A new structural modification of superconducting $La_{2-x}M_xCuO_4$

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$La_{1.9}Ba_{0.1}CuO_4$ has been observed to undergo the following sequence of transformations upon cooling from 300 K: tetragonal ($I4/mmm$) $\xrightarrow{T_0=270\ K}$ orthorhombic ($Cmca$) $\xrightarrow{T_1=52\ K}$ tetragonal ($P4_2/ncm$). The newly discovered low-temperature tetragonal structure can be understood geometrically as arising from a coherent superposition of the two domain modifications of the orthorhombic structure. Dynamically, it results from a second instability in the twofold degenerate soft modes of the high-temperature tetragonal phase. Energetically, the system can be modeled as an XY-spin system with temperature-dependent quartic anisotropy $v(T)$, and the low-temperature transformation coincides with an isotropic point $v(T_1) = 0$. The relationship of the newly discovered transformation to other anomalous properties and to superconductivity is discussed briefly.

Introduction

Although subsequent developments have resulted in materials with higher superconducting transformation temperatures T_c, much interest still centers on the study of the properties of the doped La_2CuO_4 superconductors (SC) discovered by Bednorz and Müller [1]. This continued attention results in part from the relative structural simplicity of these materials, which are widely believed to share a common superconducting pairing mechanism with other high-T_c copper-oxide-based systems with similar structures. La_2CuO_4 is a layered perovskite, and perovskites have a proclivity toward structural instabilities associated with soft phonons [2]. It was therefore not surprising that inelastic neutron-scattering studies [3] revealed such a soft-phonon mechanism for the high-temperature body-centered tetragonal (HTT; space group $I4/mmm$) to low-temperature orthorhombic (LTO; space group $Cmca$) transformation in $La_{2-x}M_xCuO_{4-y}$ (M = Sr, Ba). The transformation temperature, T_0, about 515 K in undoped material ($x = y = 0$), decreases strongly with alkaline-earth doping [4]. It is widely believed that superconducting preparations of this material ($0.05 < x < 0.3$) have the LTO $Cmca$ structure [5].

There have, nonetheless, been many reports of anomalies in thermal [6], elastic [7], structural [8], and optical [9] properties of both doped and undoped La_2CuO_4 which have suggested the possibility of further low-temperature phase transformations. We report here the observation of a new low-temperature tetragonal (LTT) structure in the $La_{2-x}Ba_xCuO_{4-y}$ system. The structure of the new phase is determined and shown to result from an unresolved soft-mode instability of the HTT phase. These new findings account in a natural way for the unexplained elastic anomalies noted in these materials, and strongly suggest the occurrence of this LTT structure in strontium-doped material as well. The implications of the fact that SC occurs in a LTT as well as (conceivably rather than) the previously supposed LTO modification are briefly explored.

2. Experiment

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; the process has been described previously [10] and shown to yield a series of $La_{2-x}Ba_xCuO_{4-y}$ samples with consistent and reproducible properties. High-resolution X-ray diffraction studies were carried out in a closed-cycle He refrigerator at temperatures between 10 K and 300 K using a 12-kW Cu rotating anode source. $K_{\alpha 1}$ radiation was used, the necessary high-angular resolution being provided by a perfect Ge (111) monochromator and analyzer. Representative scans for a sample with $x = 0.1$ of the (110) La_2CuO_4 Bragg reflection are shown in **Figure 1**. (We use throughout an indexing scheme based upon the HTT $I4/mmm$ structure: $a_0 = b_0 = 5.39$ Å, $c_0 = 13.15$ Å.) The splitting characteristic of the LTO phase, absent at 300 K, is evident on cooling to 180 K and 53 K. The 52 K scan reveals a recovered unsplit tetragonal component which is first barely anticipated at 53 K. On further cooling, the LTO peaks decrease, but they are still weakly visible at 10 K, even after several days. The (200) scan is virtually unchanged over the same temperature interval. The redistribution of the (110) intensity for $T <$ 52 K is sluggish, and if the sample is cooled rapidly (30 min) from room temperature to 10 K, the transformation occurs slowly over a period of several hours. Similar but less pronounced hysteretic effects are evident upon heating above 53 K. The noticeable increase in width of the LTT (110) reflection is attributed to residual strain effects. We interpret this behavior to signify a discontinuous transformation to a new LTT phase, as shown in **Figure 2**.

