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Lattice Instabilities and Structural Phase Transformations in La_2CuO_4 Superconductors and Insulators.

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Abstract.

Soft-mode structural phase transformations, common in many perovskite-based materials, are also found in La_2CuO_4 and structurally related oxides. The resulting phase behavior is rather complex, but is a natural consequence of the degeneracy of the soft phonon order parameters. This paper reviews the structural and lattice-dynamical results and their interpretation based upon mean-field statistical mechanical models.

1. Introduction. Following the discovery of multiple structural phase transformations in Ba-doped La_2CuO_4, there has been considerable study and interest in these transformations *per se* and with reference to their influence on superconductivity in copper oxide systems. This paper will review the structural aspects of these studies with emphasis on a simple but reasonably satisfactory phenomenological interpretation based on phonon instabilities and the interplay of degenerate order parameters. This provides an important foundation for the subsequent understanding of the electrical and magnetic properties of these materials, which are topics of subsequent papers in these proceedings.

2. Soft Phonon Modes. La_2CuO_4 has a well known high temperature tetragonal (HTT, space-group I4/mmm) perovskite-like structure, but transforms upon cooling to a less symmetric low temperature orthorhombic (LTO, space-group Bmab) structure.

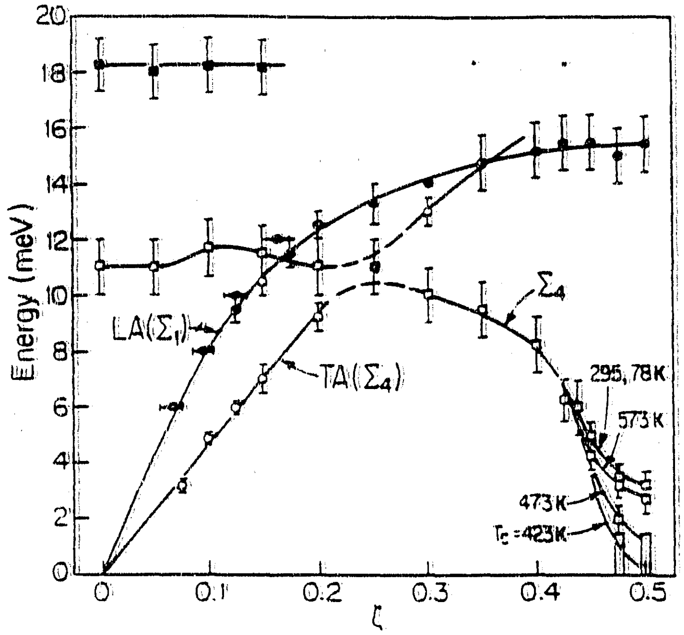

Fig. 1. Soft phonon dispersion from Γ (q=0) to M (q=1/2,1/2,0) in La_2CuO_4. (From Ref. 2.)

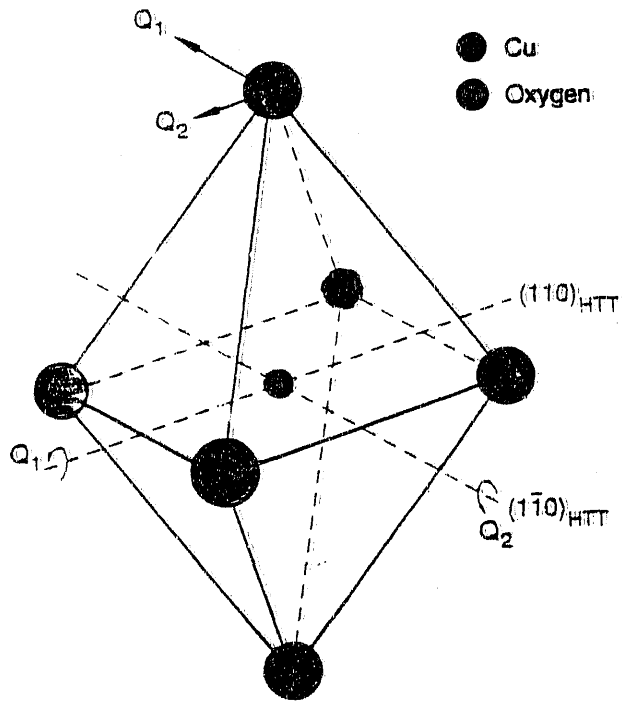

Fig. 2. Schematic representation of the tilt axes and oxygen atom displacements of copper-oxygen octahedra in La_2CuO_4. Adjacent octahedra in the ab-plane are coupled through shared corner oxygen atoms.

