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STRUCTURAL PHASE TRANSITIONS AND SUPERCONDUCTIVITY IN LANTHANUM COPPER OXIDES

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1. Introduction

Despite the enormous effort expended over the past ten years to determine the mechanism underlying high temperature superconductivity in cuprates there is still no consensus on the physical origin of this fascinating phenomenon. This is a consequence of a number of factors, among which are the intrinsic difficulties in understanding the strong electron correlations in the copper oxides, determining the roles played by antiferromagnetic interactions and low dimensionality, analyzing the complex phonon dispersion relationships, and characterizing the phase diagrams which are functions of the physical parameters of temperature and pressure, as well as the chemical parameters of stoichiometry and hole concentration. In addition to all of these intrinsic difficulties, extrinsic materials issues such as sample quality and homogeneity present additional complications.

Within the field of high temperature superconductivity there exists a subfield centered around the material originally reported to exhibit high temperature superconductivity by Bednorz and Müller [1], Ba doped La_2CuO_4. La_2CuO_4 is structurally the simplest cuprate superconductor, consisting of single copper oxide (CuO_2) planes separated by LaO_2 rocksalt

layers [2] in which the La can be replaced by divalent alkaline earths to oxidize the CuO_2 planes and yield high temperature superconductivity (Figure 1). Thus compositions such as $La_{2-x}Sr_xCuO_4$, where x is varied between zero and 0.3, exhibit phase diagrams in which antiferromagnetic long range order exists below about 300 K when x = 0, then evolve into unusual metals for which superconductivity is observed with onset

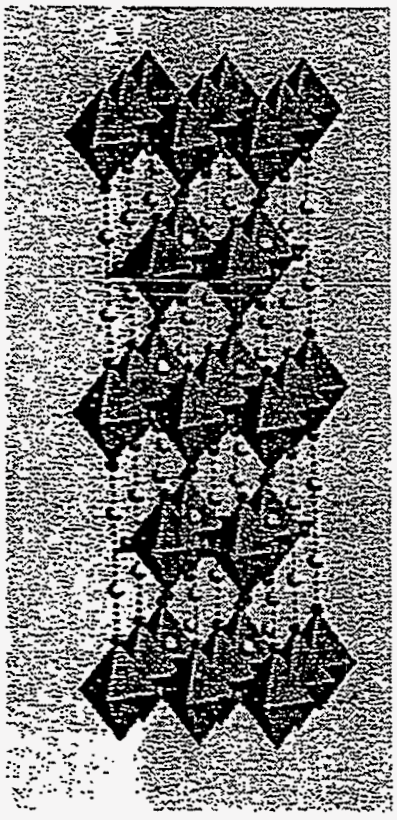

Figure 1. Crystal structure of La_2CuO_4. The layers of corner shared CuO_6 octahedra are shown with oxygen atoms as small dark spheres. The La atoms are shown as large light spheres.

temperatures as high as 38 K for $0.05 < x < 0.2$, and finally behave as normal (nonsuperconducting) metals when $x > 0.2$. This range of behavior is summarized in the phase diagram shown in Figure 2. It is believed that phase diagrams such as this are a generic feature of cuprate superconductors,

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although it is only in the lanthanum cuprates that such a clear evolution of the complete phase diagram with doping is observed.

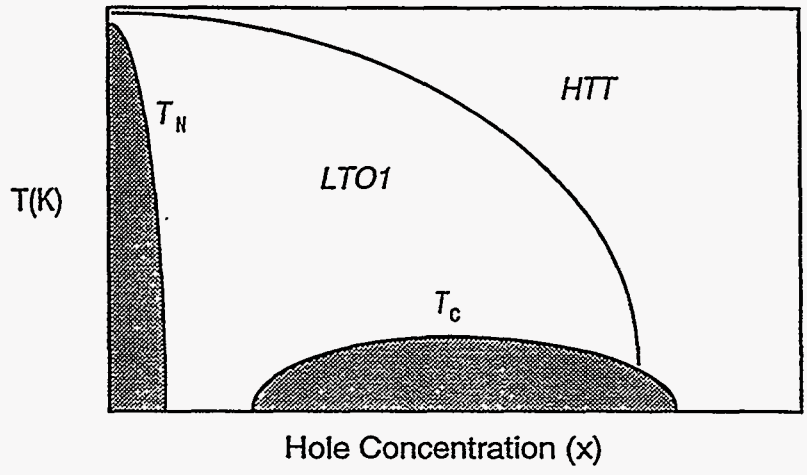

Figure 2. Phase diagram of $La_{2-x}Sr_xCuO_4$. T_N is the Neel temperature and T_c is the superconducting transition temperature. The structural designations HTT and LTO1 are described in the text and defined in Table 1.

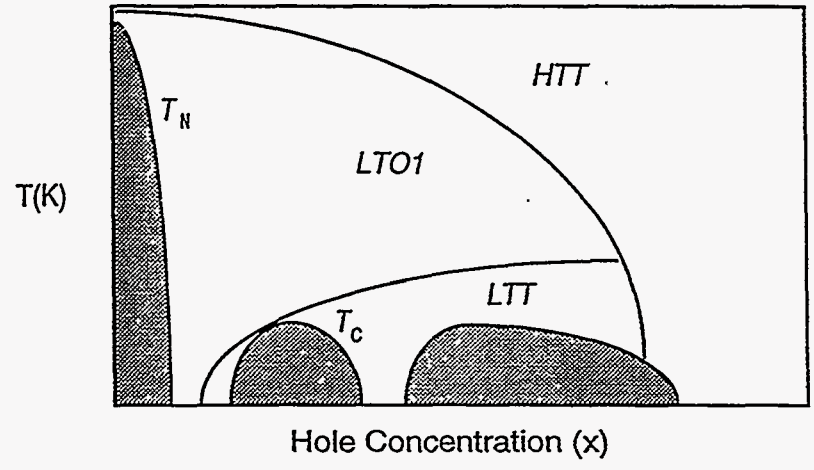

Figure 3. Phase diagram of $La_{2-x}Ba_xCuO_4$. Note the strong suppression of superconductivity in the intermediate doping regime (centered at x = 1/8). The structural designations HTT, LTO1 and LTT are described in the text and defined in Table 1.

Shown in Figure 3 is the striking difference found for the phase diagram of La_2CuO_4 doped with Ba, rather than Sr, in the range of x near 0.125. Whereas the Sr doped materials exhibit almost monotonically increasing T_cs from x = 0.1 to x = 0.15, similar to the phase diagram of Figure 2, the Ba doped materials show a deep minimum in the superconducting transition temperatures (and Meissner fractions) centered at x = 0.125. This observation, first reported in 1988 [3], has stimulated a large number of studies with the purpose of understanding the source of this distinction [4]. What these studies have revealed is a fascinating interplay of structural, magnetic and superconducting properties which is unique in the field of high temperature superconductivity and will be summarized in this contribution.

2. Structural Phase Transformations

2.1. STRUCTURES

The initial observation [3] of the suppression of superconductivity in $La_{2-x}Ba_xCuO_4$ near x = 0.12 (Figure 3) led to detailed studies of the structures of these materials as functions of temperature [5,6]. Using both synchrotron x-ray powder diffraction [Axe et al., reference 5] and neutron powder diffraction [6] it was soon discovered that the material underwent a structural phase transformation from the orthorhombic Bmab (LTO1, Low Temperature Orthorhombic 1) phase (the same phase present in superconducting $La_{2-x}Sr_xCuO_4$ samples), to an apparently non-superconducting tetragonal (LTT, Low Temperature Tetragonal) phase having $P4_2/ncm$ space group symmetry. It is important to recognize that this latter structure is different from that adopted by these materials at high temperatures, the tetragonal I4/mmm (HTT, High Temperature Tetragonal) structure. The LTO1 structure is derived from the HTT structure by tilting the CuO_6 octahedra about the $(110)_{HTT}$ or $(1\text{-}10)_{HTT}$ axis, leading to either of the two LTO1 twins (see Figure 4). The unit cell of the LTO1 phase has lattice parameters of approximately (ignoring the small, $\approx$ 1% orthorhombic distortion) $\sqrt{2}a \times \sqrt{2}a \times c$, where a and c are the lattice parameters of the high temperature HTT phase. The LTT structure develops from the LTO1 phase as a result of the condensation of the second of these degenerate modes, without a change in the conventional unit cell size (although the *primitive* cell does double as a result of this transformation).