Additional powder data were collected from a different specimen of $La_{1.9}Ba_{0.1}CuO_4$ at several temperatures between 284 K and 15 K using 2.373-Å neutrons. In agreement with Figure 2, two transformations were observed, at about 275 K and over the range 50–40 K, in which about 90% of the LTO phase transformed to the LTT phase. The remaining 10% LTO phase persisted to 15 K, but no hysteresis effects were seen in this sample. The transformation from HTT to LTO is accompanied by the appearance of weak superlattice peaks whose integrated intensity shows a slight but discernable discontinuity at the LTO-to-LTT transformation.

Extended data sets suitable for neutron Reitveld refinement were collected at 15 K and 91 K. From symmetry considerations (see below), the space group $P4_2/ncm$, with an enlarged unit cell with dimensions $\sqrt{2}a$, c with respect to the HTT structure, was chosen for the LTT structure. The residual strain broadening of reflections such as HTT (220) [which index as (400) in the LTT cell] was simulated by removing the constraint that $a = b$. It cannot be ruled out that the true structure is slightly orthorhombic (most probable space group $Pccn$), but attempts to refine the structure with this symmetry failed to produce better fits.

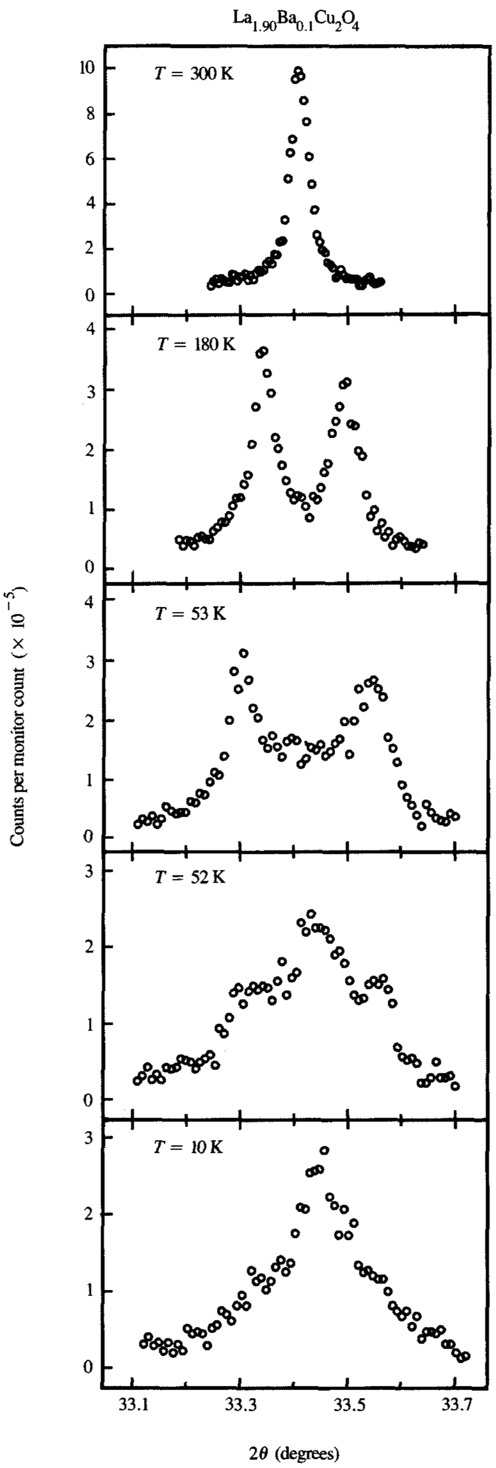

Figure 1

The temperature-dependent splitting of the tetragonal (110) reflection at several temperatures. The unsplit component, which re-emerges below 53 K, is noticeably broader than at 300 K.