Shortly after the discovery of superconductivity in these materials[1], the nature of the HTT-LTO phase transformation was studied by inelastic neutron scattering [2]. It showed that the transformation followed classical soft-mode behavior involving zone boundary phonons. A summary of phonon dispersion measurements in the HTT phase are shown in Fig. 1. There are two degenerate unstable modes with the wave-vectors $\mathbf{q}_1$=[1/2,1/2,0] and $\mathbf{q}_2$=[1/2,-1/2,0]. The displacements associated with the modes consist principally of tilting of CuO_6 octahedra about axes perpendicular to $\mathbf{q}_1$ and $\mathbf{q}_2$, as shown in Fig. 2.

3. Landau Theory. Let Q_1 and Q_2 represent the amplitude of the displacements associated with the $\mathbf{q}_1$ and $\mathbf{q}_2$ phonons, respectively. To provide a systematic way of analyzing the possible consequences of such a phonon instability, Axe, et al.[3] constructed a Landau-Ginzburg free energy function by considering symmetry-invariant combinations of the degenerate primary order parameters, together with a secondary order parameter, η, representing the orthorhombic strain (a-b)/(a+b):

$$F=1/2a(T-T_0)(Q_1^2+Q_2^2)+u(Q_1^2+Q_2^2)^2+v(Q_1^4+Q_2^4)+\ldots$$
$$+1/2c\eta^2+d(Q_1^2-Q_2^2)\eta+\ldots \qquad (1)$$

The first line of Eq. 1 is familiar as the Landau representation of the XY-model, but with additional quartic anisotropy ($v\neq0$). At T_0 both the Q_1 and Q_2 modes become unstable. The nature of the stable solutions as T approaches T_0 from below as summarized in Fig. 3, are determined by competition between the higher order (anharmonic) terms in the Landau potential. If $u>0$, second order transformations are possible to two different phases, depending upon whether v is positive or negative. If $v<0$, only Q_1 or Q_2 (but not both) is non-zero. The translational symmetry of either of these two possible (twin-related) structures is reduced from HTT, giving rise to new T-dependent superlattice reflections. The second line in Eq. 1 reflects the elastic strain energy and the coupling of the strain to the primary order parameters. Because of the $Q^2\eta$ coupling, this phase is accompanied by an orthorhombic strain, $\eta\sim Q^2$, as is observed in the LTO phase of La_2CuO_4[2]. Clearly the HTT-LTO transformation is to be associated with this solution. If $v>0$, both Q_1 and Q_2 would condense with equal amplitude, but as there is no resultant coupling to the macroscopic strain, the structure would remain tetragonal.

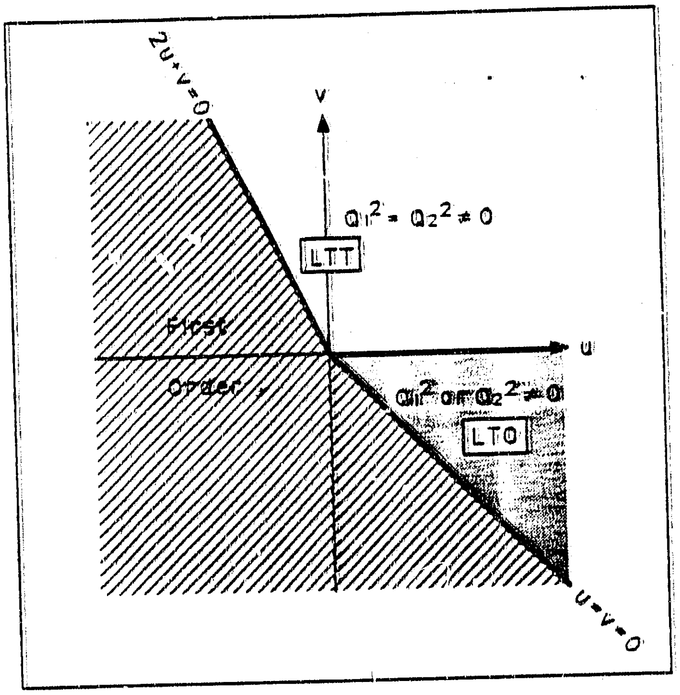

Fig. 3. Mean field phase stability diagram of the XY-model. The ground state degeneracy is resolved by the anisotropy parameter, v, giving rise to two possible stable low temperature phases.