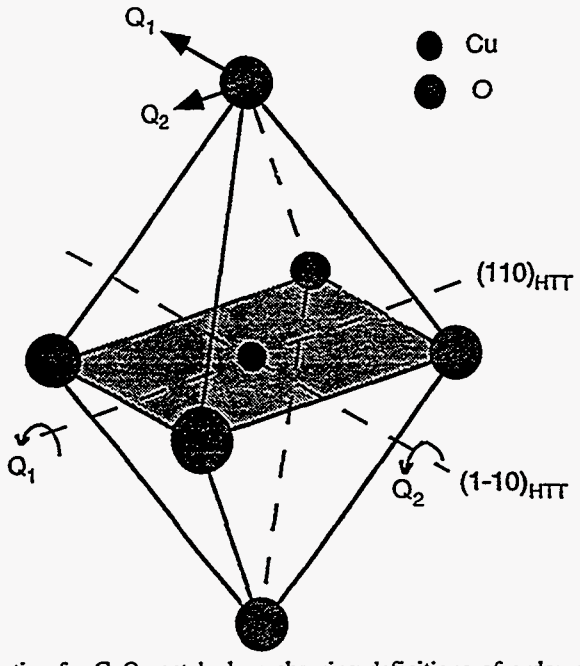

Figure 4. Schematic of a CuO_6 octahedron showing definitions of order parameters used in Equation (1) and Table 1.

2.2. LANDAU THEORY

A treatment of these structural transitions using Landau's theory of phase transitions [5], which we summarize here, leads to the conclusion that the second transition is a result of the vanishing of the quartic anisotropy, v(T), with temperature. This is based upon the following expression for the Landau free energy which is a function of the order parameters Q_1 and Q_2, where Q_1 corresponds to the magnitude of the tilt of the CuO_6 octahedra about the $(110)_{HTT}$ axis and Q_2 is the tilt magnitude about the $(1\text{-}10)_{HTT}$ axis (Figure 4):

$$F(Q_1, Q_2) = A(Q_1^2+Q_2^2) + u(T)(Q_1^2+Q_2^2)^2 + v(T)(Q_1^4+Q_2^4) + w(T)(Q_1^8+Q_2^8). \quad (1)$$

Furthermore, the fact that the $P4_2/ncm$ space group is not a subgroup of the Bmab space group is consistent with the experimental observation that the LTO1 to LTT structural transformation is first order. The four known tilt structures for lanthanum cuprates are listed in Table 1 along with definitions based upon the values of the order parameters for each structure.

If the substitutions $Q_1 = Q\cos\Theta$ and $Q_2 = Q\sin\Theta$ are made in Equation (1), the following expression results

$$F(Q,\Theta) = f(Q) + \alpha\cos 4\Theta + \beta\cos 8\Theta \qquad (2)$$

where $\alpha = v(T)Q^4 = (1/4)vQ^4 + (7/16)wQ^8$ and $\beta = (1/64)wQ^8$. In Equation (2), Q and Θ are the "amplitude" and "phase" of the tilt of the CuO_6 octahedra, where the amplitude corresponds to the magnitude of the tilt around an axis in the a-b plane and the phase is the polar rotation angle of this in-plane axis about the crystallographic *c* axis. Minimization of F with respect to Θ predicts a first order LTO1 to LTT transformation for $\beta < 0$, but a new structural phase having Pccn (LTO2, Low Temperature Orthorhombic 2) symmetry appears as an intermediary between the LTO1 and LTT phases if $\beta > 0$. Since the orthorhombicity is proportional to $(Q_1^2 - Q_2^2)$ for all four phases listed in Table 1, the LTO2 phase will in general be *less* orthorhombic than the LTO1 phase. Such an LTO2 phase was in fact first observed [7] in samples of $La_{2-x}Sr_xCuO_4$ in which the La ions were partially substituted by smaller rare earth ions such as Nd. Furthermore, in the $La_{2-x-y}Nd_ySr_xCuO_4$ system it was observed that the LTO1 to LTO2

TABLE 1. The four known tilt structures in lanthanum cuprates. Q_1 and Q_2 are the order parameters in Equation (1), and Q and Θ are the (polar) order parameters in Equation (2).

Space Group	Notation	Unit Cell Size	(Q_1,Q_2)
I4/mmm	HTT	$a \times a \times c$	$Q_1 = Q_2 = 0$ $Q = 0$
Bmab	LTO1	$\sqrt{2}a \times \sqrt{2}a \times c$	$Q_1 \neq 0$ ($Q_1 = 0$) $Q_2 = 0$ ($Q_2 \neq 0$) $Q \neq 0, \Theta = 0$
Pccn	LTO2	$\sqrt{2}a \times \sqrt{2}a \times c$	$Q_1 \neq 0$ $Q_2 \neq 0$ $\lvert Q_1\rvert \neq \lvert Q_2\rvert$ $Q \neq 0,$ $0 < \Theta < 45°$
$P4_2/ncm$	LTT	$\sqrt{2}a \times \sqrt{2}a \times c$	$\lvert Q_1\rvert = \lvert Q_2\rvert \neq 0$ $Q \neq 0, \Theta = 45°$

and LTO2 to LTT transformations were second order, as permitted by space group-subgroup relationships and Landau theory, for low values of y ($y < 0.3$), but that at higher values of y the LTO1 to LTO2 transformation became first order, as evidenced by the coexistence of the LTO1 and LTO2 phases. The appearance of a first order LTO1 to LTO2 transformation can be rationalized [7] by including higher order terms than shown in Equation (2) in the Landau expansion for the free energy.

2.3. SHORT VERSUS LONG RANGE STRUCTURAL ORDER

There has been considerable discussion concerning the nature of the low temperature structures in these materials, primarily because of the broadening exhibited by, for example, the (h00) and (0h0) reflections in the LTT phase. The origin of this broadening has been attributed to small domains several hundred Å in size [7], or unresolved orthorhombic splitting indicating that the true structure is LTO2. Other authors have presented evidence, primarily based upon experimental probes sensitive to short range order such as Pair Distribution Function (PDF) analysis of neutron scattering data [8], that all the structures determined by conventional diffraction techniques are averages over structures which are locally LTT but lack long range coherence. The presence of long range structural coherence, where long can be loosely defined as exceeding the superconducting coherence length in the CuO_2 planes (about 30 Å), has also been described as a structural prerequisite for superconductivity [9]. Similar arguments have been applied to the HTT to LTO1 transformation based upon Extended X-ray Absorption Fine Structure (EXAFS) and Perturbed Angular Correlation Spectroscopy (PACS) measurements [10], viewing the structural transformation at high doping levels ($x > 0.15$) in $La_{2-x}Sr_xCuO_4$ as an order-disorder transition (in which long range correlation of the CuO_6 octahedra tilt direction serves as the order parameter), rather than as a classical second order phase transformation where the order parameter is the magnitude of the tilt. The Potts model described in reference [7] gives a theoretical description of a similar order-disorder scenario in which the temperature dependent competition between energy and entropy determines the structural phase diagram. The complete reconciliation of these different views of structural transitions in lanthanum cuprates has not yet been presented and perhaps must wait until the various types of experiments have been performed on identical samples, allowing a more accurate basis for comparison. Nevertheless, it is perhaps significant that an electron diffraction study [11] found that the LTT phase nucleates at the LTO1 twin boundaries through an intermediate LTO2 phase. Such complex domain

microstructures might influence results of experimental techniques which are sensitive to large Q differently than results of techniques which emphasize smaller Q values. It is possible that such considerations will reconcile the short and long range structural data for the lanthanum cuprates.