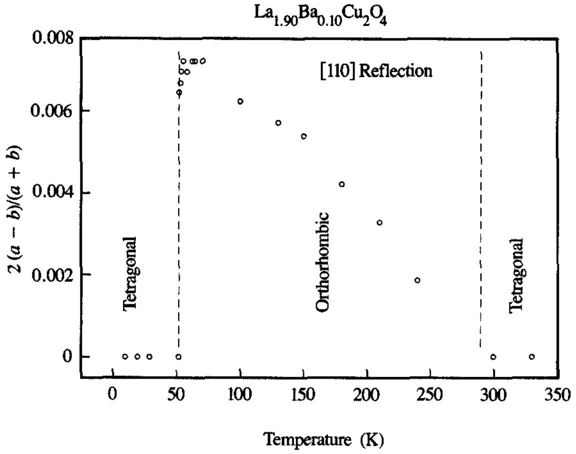

Figure 2

Summary of the behavior of the orthorhombic order parameter vs. temperature.

Table 1 Results of Reitveld refinement of neutron data from $La_{1.9}Ba_{0.1}CuO_4$ at 91 K. Figures in parentheses are estimated standard deviations in the least significant digit. Space group *Bmab*.

Atom	*Site*	*x*	*y*	*z*	*B* (Å)
La, Ba	8(f)	0	0.0056(3)	0.3609(1)	0.0(1)
Cu	4(a)	0	0	0	−0.2(1)
O(1)	8(e)	1/4	1/4	0.0055(2)	0.2(1)
O(2)	8(f)	0	−0.0285(5)	0.1826(2)	0.7(1)

$a = 5.3455(2)$ Å; $b = 5.3793(2)$ Å; $c = 13.2438(6)$ Å.
$R_I = 0.024$; $R_{wp} = 0.076$; $R_E = 0.060$.

Table 2 Results of Reitveld refinement of neutron data from $La_{1.9}Ba_{0.1}CuO_4$ at 15 K. Scattering lengths of 0.827, 0.525, 0.772, and 0.5805×10^{-12} cm were taken for La, Ba, Cu, and O, respectively. Figures in parentheses are estimated standard deviations in the least significant digit. Space group $P4_2/ncm$.

Atom	*Site*	*x*	*y*	*z*	*B* (Å)
La, Ba	8(i)	0.0040(3)	0.0040	0.3610(1)	0.1(1)
Cu	4(d)	0	0	0	0.1(1)
O(1)	4(e)	1/4	1/4	0.0079(4)	0.0(3)
O(1′)	4(a)	3/4	1/4	0	0.7(4)
O(2)	8(i)	−0.0213(4)	−0.0213(4)	0.1824(2)	0.6(1)

$a = 5.3559(2)$ Å; $b = 5.3665(3)$ Å; $c = 13.2381(7)$ Å.
$R_I = 0.031$; $R_{wp} = 0.088$; $R_E = 0.063$.

Likewise, the fits did not reveal any deviation from full oxygen stoichiometry ($y = 0$).

The results for the LTO structure at 91 K are listed in **Table 1**. (For ease of comparison, the space-group setting *Bmab*, related to the conventional *Cmca* setting by an interchange of *b* and *c*, has been chosen.) The results for the LTT structure at 15 K are shown in **Table 2**. The fits, as judged by the R-factors, profile, and difference plots [**Figures 3(a)** and **3(b)**] are very good at both temperatures. The slightly worse fit for the LTT structure is probably due to small residual amounts of the LTO phase which have not been allowed for in the refinement. A more detailed account of the neutron refinements will be given in a subsequent paper.