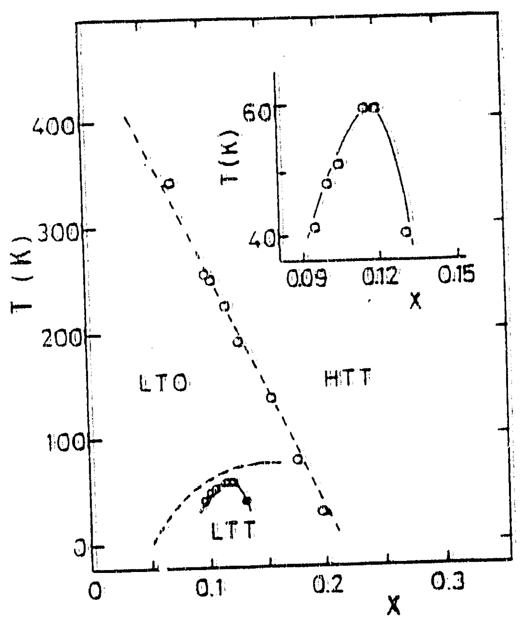

Fig. 4. Structural phase diagram for $La_{2-x}Ba_xCuO_4$, showing the stability range of the LTT phase. The dotted curve is from Ref. 4. The open circles are determined by thermal measurements. [Kumagai, et al., J. Phys. Soc. Japan, 60, 1448 (1991)].

4. The Low Temperature Tetragonal Modification. In an x-ray study Axe, et al.[3] found that over a narrow range of doping $La_{2-x}Ba_xCuO_4$ not only showed the expected HTT-LTO transformation, but changed abruptly to a low temperature tetragonal (LTT) modification upon further cooling, as shown in Fig. 4. A subsequent neutron powder diffraction study revealed the persistence of superlattice reflections in the LTT phase, ruling out the possibility that LTO had simply reverted to HTT, and the resulting diffraction pattern could be satisfactorily explained on the basis of a $P4_2/ncm$ structure[3,4].

An examination of the relevant displacements shows that the ($P4_2/ncm$) LTT structure represents the second stable solution of the Landau potential discussed above. It can be viewed as a *coherent* superposition of two twin-related ($Q_1=0$ and $Q_2=0$) LTO structures. The lack of substantial changes in either the primary or allowed superlattice intensities upon crossing the LTO-LTT phase boundary indicates that $Q_1^2+Q_2^2$ does not change appreciably in passing from LTO to LTT, yet η does vanish abruptly. The LTT modification, although only subtly different from the LTO (or for that matter the HTT) phase, has a much reduced superconducting T_c[5], which has motivated substantial further (and ongoing) interest in the nature of these phases.

5. The LTO-LTT Phase Transformation. The relative stability of LTO vs. LTT phases is determined by the positivity of v. Although $v<0$ when T is near T_0, v will in general vary with temperature. We need to investigate the behavior of Eq.1 in the neighborhood of the temperature where the quartic anisotropy, v(T), changes algebraic sign. However Eq. 1 is inadequate as it stands since it omits higher order anisotropy terms which become relevant if $v(T)\to 0$. This leads us to study the following free-energy function:

$$F=1/2a(Q_1^2+Q_2^2)+u(Q_1^2+Q_2^2)^2+v(Q_1^4+Q_2^4)+w(Q_1^8+Q_2^8). \quad (2)$$

[Two comments. a). Other low order invariants are either isotropic or, as e.g. $(Q_1^2+Q_2^2)(Q_1^4+Q_2^4)$, can be absorbed into the temperature dependence of v(T). $(Q_1^8+Q_2^8)$ is the leading order term isotropy breaking term when $v(T)\to 0$. b). Without loss of generality, we may take d=0. The principal effect of the coupling to the strain is to renormalize the anisotropy constants, e.g. $v'=v-d^2/c$.]