2.4. RARE EARTH SUBSTITUTION

The effect of rare earth size in samples of composition $La_{2-x-y}RE_ySr_xCuO_4$ has also been investigated [12, 13]. The LTO1 to LTO2 and LTT structural transformations occur at higher temperatures for equal amounts of smaller rare earths such as Sm and Gd. In Figure 5, for example, $La_{1.675}Sm_{0.2}Sr_{0.125}CuO_4$ is seen to transform from LTO1 to LTT at a temperature of 125 K, well above the maximum temperature (80 K) at which $La_{1.875-y}Nd_ySr_{0.125}CuO_4$ samples transform. This leads to the general conclusion that *the primary effect of rare earth substitution is to increase the tendency toward structural instability in lanthanum cuprates, and the smaller the rare earth the greater the tendency toward instability.*

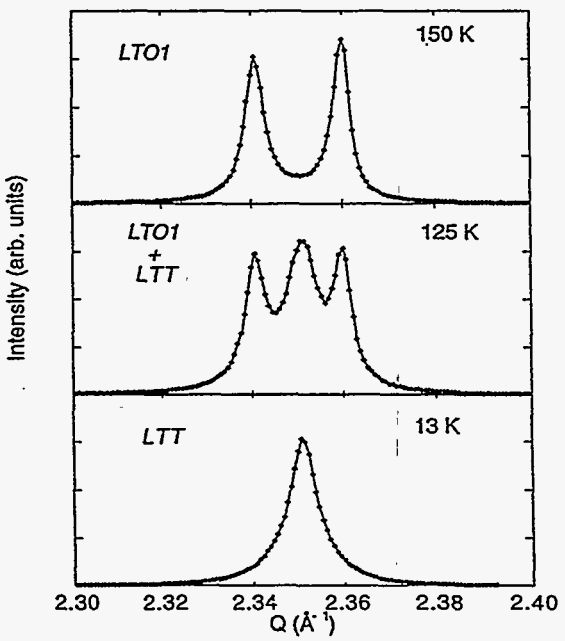

Figure 5. Synchrotron x-ray powder diffraction scans of the $(110)_{HTT}$ reflection of $La_{1.675}Sm_{0.2}Sr_{0.125}CuO_4$. Data was collected at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. $Q = (4\pi\sin\theta)/\lambda$, where $\lambda = 0.70377$ Å and θ is the x-ray scattering angle. The coexistence of LTO1 and LTT phases at 125 K shows that the transformation is first-order.

It is interesting to note that the transitions described so far involve rotations of the CuO_6 octahedra about the in-plane (*a* and *b*) axes of the La_2CuO_4 structure, but rotations of the CuO_6 octahedra about the third axis (the *c* axis) have not yet been reported, although distortions of this type have been described [14] in cuprates with the T' (Nd_2CuO_4) type structure in which there is no apical oxygen atom. There are several examples [15] of isostructural materials which do exhibit rotations of the metal-oxygen octahedra about the *c*-axis, among which are Sr_2RhO_4 and Sr_2IrO_4. In these materials the RhO_6 and IrO_6 octahedra are rotated by approximately 10 degrees about the *c* axes, reducing the space group symmetry from I4/mmm to $I4_1$/acd. The latter unit cell has dimensions of $\sqrt{2}a \times \sqrt{2}a \times 2c$, where *a* and *c* are the lattice dimensions for the I4/mmm cell.

3. Structural Phase Transitions and Magnetism

The effect of the HTT $\rightarrow$ LTO1 transformation upon the magnetic properties of La_2CuO_4 has been extensively studied using magnetic susceptibility [16] and neutron scattering techniques [17]. The magnetism in the lanthanum cuprates is well described by the spin 1/2 two-dimensional Heisenberg model on a square lattice,

$$\mathbf{H} = J \sum \mathbf{S}_i \bullet \mathbf{S}_j \qquad (3)$$

where the sum is over adjacent lattice sites <i, j>, and the superexchange interaction (*J*) has a magnitude of approximately 1500 K [17]. The primary effects of the structural transformation upon the magnetic properties can be attributed to an additional antisymmetric superexchange term in the spin Hamiltonian [18], the Dzyaloshinsky-Moriya (D-M) interaction [19],

$$\mathbf{H}_{D\text{-}M} = \mathbf{D}_{ij} \bullet \mathbf{S}_i \times \mathbf{S}_j \qquad (4)$$

where $\mathbf{S}_i$ and $\mathbf{S}_j$ are the Cu spin vectors for adjacent lattice sites and $\mathbf{D}_{ij}$ is the D-M spin-orbit coupling constant. This interaction can introduce a canted component to the staggered magnetization in the Néel state if the in-plane oxygen ions are not located on sites with inversion symmetry. That is the case for the LTO1, LTO2 and LTT (*but not the HTT*) structures. Initially the observed effect of the low temperature structural phase transitions upon the magnetism was attributed to this interaction, although recently it has become apparent that a more comprehensive treatment is necessary to account for the experimental observations (see below). Here we will briefly describe the

results of experimental measurements of the magnetic susceptibility, spin structure and spin wave gaps in several LTO2 and LTT phases.

3.1. $La_{2-x}Nd_xCuO_{4+\delta}$

The first insulating cuprate system studied [20-22] which exhibited structural transformations to the LTO2 and LTT phases was $La_{2-x}Nd_xCuO_{4+\delta}$. Studies of ceramic samples [20] demonstrated that the substitution of Nd for La induced these low temperature structural transformations, and that the transformations were rather sensitive to the amount of excess oxygen present in the samples. It is therefore very important in studies of structure and magnetism to ensure that the samples are oxygen stoichiometric, a situation which can be obtained by reducing the samples in a N_2 atmosphere at 400 C for extended periods of time.

The magnetic properties of Nd substituted materials are distinctly different from those of the La_2CuO_4 parent compound at low temperatures. Whereas La_2CuO_4 is metamagnetic below the Néel temperature [17, 23], and remains so to 2 K, $La_{2-x}Nd_xCuO_4$ samples exhibit spontaneous magnetization at low temperatures in the LTO2 and LTT phases, that is they are weak ferromagnets [20-22]. This conclusion has been arrived at by observation of remanence in the magnetic susceptibility at low temperatures [19, 21] and by magnetic neutron diffraction measurements on both ceramics [19] and single crystals [21, 22] which demonstrate that a magnetic phase transition occurs in the low temperature phases in zero field which is analogous to that observed in La_2CuO_4 crystals in a magnetic field [17]. The magnitude of the ferromagnetic moment is comparable to that of the canted moment in the metamagnetic state of La_2CuO_4 ($\approx 10^{-3}\ \mu_B$).

An important question in that regard concerns the presence of weak ferromagnetism in the LTT phase, where theory predicts there is zero ferromagnetic moment per CuO_2 plane [24, 25]. In general, the samples studied have either LTO2 symmetry at low temperature, or LTT-like symmetry in which the width of the (220) reflection is considerably greater than other diffraction peaks. This residual width may have several origins, including domain size broadening or unresolved orthorhombic splitting (that is, the strcutures are LTO2, not LTT). Thus the question of whether or not LTT phases are weak ferromagnets (that is, the Cu spins are canted) remains unresolved. It was suggested that the Nd ions might cause the out-of-plane spin canting [Stein et al, reference 25], and in the next Section we describe data for Sm doped La_2CuO_4 which support this suggestion. The presence of a fairly large (4 μ_B) magnetic moments on the Nd ions will enhance coupling between the Nd and Cu spins. Nevertheless, it is clear that the sign

of the magnetic coupling between CuO_2 layers is changed by the structural transformations in $La_{2-x}Nd_xCuO_4$ [20 - 22].