3. Discussion

The essential features of the LTT structure and its relationship to the HTT and LTO structures are shown schematically in **Figure 4**. In the LTO structure, sheets of CuO_6 octahedra are buckled by alternate rotations of about 3.5° about one of the two equivalent [110] axes as in Figure 4(a). Figure 4(b) shows the LTT buckling pattern, which is obtained by the superposition of the pattern of Figure 4(a) with buckling of equal amplitude about both of the [110] axes. The resulting rotations of the octahedra are about {100} axes, adjacent layers being related by a fourfold glide operation which restores tetragonal symmetry.

Insight into the factors which favor the LTT or LTO structures is obtained from a simple Landau theoretical analysis of the soft-mode instability. Represent the amplitude of the degenerate soft modes associated with the wavevectors $q_1 = \frac{1}{2}(110)$ and $q_2 = \frac{1}{2}(1\text{-}10)$ as (Q_1, Q_2). The symmetry-invariant free-energy expansion with a soft-mode instability below T_0 takes the form

$$F = \tfrac{1}{2}a(T - T_0)(Q_1^2 + Q_2^2) + u(Q_1^2 + Q_2^2)^2 + v(Q_1^4 + Q_2^4) + \cdots \qquad (1)$$

where the terms represent, respectively, harmonic and isotropic anharmonic and quartic anharmonic contributions. Since both modes become unstable at T_0, the form of the instability is determined by the competition between anharmonic terms. Minimization of Equation (1), which has been studied in the context of *XY*-magnetic spin models [11], yields only two stable regions in the space of (u, v):

1. $v < 0$; $(u + v) > 0$, for which either Q_1 or Q_2 separately is nonzero, corresponding to the LTO structure.
2. $v > 0$; $(2u + v > 0$, for which $Q_1 = Q_2 \neq 0$, corresponding to the LTT structure.

Thus, the LTO–LTT transformation temperature T_1 is defined by $v(T_1) = 0$, with $v(T > T_1) < 0$ and $v(T < T_1) > 0$.

In principle the model prediction $v(T_1) = 0$ can be tested by measuring the soft-phonon frequencies in the various