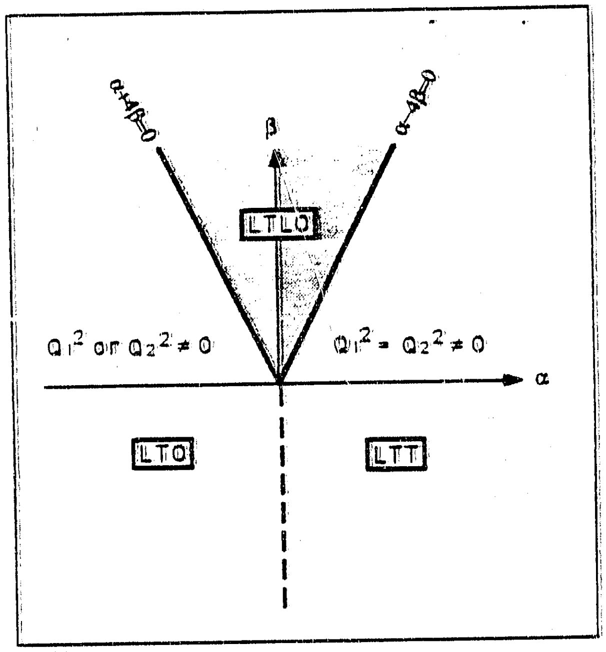

Fig. 5. Phase diagram in the vicinity of the bicritical point, formed by the bifurcation of a first order phase boundary (dashed line) into two second order boundaries (solid lines), producing an intermediate LTLO phase.

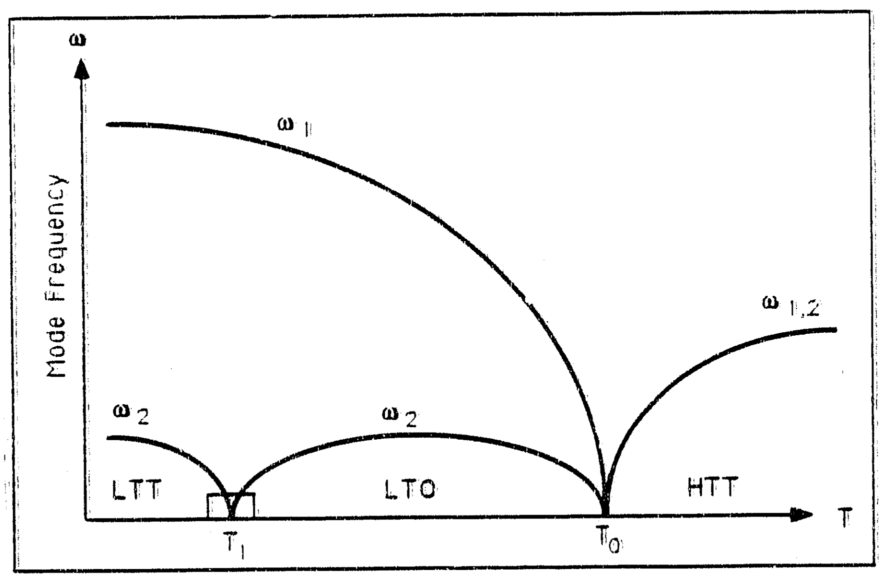

Fig. 6. Schematic representation of the temperature dependence of the soft modes in the LTT, LTO and LTT phases. The behavior near T_1 is shown in more detail in Fig. 7.

It is convenient to introduce a polar representation, $Q_1 = Q\cos\theta$ and $Q_2 = Q\sin\theta$, so that Eq. 2 becomes

$$F(Q,\theta) = f(Q) + \alpha(T)\cos 4\theta + \beta\cos 8\theta, \qquad (3)$$

where $\alpha(T) = 1/4\, vQ^4 + 7/16\, wQ^8$ and $\beta = 1/64\, wQ^8$, and we are interested in the behavior of $F(Q,\theta)$ in the vicinity of $\alpha(T) \sim (T-T_1)$. Because taking linear combinations of Q_1 and Q_2 have the effect of rotating the tilt axis of the CuO_6 octahedra, the most physical interpretation of θ is as the orientation of the tilt axis in the a-b plane. $\theta = 0$ (mod $\pi/2$) represent LTO-like displacements, while $\theta = \pi/4$ (mod $\pi/2$) represent LTT-like displacements.