There has also been a measurement of the magnitude of the spin wave gap in a single crystal of $La_{1.65}Nd_{0.35}CuO_4$ at temperatures above and below the LTO1 to LTT (or LTO2) transition temperature [21]. There it was found that the in-plane gap in the LTO2 phase was twice as large as that of the LTO1 phase. This result could not be explained using the D-M interaction in combination with several other sources of magnetic anisotropy, including interlayer anisotropy [24], and will require consideration of additional anisotropy terms in the spin Hamiltonian. It is reasonable to conclude at this point in time that we have a good understanding of magnetism in the HTT and LTO1 phases, including issues such as the source of the easy-plane anisotropy in tetragonal materials, but questions remain concerning the interactions which are necessary to obtain a complete description of the magnetic properties of the LTO2 and LTT phases of lanthanum cuprates [25].

3.2. $La_{2-y}RE_yCuO_4$

The magnetic behavior of the low temperature phases of La_2CuO_4 substituted with other rare earth ions is different from that found for Nd substitution. In Figure 6 we show the $(110)_{HTT}$ reflection measured by synchrotron x-ray powder diffraction for $La_{1.9}Sm_{0.1}CuO_4$ and $La_{1.8}Sm_{0.2}CuO_4$. Both materials transform from the LTO1 to the LTO2 structure upon cooling, with the $Sm_{0.1}$ sample transforming at about 80 K and the $Sm_{0.2}$ sample transforming at about 115 K. In Figure 7 we show the magnetic susceptibilities for both samples. The susceptibility peaks at about 310 K indicate the onset of long range antiferromagnetic order (the Néel temperature T_N). The anomalies in the susceptibilities at 80 K and 120 K are associated with the LTO1 to LT02 transformations, as clearly indicated by the orthorhombicity versus temperature plot for the $Sm_{0.1}$ sample (Figure 7). These anomalies are probably due to the canted components of the staggered magnetization, as suggested by their magnitudes which are similar to those of the peaks at T_N. (It is known that the peak at T_N arises from spin canting induced by the D-M interaction described in Section 3.) Although Sm doped La_2CuO_4 undergoes structural transformations to the LTO2 and/or LTT phases, depending upon the Sm concentration (Figure 6), neither structure exhibits weak ferromagnetism at temperatures as low as 2 K. Magnetization versus field isotherms (not shown) suggest that the metamagnetic critical field decreases considerably at the LTO1 to LTO2 transformation, but evidence for a metamagnetic transition vanishes with

further decrease of temperature. A powder neutron diffraction study [26] of a sample of $La_{1.9}{}^{154}Sm_{0.1}CuO_4$ (the ^{154}Sm isotope was used to avoid the strong neutron absorption of ^{149}Sm present at 13.8% natural abundance) shows (Figure 8) that the magnetic structure adopted by the Cu spins is subtly affected by the LTO1 to LTO2 transformation, in contrast to the situation for Nd substitution [20 - 22]. One possibility which is consistent with the magnetic susceptibility and neutron data is that the Cu spins rotate to lie parallel to the tilt axes of the CuO_6 octahedra in the Sm doped samples at

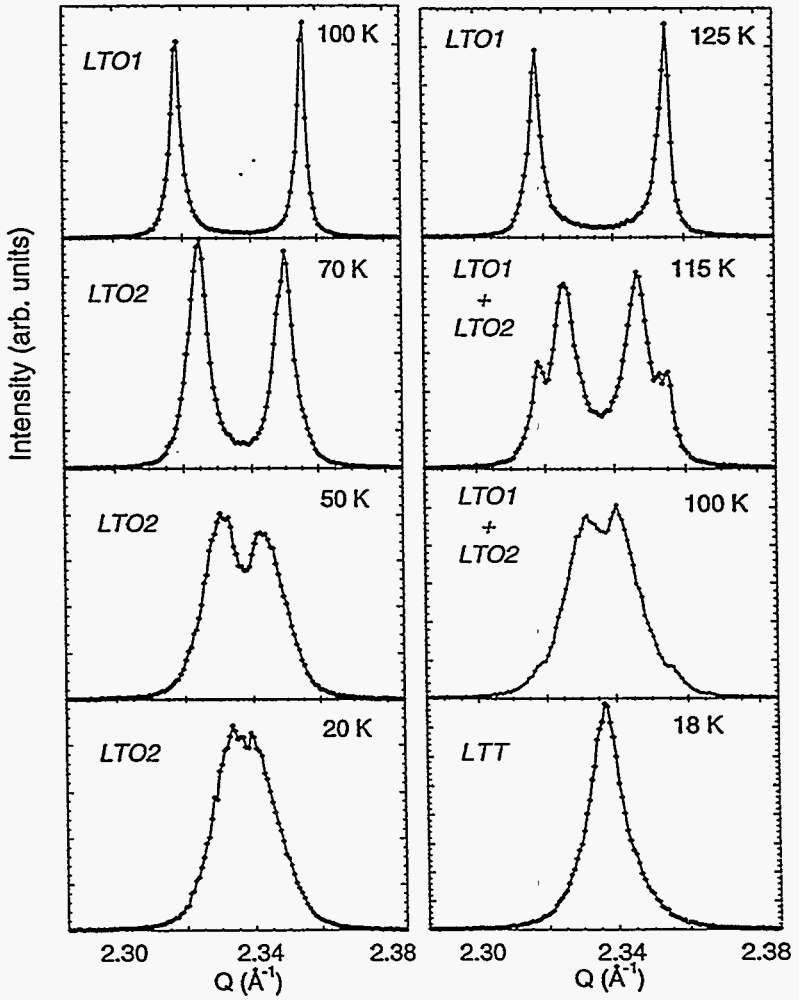

Figure 6. (left) Synchrotron x-ray diffraction scans of the $(110)_{HTT}$ peak of $La_{1.9}Sm_{0.1}CuO_4$. (right) Synchrotron x-ray diffraction scans of the $(110)_{HTT}$ peak of $La_{1.8}Sm_{0.2}CuO_4$. X-ray wavelength was 0.70059 Å. Data were collected at the NSLS.