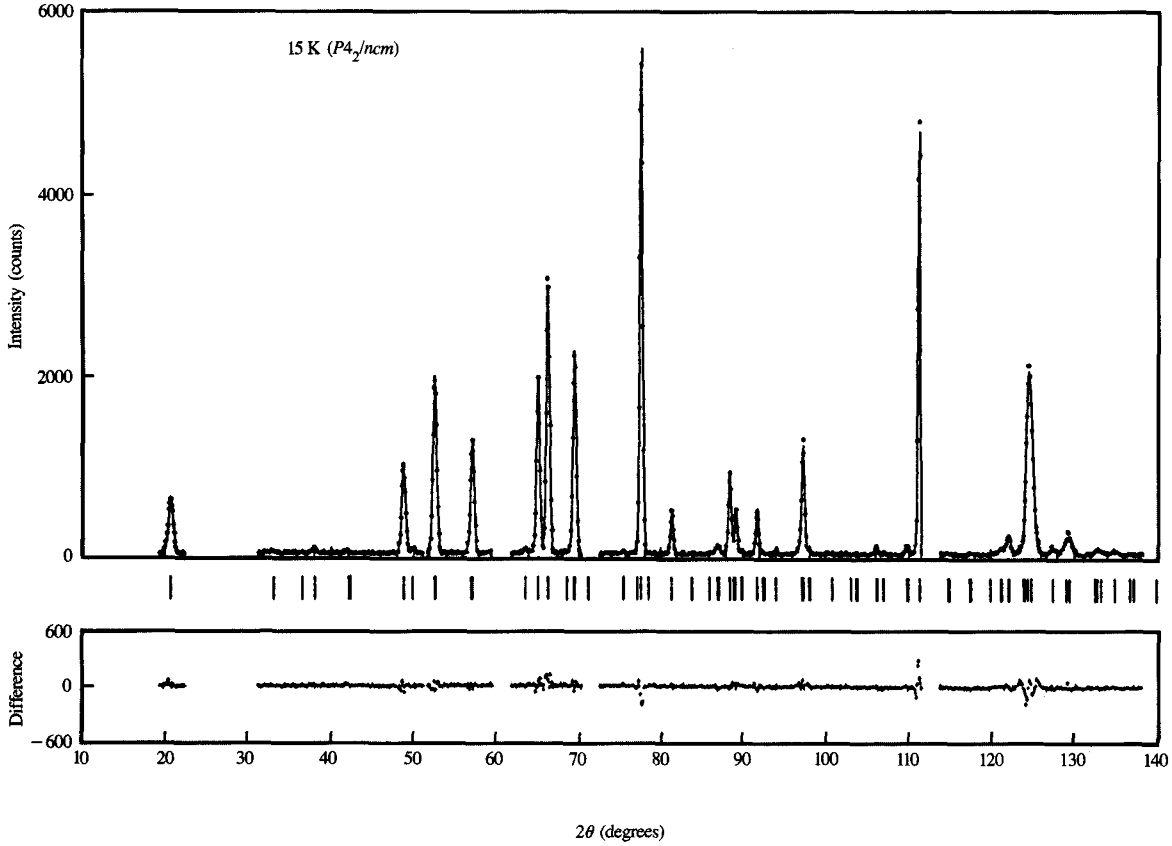

Figure 3

Comparison of calculated and observed powder profile data for the low-temperature tetragonal phase, assuming a $P4_2/ncm$ structure.

phases, as sketched schematically in **Figure 5**. The mode frequencies, degenerate in the HTT, are split in the LT phases. It can be shown that the frequency of the uncondensed LTO mode (Q_2, say) vanishes as $v \rightarrow 0$. Unfortunately, single crystals of $La_{2-x}Ba_xCuO_{4-y}$ suitable for inelastic neutron-scattering determination of ω_2 in the LT phases are not at present available [12]. Referring to Figure 5, if $|v| \ll u$, ω_2 will remain relatively soft throughout the LTO phase. This undoubtedly explains the ultrasonic anomalies observed by Fossheim et al. in $La_{1.85}Ba_{0.15}CuO_{4-y}$ [7]. Their "instability" region corresponds well with the LTO region, $T_1 > T > T_0$, which we have observed for $x = 0.15$ [13].

The sequence HTT–LTO–LTT with structures identical to those found here has been previously observed in other compounds with the K_2NiF_4 structure, and has been analyzed group-theoretically in terms of tilt structures [14]. Onoda et al. [15] have reported an orthorhombic *Pccn* structure which, within experimental error, is identical to the LTT structure described here for a single crystal of $La_{1.85}Ba_{0.15}CuO_{4-y}$ at room temperature. Our study [13] of $La_{2-x}Ba_xCuO_4$ vs. x, for $x = 0.15$, shows an LTO–LTT transformation, but at much lower temperature ($T_1 = 65$ K). More complete understanding of this and other structural anomalies and inconsistencies may involve a careful assessment of the role of oxygen vacancy doping, which is known to accompany high Sr doping in $La_{2-x}Sr_xCuO_{4-y}$ unless special precautions are taken [16].