6. The LTLO Phase and Bicriticality. By minimizing $F(Q,\theta)$ with respect to θ, we determine the linear combination of (Q_1, Q_2) favored by the competition between 4th and 8th order anisotropy. The algebraic sign of β makes a qualitative difference in the nature of the solutions, as may be seen by considering $\alpha(T)=0$, the situation just at $T=T_1$. For $\beta<0$, Eq. 3 has minima for $\theta=0$ (mod $\pi/4$), showing that LTO and LTT are degenerate at T_1 and that a first order transformation between the two occurs at that temperature as $\alpha(T)$ passes through zero. By contrast, when $\alpha(T)=0$ and $\beta>0$, Eq. 3 is minimized for $\theta=\pi/8$ (mod $\pi/4$), neither LTO or LTT. It is rather a predicted new structure obtained by a *coherent superposition of HTT and LTO phases.*

The phase diagram resulting form the minimization of Eq. 3 is shown in Fig. 5.[6] If $\beta>0$, the LTT-LTO phase boundary is split by the appearance of this new phase, intermediate also in the sense that it interpolates smoothly between $\theta=0$ (LTO) and $\theta=\pi/4$ (LTT) as a function of $\alpha(T)$. The orthorhombic strain, although smaller than for LTO is still present, since $(Q_1^2-Q_2^2)\neq 0$. For convenience, we call this the low temperature *less* orthorhombic (LTLO) phase. The space group for the LTLO structure is Pccn, which is a subgroup of both Bmab and $P4_2/ncm$ (and thus necessarily a subgroup of I4/mmm.) However neither Bmab or $P4_2/ncm$ are subgroups of the other. We shall see that both the LTO-LTLO and LTLO-LTT transformations can, and in this model are predicted to be, continuous. They join the first order LTO-LTT phase boundary at a singularity known in the terminology of critical phenomena as a *bicritical point.*

[Comment. For intercomparison of the four phases it is helpful to use a non-standard face-centered (F4/mmm) HTT unit cell containing four formula units (z=4) rather than the conventional (z=2) body centered cell. With this choice all structures have approximately the same unit cell size ($a \cong b \cong 5.4$Å, $c \cong 13.2$Å). In the base-centered LTO cell two of the three face-center equivalences are lost, and in both the LTLO and LTT phases all face-center equivalences are lost. Consequently, an LTO diffraction pattern differs from LTT or LTLO by systematic missing reflections. The only qualitative difference between LTT and LTLO is the orthorhombic strain.]

Based upon the abrupt disappearance of η, the LTO-LTT transformation in $La_{2-x}Ba_xCuO_4$ would appear to be discontinuous, in agreement with these predictions. However, recent work by Crawford, et. al. demonstrates that the La_2CuO_4 system can be nudged close to bicriticality[7]. These authors have shown that partial replacement of La with heavier rare earths (e.g. Nd or Gd) provides an additional variable with which to tune these low temperature transformations. For example, $La_{1.6}Nd_{0.4}CuO_4$, an insulator, undergoes the transformation sequence HTT->LTO->LTLO with decreasing temperature. Adding strontium causes $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ ($x=0.12$) to augment the sequence, HTT->LTO ->LTLO->LTT. By $x=0.18$ the LTLO phase has been squeezed out, and the sequence is HTT->LTO->LTT, as observed in $La_{2-x}Ba_xCuO_4$. (The Sr concentration for bicriticality is $x \cong 0.15$.) The experimentally determined phase diagram is qualitatively similar to Fig. 4, with $\alpha(T)$ replaced by T_1-T and β by $(x-0.15)$. For $x \geq 0.075$, all of these materials are metallic superconductors[7].