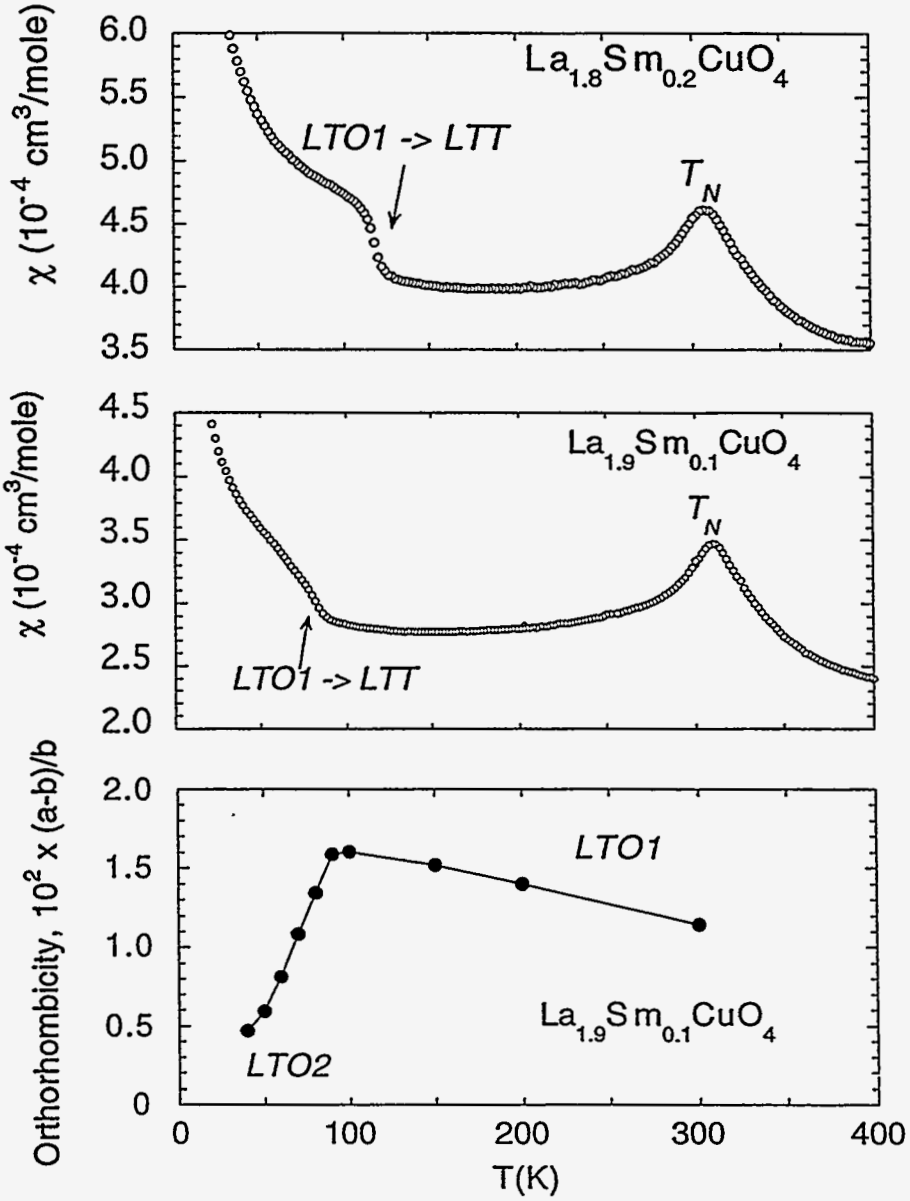

Figure 7. Magnetic susceptibilities of $La_{1.8}Sm_{0.2}CuO_4$ (top) and $La_{1.9}Sm_{0.1}CuO_4$ (middle) measured in a magnetic field of 1.0 T showing the magnetic signatures of the Néel temperatures (T_N) near 310 K and the LTO1 to LTT structural transformations at 120 K (top) and 80 K (middle). Orthorhombicity versus temperature for $La_{1.9}Sm_{0.1}CuO_4$ (bottom) showing the LTO1 to LTO2 structural transition below 100 K. Note the correspondence with the magnetic data (middle). All three temperature scales (x axes) are the same.

low temperatures, and are therefore not canted because the D-M interaction vanishes for such a spin structure. This picture is consistent with the suggestion [25] that weak ferromagnetism in Nd doped La_2CuO_4 is induced by coupling between the Nd and Cu moments, and that without this coupling the canted moment in the LTT phase vanishes [24, 25]. Additional studies are desirable to prove this interpretation. Nevertheless, the sensitivity of the in- and out-of-plane magnetic anisotropies in lanthanum cuprates to rare earth substitution on the La site is remarkable and should be further addressed by experimental (single crystal) and theoretical studies. For example, single crystal studies (described below) of $La_{1.475}Nd_{0.4}Sr_{0.125}CuO_4$ have shown that the Nd spins are coupled to the Cu spins and participate in magnetic order of the Cu sublattice at low temperatures [27], and it is also possible (although less likely) that the Sm spins participate in the magnetic order of the Cu sublattice in Sm doped La_2CuO_4.

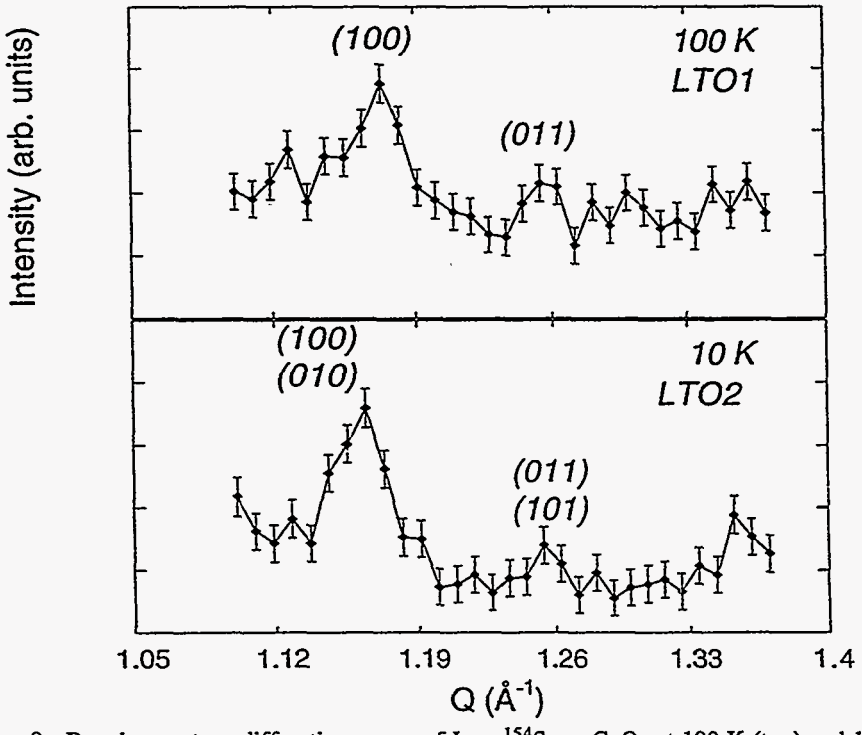

Figure 8. Powder neutron diffraction scans of $La_{1.9}{}^{154}Sm_{0.1}CuO_4$ at 100 K (top) and 10 K (bottom) collected at the High Flux Beam Reactor at Brookhaven National Laboratory. The magnetic diffraction peaks are labelled. The neutron wavelength was 2.37 Å.

4. Structural Phase Transitions and Superconductivity

The great interest in the structural transformations exhibited by the various materials described above is a direct result of the remarkable suppression of superconductivity observed in the LTT (and LTO2) structures [3, 4]. That such a subtle change in the tilt pattern of the CuO_6 octahedra in the CuO_2 layers can so strongly affect the superconducting state is fascinating and is likely to be directly related to the fundamental mechanism of high temperature superconductivity.

Perhaps the most important aspect of the suppression of superconductivity in the LTT phase is its dependence upon the doped hole concentration (Figure 9). Although the initial studies [4, 5] of the $La_{2-x}Ba_xCuO_4$ system attributed the loss of superconductivity to the appearance of the LTT phase, later studies [7] of the rare earth substituted

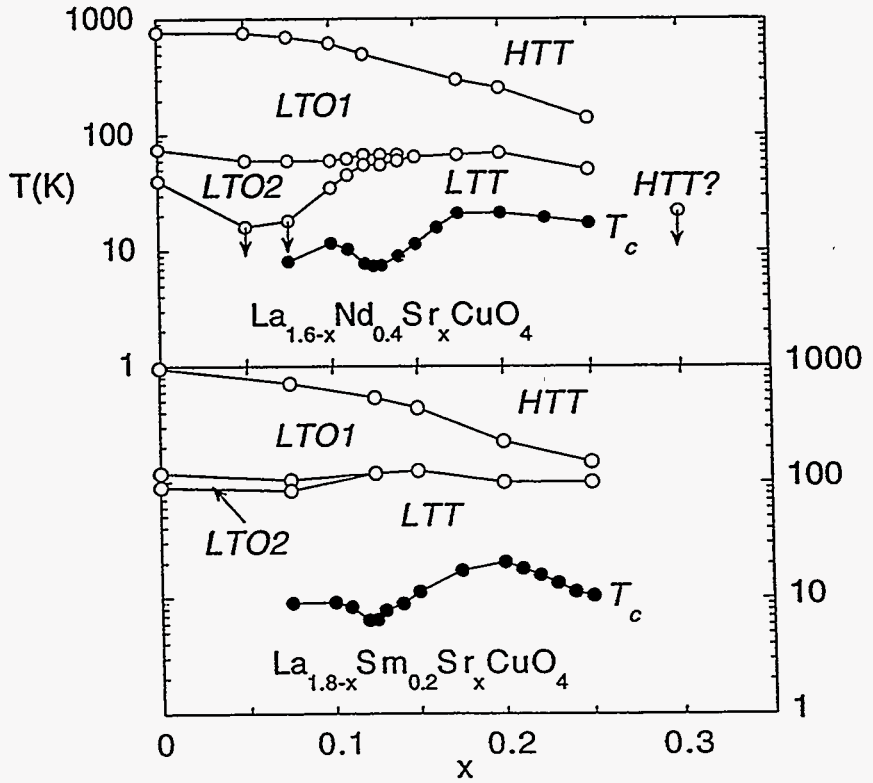

Figure 9. Structural and superconducting phase diagrams for $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ and $La_{1.8-x}Sm_{0.2}Sr_xCuO_4$. Note the minima in superconducting T_c at x = 1/8.