Finally, we comment on the possible relevance of these new observations to superconductivity:

1. As a consequence of short coherence lengths in the high-T_c oxides, the SC order is expected to be strongly depressed and perhaps to vanish at twin grain boundaries [17]. Tunneling and flux trapping in such barriers may have significant effects on the current-carrying capacity of

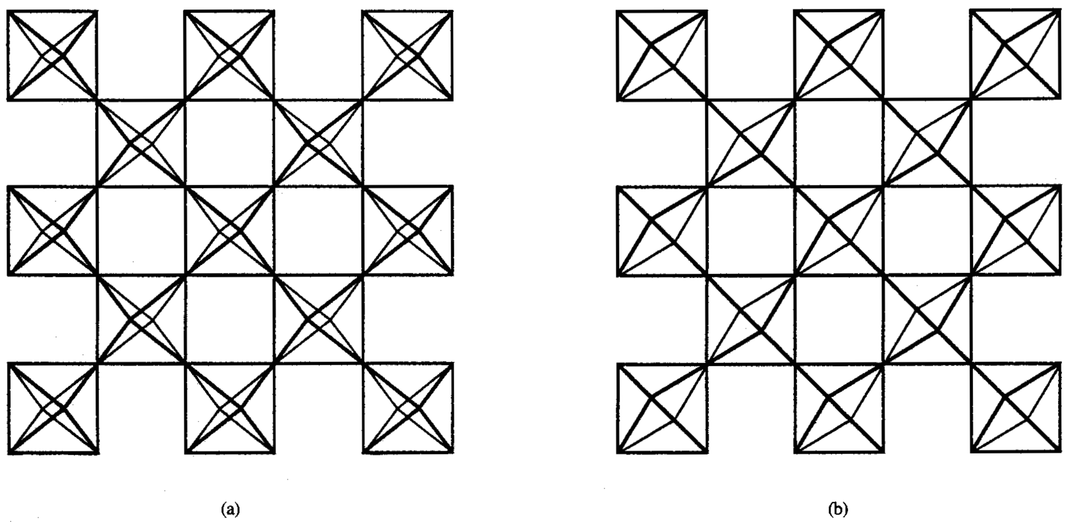

Figure 4

Schematic representation of the tilt pattern within one plane of CuO_6 octahedra in the LTO and LTT phases. In the LTT phase the pattern is rotated by 90° (fourfold glide) in the next layer to establish tetragonal symmetry.

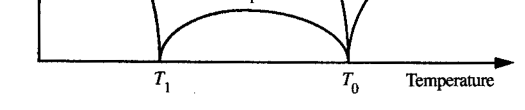

Figure 5

Schematic representation of the behavior of the soft-X-point phonon modes in the low-temperature phases. $\omega_1(T_0) = \omega_2(T_0) = 0$ due to vanishing harmonic energy terms. $\omega_2(T_1) = 0$ due to vanishing quartic anisotropy energy.

such materials. Since the domain configurations of the LTO and LTT structures are quite different, it would be interesting to compare the SC transport properties of LTT and LTO materials which are nearly identical in other respects. (Of course, this presupposes the existence of SC in LTO modifications, in accordance with accepted common belief.)

2. As pointed out by Thio et al. [18], the weak buckling of the CuO_6 planes associated with the LT phases causes a canting of the antiferromagnetic (AF) spin structure. Because of frustration effects, even small canting can greatly influence the magnetic interplanar coupling. Although doping destroys AF long-range order, AF correlations are still significant at doping levels necessary for SC, and may mediate SC spin-pairing. If this is so, both the interplanar SC and AF coupling are directly influenced by the spin-canting and structural buckling in the CuO planes. This suggests that the SC transformation temperatures of the LTO and LTT modifications may differ significantly.

In this connection it is noteworthy that for a sequence of $La_{2-x}Ba_xCuO_{4-y}$ samples prepared identically to those of this study, Moodenbaugh et al. [10] find that with increasing x the SC transformation first increases to about 20 K for $x = 0.08$, then broadens and decreases to about 5 K near $x = 0.12$, increases again to near 25 K at $x = 0.15$, and then drops off again. The lowering of T_c at intermediate doping roughly correlates with the occurrence of a major fraction of LTT phase present at low temperatures [13]. A related observation is that Fujita et al. have reported two distinct T_c's in highly Ba-doped samples of La_2CuO_4 [4]. Further discussion of the interrelation of the structural and superconducting properties of these materials will be reported in a future publication [13].

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