7. Soft Mode Dynamics. The soft mode associated with the HTT instability has already been discussed. Below T_0 the degeneracy of the Q_1- and Q_2-modes is removed by the LTO distortions. As shown schematically in Fig. 6, there is an upper branch involving fluctuations in the condensed (say Q_1)-mode, and a lower branch involving the uncondensed (say Q_2)-mode. More generally, the upper branch involves fluctuations in the *amplitude* of the tilts of the CuO_6 octahedra, while the lower one involves fluctuation in the *direction of the tilt axis.* The LTO-LTT transformation involves an instability in the tilt direction and a re-softening of the lower branch. Although single crystals of $La_{2-x}Ba_xCuO_4$ suitable for inelastic neutron scattering have not been produced, neutron and Raman scattering measurements on isomorphous La_2NiO_4 [8] and Pr_2NiO_4 [9], which also exhibit LTT phases at low temperature, show the expected re-softening. It is worth noting that the critical fluctuations in the HTT phase are governed by the harmonic terms in Eq. 1, fluctuations in the low temperature phases are governed by the anharmonic terms. Analyzing the dynamical response of Eq. 1, Thurston, et al.[10] showed that $\omega_2^2 \sim -v(T)$, and estimated the temperature dependence of v(T) from measured phonon frequencies.

A more complete discussion of the soft mode dynamics in the vicinity of the bicritical point can be obtained by an analysis of Eq. 3. The square of the soft mode frequency is inversely proportional to χ, the susceptibility for fluctuations in the tilt direction, where $\chi^{-1}=\partial^2F/\partial\theta^2 \sim \omega^2$. It can be shown that near the first order LTO-LTT phase boundary ($\beta<0$),

$$\chi_{LTO}^{-1} = -16\alpha - 64\beta;$$
$$\chi_{LTT}^{-1} = +16\alpha - 64\beta,$$

whereas when $\beta>0$,

$$\chi_{LTO}^{-1} = -16\alpha - 64\beta;$$
$$\chi_{LTT}^{-1} = +16\alpha - 64\beta;$$
$$\chi_{LTLO}^{-1} = 64\beta[1-(\alpha/4\beta)^2],$$

over the appropriate range of stability. These results are summarized in Fig. 7. While the LTO and LTT susceptibilities have the familiar mean field Curie-like behavior, χ_{LTLO}^{-1} shows an unusual parabolic temperature dependence. The LTLO soft mode should be Raman active, but with an intensity that vanishes at the LTLO-LTO phase boundary. It will be interesting to see whether experiments will be adequately described by these mean-field predictions.

8. A Statistical Order-Disorder Model. While Landau theory provides a satisfactory phenomenological picture of how degenerate soft modes bring about the LTO-LTT transformation (with or without intervening LTLO), it provides no insight into the temperature

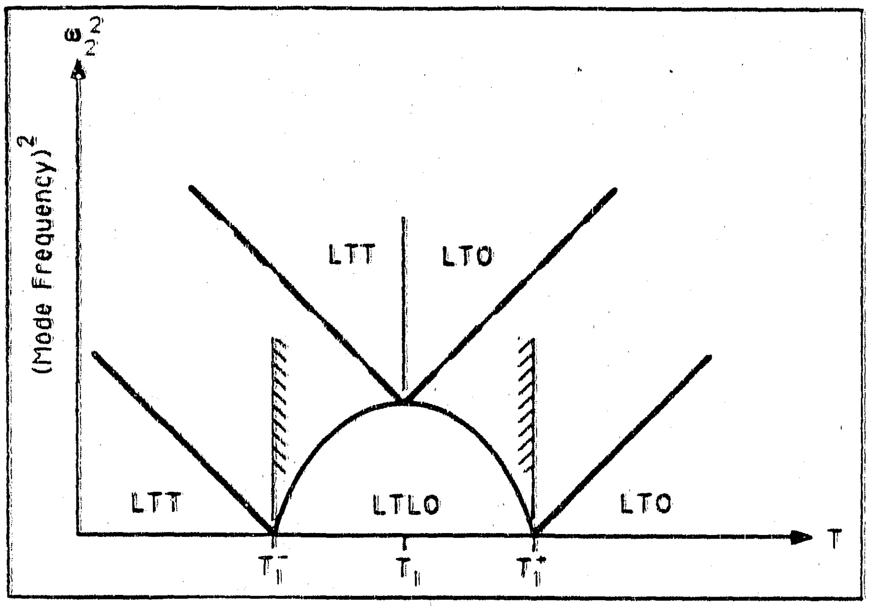

Fig. 7. Behavior of the soft mode inverse susceptibility (proportional to mode-frequency-squared) near the bicritical point. The dashed line is for first order LTO-LTT boundary. The solid lines are for the continuous LTO-LTLO-LTT case.