TABLE 2. Lattice parameters and CuO_6 tilt angles determined by Rietveld refinement of neutron powder diffraction data collected at the National Institute of Standards and Technology (NIST) for materials with composition $La_{2-x-y}Nd_ySr_xCuO_4$. Q is the angle between the CuO_6 four-fold axis and the crystallographic *c* axis, and Θ is the angle between the in-plane rotation axis and the *a* axis.

T = 15 K

x	y	Lattice Parameters (Å)	Q (degrees)	Θ (degrees)
0.125	0.0	5.32216(6) 5.35720(6) 13.1761(2)	3.37	0 (LTO1)
0.12	0.2	5.3286(2) 5.3553(2) 13.1388(4)	4.02	25.9 (LTO2)
0.125	0.4	5.3417(1) 13.0938(4)	4.68	45 (LTT)
0.125	0.5	5.3399(1) 13.0701(3)	4.83	45 (LTT)
0.125	0.6	5.3392(1) 13.0470(3)	5.03	45 (LTT)
0.125	0.7	5.3383(2) 13.0297(4)	5.46	45 (LTT)
0.125	0.8	5.3369(2) 13.0183(6)	5.72	45 (LTT)
0.15	0.4	5.3350(1) 13.1079(3)	4.22	45 (LTT)
0.20	0.4	5.32261(8) 13.1246(2)	3.43	45 (LTT)

		T = 100 K		
0.125	0	5.32636(6) 5.35499(6) 13.1815(2)	3.10	0 (LT01)
0.125	0.4	5.33130(1) 5.3669(1) 13.1064(3)	4.41	0 (LT01)
0.125	0.6	5.3061(1) 5.3718(1) 13.0654(3)	4.89	0 (LT01)
0.15	0.4	5.3134(1) 5.3601(1) 13.1131(3)	4.07	0 (LTO1)
0.20	0.4	5.3105(1) 5.3362(1) 13.1298(2)	3.14	0 (LTO1)

systems (Figure 9) clearly demonstrated that the LTT phase could support bulk superconductivity when the hole concentration was adjusted independently of the structure. These studies and others [28, 29] concluded that the suppression of superconductivity in the LTT phase was strongest at the doping level of 1/8 hole per Cu atom. Earlier studies of the oxygen isotope effect in $La_{2-x}Sr_xCuO_4$ also found that this hole concentration was unique [30]. It was speculated at that time that the value of 1/8 was related to some commensurability of the electronic and crystal structures and recently studies of single crystals of $La_{1.475}Nd_{0.4}Sr_{0.125}CuO_4$ have shed considerable light on the source of this commensurability.

Tranquada and coworkers have presented evidence [27] for the formation of striped phases in single crystal $La_{1.475}Nd_{0.4}Sr_{0.125}CuO_4$ in which regions of antiferromagnetically ordered Cu spins are separated by antiphase domain wall boundaries composed of (metallic) hole doped regions. In that picture, the stripes are dynamically fluctuating in the superconducting phases such as $La_{2-x}Sr_xCuO_4$, but become pinned by the LTT lattice distortion in $La_{1.475}Nd_{0.4}Sr_{0.125}CuO_4$. This picture was strongly motivated by earlier results [31, 32] in the $La_2NiO_{4+\delta}$ system in which similar charge and spin orderings occur. It is also interesting that in

manganates such as $La_{1-x}Ca_xMnO_3$, which show colossal magnetoresistance, charge and spin ordering have been observed [33], presumably driven by formation of Jahn-Teller polarons [34]. In the cuprates charge and spin ordering, for example the incommensurability appearing in inelastic neutron scattering data in $La_{2-x}Sr_xCuO_4$ [35], have been attributed either to Fermi surface effects [36] or to frustrated phase separation [37]. The charge ordering wavevectors do not nest the Fermi surface in $La_{1.475}Nd_{0.4}Sr_{0.125}CuO_4$, which lends support to the latter interpretation for that material [38]. One question which remains is the connection between charge and spin stripes and the oxygen isotope effect on the

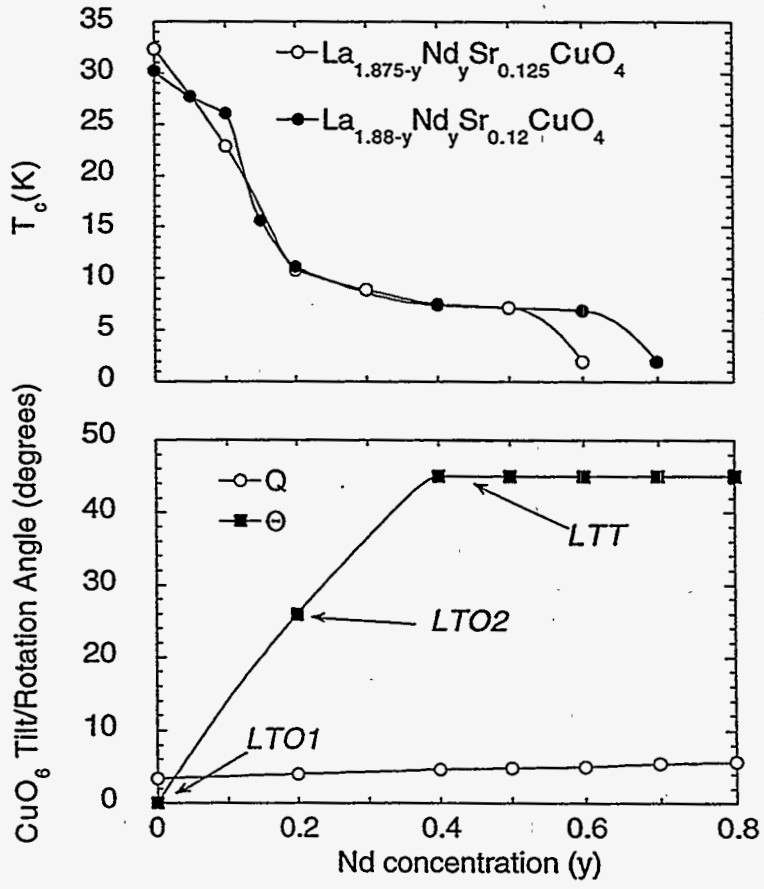

Figure 10. Superconducting T_c (top) and CuO_6 octahedra tilt angles for $La_{2-x-y}Nd_ySr_xCuO_4$ samples. The rapid drop in T_c between y = 0 and y = 0.4 is associated with the increase of Θ, whereas the loss of superconductivity at high Nd concentrations apparently has a different origin and may be related to the magnitude of Q.

superconducting transition temperature. Understanding this connection would be a further step toward elucidating the charge and spin stripe description of superconductivity in the cuprates. It is also worthwhile to further consider the stripe pinning mechanism itself and how it should depend upon both the direction and magnitude of the tilting of the CuO_6 octahedra, particularly since at high Nd concentrations the superconductivity vanishes even when x is not equal to 1/8 (Figure 10). This result has been interpreted [39] to imply the existence of a "critical" tilt angle beyond which superconductivity is replaced by a magnetic ground state stabilized by spin-orbit coupling due to a D-M type interaction [40]. The presence of magnetic order in the low temperature phases, first observed by muon spin resonance studies [41], is also consistent with the striped phase description [42]. An interesting question which thus naturally arises is whether spin-orbit coupling is important in the pinning of stripes, although the fact that charge order seems to precede spin order upon cooling [27] perhaps argues against this.

