been reported. However, it is unclear to us whether these data might not also be equally well explained by coexistent but sufficiently resolved LTT and LTO phases.

The recent interest in high-T_c superconductivity has uncovered fresh examples of such modifications in related materials. in La_2CoO_4 a discontinuous transformation from the *Bmab* structure to a new tetragonal structure (which we suggest is $P4_2/ncm$) is observed.[19] In La_2NiO_4 a similar transformation has been interpreted as producing a low-temperature phase with smaller orthorhombic strain but no change of space group.[20] However, the authors state that the data are also compatible with a *Pccn* structure. The transformation is abrupt, and seems to us that a higher-resolution study might instead reveal the coexistence of $P4_2/ncm$ and *Bmab* phases just as we observe in $La_{2-x}Ba_xCuO_4$. In La_2NiO_4 the low-temperature transformation is very sensitive to oxygen stoichiometry. It is quite possible that a similar sensitivity occurs in the $La_{2-x}Ba_xCuO_4$ system.

In writing this paper we learned of the existence of *Bmab*, $P4_2/ncm$, and *Pccn* tilt structures in materials such as methyl-ammonium manganese chloride with the

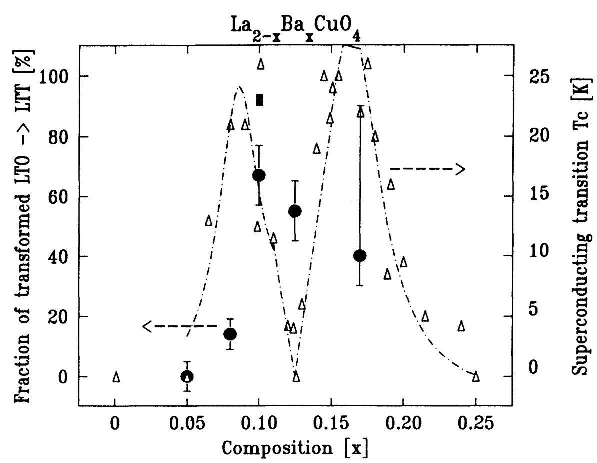

FIG. 3. Mutual-inductance T_c vs composition for Ba-doped La_2CuO_4 (triangles), which correlates well with the fraction of LTT phase present in low-temperature x-ray (circles) and neutron (rectangle) data.

K_2NiF_4 structure.[21] Their interrelation has been discussed group theoretically[22] and subjected to a Landau theoretical analysis[23] in the manner of Eq. (1). The discussion of the extended anisotropy and the bicritical point is new.

The investigation of the superconducting (SC) properties of these same $La_{2-x}Ba_xCuO_4$ samples has proceeded in a parallel manner with the structural studies.[11] The bulk SC transformation temperature, T_c, as a function of x has two maxima separated by a local minimum at $x=0.12$ (see Fig. 3). This feature has been independently verified by Kumagai and co-workers.[24] Samples with low bulk T_c's as determined inductively, when observed resistively show, in addition to the bulk T_c, a second T_c onset near 30 K.[11] For $x<0.12$ there is a general correlation between the fraction of LTT phase present in low temperature (as determined by the relative intensities of the split Bragg reflections) and the suppression of the bulk T_c (Fig. 3). Although our x-ray results are inconclusive on this point, the resistivity data[11,12] show that the effects of a second low-temperature phase also disappear for $x>0.15$. It is tempting to associate the relatively high T_c (25-30 K) with the LTO phase and a much lower T_c (<5 K and possibly vanishing) with the LTT phase. Production of LTT single-phase material, which would facilitate the testing of this interference, has so far proven unsuccessful.

In view of the subtle differences between them, it is not clear why the LTO and LTT phases should have such different SC properties. There are anomalies in the electrical resistivity,[11,12] Hall effect, and thermoelectric power,[12] which occur below T_1 in $La_{2-x}Ba_xCuO_4$ samples with $0.10<x<0.125$, indicative of substantial changes in the electronic structure.[12] Other possible explanations can be found. An increase in magnetic susceptibility occurs at the LTO-LTT transformation.[12] Because of magnetic frustration effects, even weak buckling of the CuO_6 octahedra greatly influences the magnetic interplanar coupling in antiferromagnetic La_2CuO_4 (Ref. 26) [as well as in La_2CoO_4 (Ref. 22)]. Although doping destroys antiferromagnetic long-range order, magnetic correlations persist in the SC region[27] and may mediate the SC spin pairing.[28] As a consequence, rearrangements in the structural buckling may profoundly influence the interplanar magnetic coupling and thus superconductivity.

It is a pleasure to acknowledge helpful discussions with K. S. Alexandrov, M. Sato, T. R. Thurston, K. Yamada, and especially with A. Aharony on various aspects of this work, which was supported by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

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