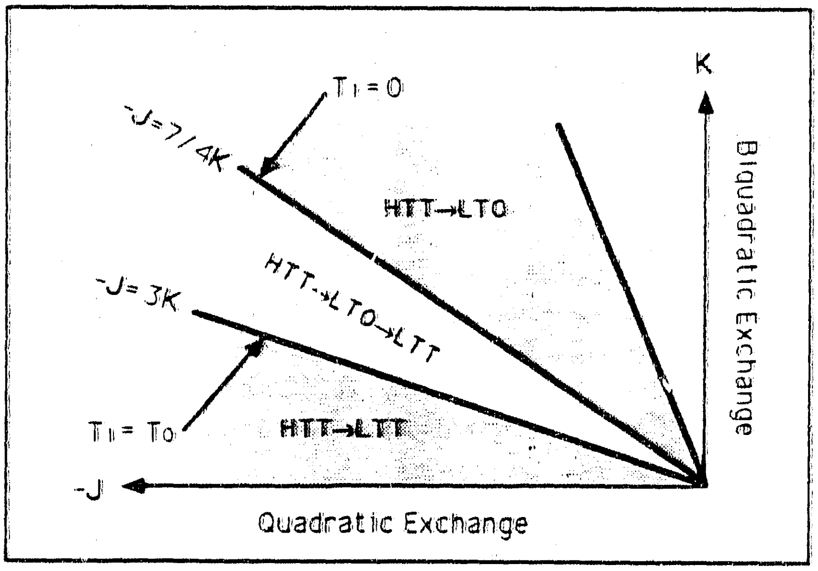

Fig. 8. Phase stability diagram for a Potts-like model of the LTO-LTT system. The shaded are represent the region where an LTO-LTT transformation can occur. T varies smoothly between T_0 and T=0 on passing from the lower to upper boundary lines.

dependences of the model parameters, a and v, which are essential for the transformations. This led Crawford, et al.[8] to discuss a rudimentary model capable of more detailed statistical mechanical analysis. Suppose states 1 and 3 represent fixed amplitude LTT-like tilts in the positive and negative sense about one axis, states 2 and 4 represent similar tilts about an orthogonal axis in the ab-plane, and n_i (i=1,4) represent their statistical occupancies. These states provide a minimal representation for constructing a Hamiltonian with the requisite tetragonal permutation symmetry of the HTT phase. A combination of quadratic and bi-quadratic exchange leads to a mean field free energy expression of the form

$$F = \mathbf{J}[(n_1-n_3)^2+(n_2-n_4)^2] + \mathbf{K}[(n_1-n_3)^4+(n_2-n_4)^4] + kTn_i\sum \ln n_i. \quad (6)$$

The phase stability relations are summarized in Fig. 8. For $\mathbf{K}=0$ (no biquadratic exchange) and $\mathbf{J}<0$, there is a single continuous transformation from a completely disordered (all $n_i=1/4$) HTT-like state to an ordered LTT-like phase with, for example, $n_1 \neq n_3 \neq 0$, $n_2=n_4=1/2(1-n_1-n_3)$. With $\mathbf{K}>0$ and $1/3<-(\mathbf{K}/\mathbf{J})<4/7$, a second LTO-like ordered phase with, for example, $n_1 \neq n_2$, $n_3=n_4=1/2(1-2n_1)$, is stable at intermediate temperatures between the HTT- and LTT-like phases. Near the lower stability line, $\mathbf{K}=-1/3\mathbf{J}$, T_1 approaches T_0, and Eq. 6 can be expanded about the HTT solution. Comparing the resulting expression with Eq. 1 gives the following estimates for the critical temperatures near the lower stability line:

$$kT_0=-\mathbf{J}, \text{ and } kT_1=3\mathbf{K} \text{ (as } T_1\text{->}T_0),$$