At low temperatures the Nd moments participate in the magnetic order of the Cu sublattices in $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$ [27] and $La_{2-y}Nd_yCuO_4$ [22]. It would therefore be worth comparing results obtained for crystals doped with Sm, rather than Nd, for several reasons. First, the Sm concentrations needed to induce the structural phase transitions are smaller [10, 12] than those required for Nd. Second, the Sm magnetic moment is considerably smaller than that of Nd [43, 44]. For these two reasons Sm would be less likely than Nd to influence the Cu spin sublattice. In support of this expectation, different spin structures are found for these two ions in the T' materials Nd_2CuO_4 and Sm_2CuO_4 [44]. The former material has Nd spins ordered antiferromagnetically parallel to the *a-b* plane, whereas the latter material has the Sm spins arranged in ferromagnetic sheets with spin direction parallel to the *c* axis. It also appears that the Nd spins couple to the Cu spins, whereas the Sm spins appear to be more independent of the Cu spins, in the T' materials. A similar situation would hopefully occur in lanthanum cuprates. Finally, the LTO1 to LTT structural transition ocurs at a much higher temperature in Sm (compared with Nd) doped samples, and it would be of great interest to see what effect this has upon the charge and spin ordering temperatures.

5. High Pressure Structural Studies of $La_{1.875}Ba_{0.125}CuO_4$

Pressure offers another degree of freedom in the study of the phase diagrams of lanthanum cuprates [45,46], and its effects are particularly

interesting with respect to the structural phase transitions in these materials. We have chosen to begin our high pressure studies with the compound $La_{1.875}Ba_{0.125}CuO_4$ due to the fact that measurements of the superconducting T_c of this material have been reported [47] for hydrostatic pressures as high as 20 kbar, and the results of those studies are anomalous.

The superconducting T_cs of a number of compositions in the $La_{2-x}Ba_xCuO_4$ phase diagram have been measured as a function of pressure [47]. The results of those measurements show that the effect of pressure is to increase T_c for all values of x, but that even at pressures as high as 20 kbar the T_c of the sample with $x = 1/8$ is still quite low, about 15 K, whereas

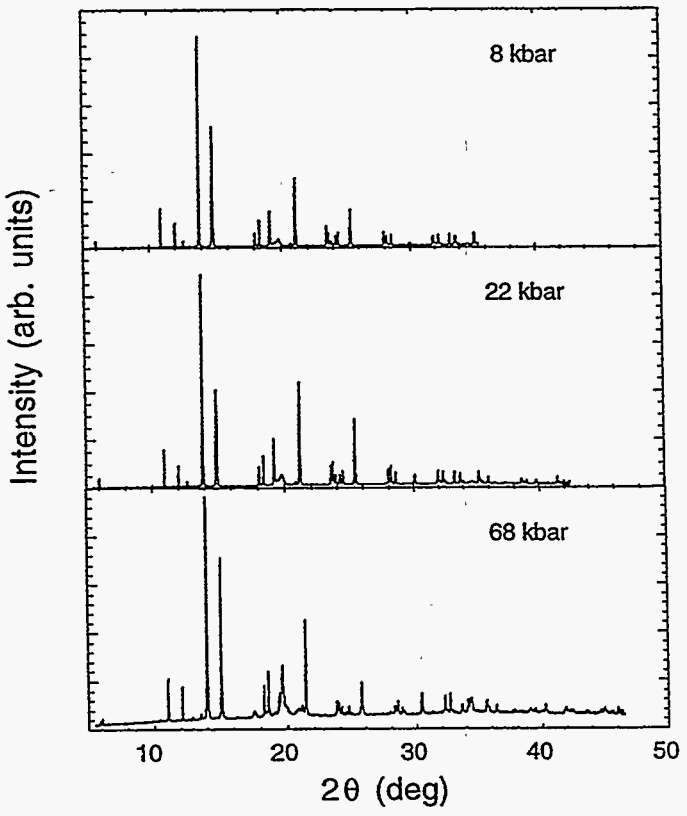

Figure 11. Synchrotron x-ray diffraction scans of $La_{1.875}Ba_{0.125}CuO_4$ at T = 15 K measured in a diamond anvil cell at 8, 22 and 68 kbar. X-ray wavelength was 0.692455 Å. Data were collected at the NSLS.

neighboring compositions have T_cs near 30 K. In addition, the authors of that study had observed the presence of resistance anomalies at the HTT to LTO1 transition temperature, and utilized these anomalies to monitor the structural transition temperature as a function of pressure. Based upon those measurements it was concluded that the HTT to LTO1 transition was completely suppressed at pressures above 14 kbar. High pressure structural studies of $La_{1.875}Ba_{0.125}CuO_4$ using neutron diffraction [46] were limited to pressures of 7 kbar or less and thus could not shed much light on the structural phase diagram at pressures near 20 kbar. Thus the low T_c of 15 K for the x = 1/8 sample at 20 kbar suggested that there was a suppression of superconductivity at this doping level *even for the HTT structure*. Since most of the theoretical discussions of the T_c suppression in $La_{1.875}Ba_{0.125}CuO_4$ rely upon the presence of the LTT (or LTO2) type distortion, and would not apply to the HTT structure [see, for example, reference 4], this was potentially a very important finding. It therefore was essential to directly determine the crystal structure at pressures at least as high as 20 kbar. We have therefore performed a series of high pressure structural studies [48] of $La_{1.875}Ba_{0.125}CuO_4$ using synchrotron x-ray radiation and Merrill-Bassett diamond anvil cells with a hydrostatic pressure medium.

In Figure 11 we show representative synchrotron x-ray powder diffraction patterns of $La_{1.875}Ba_{0.125}CuO_4$ measured at temperatures near 10 K and at the hydrostatic pressures labeled on each pattern. It is clear from our data that at pressures above 30 kbar the samples remain in the HTT structure to temperatures as low as 10 K. The important question is what structure is present at pressures near 20 kbar in the low temperature region: LTT, LTO2, LTO1, or HTT? This is a rather difficult question to answer because the orthorhombic distortion in the LTO1 phase at a fixed temperature decreases with increasing pressure (which is the same as saying that the HTT to LTO1 transition temperature decreases with pressure), and it becomes progressively more difficult to tell which structure is present as pressure increases. Nevertheless, our high pressure measurements clearly demonstrate that as pressure increases above ambient the LTT structure which is present at low temperatures is replaced by an orthorhombic structure (Figure 12), and this orthorhombic structure appears as the result of a structural phase transformation from the LTO1 structure at temperatures close to the LTO1 to LTT transition temperature under ambient pressure, 60 K. This second orthorhombic structure is less orthorhombic than the LTO1 structure and we therefore believe it to be the LTO2 structure by analogy with the LTO2 structure described above for the rare earth substituted materials. As the pressure approaches 20 kbar the orthorhombicity of this phase decreases, but we can still clearly discern a structural transition from

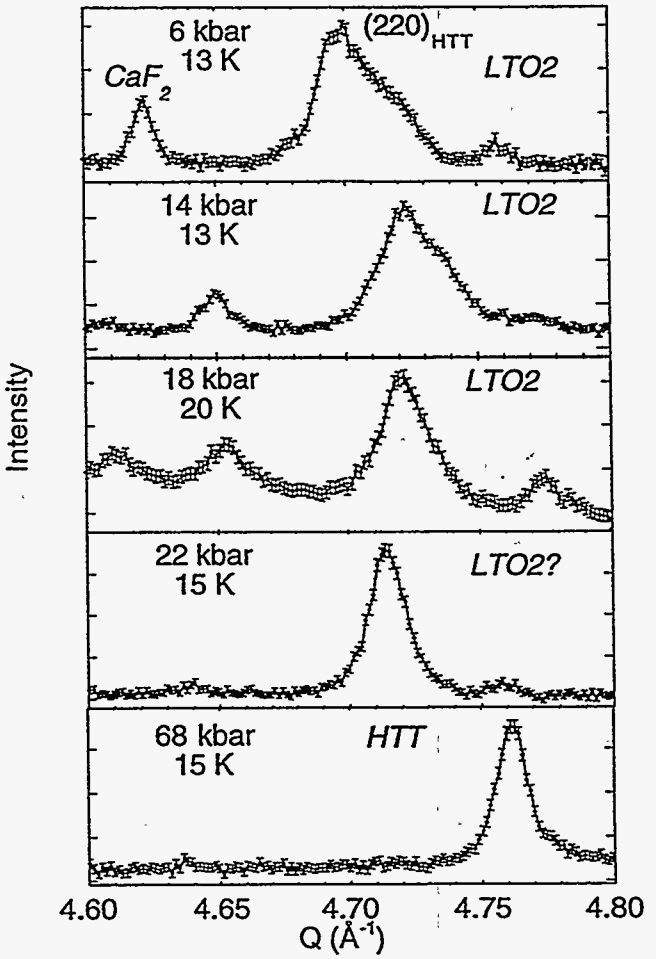

Figure 12. Synchrotron x-ray diffraction scans of the $(220)_{HTT}$ reflection at temperatures of 13 - 20 K, clearly showing an orthorhombic distortion at 22 kbar (and lower) pressures. Data were collected at the NSLS.

the LTO1 phase to this LTO2 phase at pressures as high as 18 kbar (Figure 13). At a pressure of 22 kbar, although we do not have measurements at many temperatures, the width of the $(110)_{HTT}$ reflection at 10 K is still greater than at 300 K (at a similar pressure), so even at 22 kbar the sample is clearly orthorhombic at low temperatures. Whether this orthorhombic phase is LTO1 or LTO2 we can not determine, but apparently *pressures in excess of 22 kbar are necessary to completely suppress all the structural transitions in* $La_{1.875}Ba_{0.125}CuO_4$.

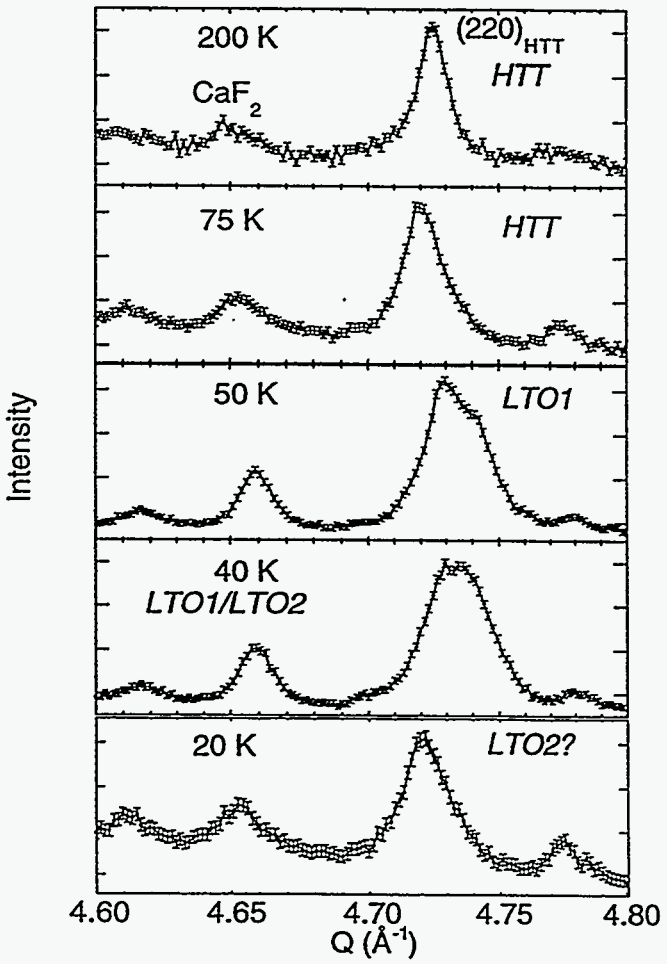

Figure 13. Synchrotron x-ray diffraction scans of the $(220)_{HTT}$ reflection as a function of temperature at a pressure of 18 kbar. There is a structural phase transformation from the LTO1 phase present at 50 K to the LTO2 phase at 40 K and below. Data were collected at the NSLS.

In Figure 14 we show a schematic of the temperature-pressure phase diagram for $La_{1.875}Ba_{0.125}CuO_4$ determined in this study. There is still some uncertainty concerning precise details in the region near 20 kbar, but our general conclusion is that *the low temperature structure near 20 kbar is orthorhombic, either LTO1 or LTO2, and the LTO2 structure is present at pressures at least as high as 18 kbar.* Thus it now seems that the

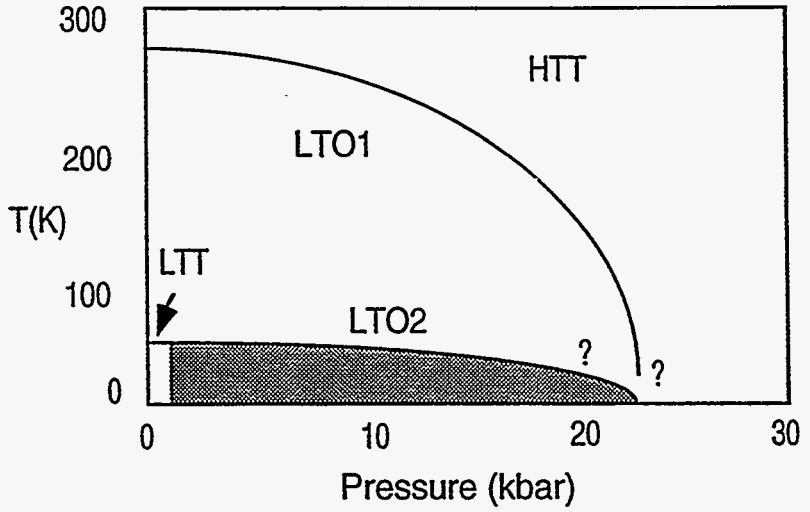

Figure 14. Temperature-pressure phase diagram of $La_{1.875}Ba_{0.125}CuO_4$.

explanation for the dependence of T_c upon pressure [47] is that $La_{1.875}Ba_{0.125}CuO_4$ is still in the LTO2 phase at 20 kbar and temperatures below about 30 K. We therefore expect that application of pressures in excess of 25 kbar will stabilize the HTT structure and restore T_c to values near 30 K.

The high pressure experiments described above indicate that the rotation of the tilt direction of the CuO_6 octahedra about the crystallographic *c* axis (the phase mode) is more important for determining the superconducting T_c than is the tilt angle of the CuO_6 axis away from the crystallographic *c* axis (the amplitude mode), at least when the hole concentration is 1/8 per Cu. This is consistent with the results described above for the $La_{2-x-y}Nd_ySr_xCuO_4$ system (Figure 10). There are at present no detailed theoretical discussions in the literature of the relative importance of the phase and amplitude of the CuO_6 octahedra tilts on any of the mechanisms suggested to account for the strong coupling of superconductivity to these distortions. There are detailed discussions [24, 25] of the dependencies of various sources of magnetic anisotropy upon these structural parameters, and a careful comparison of the results of those studies with the behavior of T_c as a function of the structural parameters might yield insight into the connection between magnetism and superconductivity in the cuprates. In any case, the coupling of the tilt structure to magnetic anisotropy, charge and spin order, superconductivity, and lattice dynamics is worthy of further detailed study and will furnish a stringent test of theoretical models for high temperature superconductivity.

5. Conclusion

Lanthanum cuprates display a rich variety of structural phase transitions which can be well-controlled through substitution of smaller rare earth ions for La. These subtle distortions of the CuO_2 layers have strong effects on superconductivity. The distortions also noticeably affect the magnetic properties of insulating cuprates through their influence on magnetic anisotropy terms in the spin Hamiltonian. In order to evaluate the connection of the relatively well understood physics of the magnetic insulators to the superconducting phases it is necessary to understand how various types of magnetic interactions evolve when doping the insulators with charge carriers. In particular, the sensitivity of the magnetic anisotropy to crystal symmetry offers a possible microscopic explanation of the effect of the structural phase transitions on superconductivity. The development of a theoretical model which can account for these effects, including the influence of hole concentration, should lead to a deeper understanding of the physics underlying the remarkable phenomenon of high temperature superconducitivity discovered by Bednorz and Müller ten years ago.

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