Near the lower stability line, $\mathbf{K}=-4/7\mathbf{J}$, T_1->0 and the transformation is between essentially fully ordered HTT- and HTO-phases which (in this model) have zero point entropies of zero and ln2, respectively. In this limit, an estimate for T_1 is obtained by equating ln2 kT_1 with the difference in ground state energies:

$$\ln 2\ kT_1=-1/2\mathbf{J}-7/8\mathbf{K} \text{ (as } T_1\text{->}0).$$

The primitive nature of this Potts representation is its strength and weakness. It is certainly not a realistic model for the La_2CuO_4 system (for example, it exhibits diffusive rather that soft mode dynamics), but it does clearly demonstrate the powerful role of entropy in stabilizing new phases in systems with degenerate order parameters.

9. Spin-Orbit Induced Electron-Phonon Coupling. Undoped La_2CuO_4 is a near-perfect example of a quasi-two-dimensional Heisenberg antiferromagnet (AF). Magnetic anisotropy, although several orders of magnitude smaller that the dominant in-plane isotropic near-neighbor exchange, ultimately determines the direction along which the ground state moments lie. The in-plane anisotropy results from the Dzyaloshinskii-Moriya (DM) interaction,

$$H_{DM}=\sum \mathbf{D}_{ij}\cdot(\mathbf{S}_i \times \mathbf{S}_j).$$

The coupling vector $\mathbf{D}_{ij}$ is due to virtual excitations of higher energy Cu^{+2} crystal field levels through spin-orbit coupling. The crystal field levels are, in turn, very sensitive to breaking of the local tetragonal symmetry of the Cu^{+2} site. It can be shown[11] that $\mathbf{D}_{ij}$ is proportional to θ, the rotation vector specifying the tilt of the Cu-O octahedra. H_{DM} is minimized when the spins lie in a plane perpendicular to $\mathbf{D}_{ij}$. Thus LTO-LTT structural rearrangements can be expected to cause large reorientations in the directions of cuprate moments. This prediction has not been experimentally verified in the insulating cuprates, although it could, in principle, be tested in the $La_{2-x}Nd_xCuO_4$ system discussed earlier.

The metallic cuprates do not support long-range AF order, but appreciable short-range AF order persists[12]. Thio, et al., have discussed interplanar magneto-conductive changes induced by spin reorientations caused by LTO-LTT transformations, with possible relevence to superconductivity. More recently Bonesteel et al.[13] have considered the effect of spin-orbit induced DM-like interactions on the spins of mobile holes in the cuprates away from half-filled bands. They find a novel electron-phonon coupling with the soft 'tilting' modes which is produced by a rotation of the spin of the holes upon hopping from site i to j. Since the rms fluctuations in the tilt angles is large due to the high low-energy density-of-phonon-states, they suggest that this mechanism could be a primary cause of electron scattering in these materials, and suggest that it might explain their observed linear electrical resistivity at temperatures high enough that the phonons are thermally saturated.

10. Conclusion: It is the intent of this review to illustrate that there exists a considerable understanding of the structural phase transformations in La_2CuO_4 from a lattice dynamical and statistical mechanical point of view. The treatment given here is very general, applying not only to cuprates but to all structural isomorphs which display similar behavior. Several efforts to provide cuprate-specific microscopic underpinning for these phenomenological considerations have met with some notable success, particularly concerning ground-state properties.[14]

Other speakers at this conference will discuss the influence of the LTO-HTT transformation on the normal and superconducting state electronic and magnetic properties. It is worth emphasizing that extensive work involving replacement of lanthanum with iso- and heterovalent cations[7,15], show that although the onset of superconductivity is inhibited by the LTT transformation *per se*,[4,5] a further reduction in the superconducting T_c is associated with a hole to copper ratio of ~1/8. Both of these phenomena appear to be remarkable and worthy of further study and understanding.

11. **Acknowledgements.** It is a pleasure to acknowledge the help of my colleagues and co-workers, in particular H. Chou, D. E. Cox, M. K. Crawford, A. R. Moodenbaugh and T. R. Thurston for assistance and valuable discussions. This work was supported by the Division of Basic Sciences, U. S. Department of Energy, under Contract No. DE-AC02-76CH00016.

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