# Lattice Instabilities, Isotope Effect, and High-$T_c$ Superconductivity in $La_{2-x}Ba_xCuO_4$

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Unlike $La_{2-x}Sr_xCuO_4$, $La_{2-x}Ba_xCuO_4$, $x \sim x_{cr}=0.12$, undergoes a structural change to a low-temperature tetragonal (LTT) phase below 60 K, and this transformation is known to suppress $T_c$ drastically. We present self-consistent local-density-functional calculations for this system that indicate the $CuO_6$ octahedrons are unstable to an $X$-point tilt in any direction, thereby leading to strongly anharmonic $X$-point vibrations. The LTT phase is most favored energetically, consistent with experiment. The effect of the LTT distortion on the electronic structure accounts for the suppression of $T_c$ in the LTT phase, and for the enhanced isotope effect at $x=x_{cr}$.

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A number of experimental data have shown an intimate connection between the phonons in copper-oxide superconductors and their high transition temperatures $T_c$, such as shifts [1] in frequencies and linewidths for $T<T_c$, short-range rearrangements of atoms [2] at $T_c$, and a greatly enhanced oxygen isotope shift [3] of $T_c$ in $La_{2-x}M_xCuO_4$ near $x=x_{cr}=0.12$ for $M=$Sr and Ba. Indeed, this latter experiment establishes lattice dynamics to be intimately involved in the pairing mechanism in the La-based system. Equally dramatic evidence of an intimate connection between the dynamics of the lattice and superconductivity is the strong suppression of $T_c$ resulting from a small change in structure. For Ba concentrations near $x_{cr}$ in $La_{2-x}Ba_xCuO_4$ there is a *second* structural transformation around 60 K, from the low-temperature orthorhombic (LTO) phase into a low-temperature tetragonal (LTT) phase with $P4_2/ncm$ space group. The LTT structure, in which the $CuO_6$ octahedra are tilted along the conventional $x$ and $y$ axes in alternating layers, was identified by Axe *et al.* [4], who also verified earlier findings [5,6] that $T_c$ was strongly suppressed in this phase. Crawford *et al.* [3] noted that the very large isotope shift is obtained at exactly the same concentration $x=0.12$ for which the transition to the LTT phase in Ba-substituted material is the most complete.

In this Letter we present local-density-functional-approximation (LDA) calculations of the energy surface for $CuO_6$ octahedra tilts of $\mathbf{q}=(1,1,0)\pi/a$ periodicity ($X$ point in the conventional cell). We have previously shown [7,8] the applicability of LDA calculations for high-$T_c$ superconductors. Precise LDA calculations [7] provide Raman-active modes (fifteen in total) in $YBa_2Cu_3O_7$ whose frequencies agree well with experiment. Earlier we had found [8] that our calculations predict the $X$-point "tilt mode" [high-$T$ tetragonal (HTT) to LTO] instability in $La_2CuO_4$. In that study we included the orthorhombic strain that is coupled to the order parameter and is present experimentally as a $\sim 2\%$ strain. Here we present results for the energy surface for pure $X$-point tilts without strain, which allows us to investigate more general instabilities. We have studied, relative to the reference HTT $I4/mmm$ structure, order parameters corresponding to LTO symmetry, LTT symmetry, and an intermediate $Pccn$ symmetry that can take one continuously from the LTO structure to the LTT structure. Details of the linearized-augmented-plane-wave (LAPW) method that we have used have been presented elsewhere [7,8]. The LTT and $Pccn$ structures involve the quadrupling of the HTT unit cell (resulting in 28 atoms) and Hamiltonian matrices up to a dimension of 3300 were necessary to give converged energy surfaces. Zone sampling was similar to earlier studies [7,8]. Since we are interested in the Ba-substituted system, we have used the lattice parameters corresponding [4,9] to $x(\mathrm{Ba})=0.10$, $a=5.360$ Å, and $c=13.236$ Å, but otherwise do not account explicitly for the Ba substitution. The volume dependence can often be quite important in perovskite structures [10].

Using the notation of Axe *et al.* [4], the HTT phase has a degenerate symmetry-related pair of soft $X$-point phonons with amplitudes $\mathbf{Q}=(Q_1,Q_2)=(Q\cos\theta,Q\sin\theta)$. The LTO phase ($\theta=0$) is characterized by $\mathbf{Q}_{\mathrm{LTO}}=(Q_a,0)$, the LTT phase ($\theta=\pi/4$) is characterized by $\mathbf{Q}_{\mathrm{LTT}}=(Q_b,Q_b)$, and we also treat an intermediate $Pccn$ structure ($\theta=0.147\pi$). Since the octahedra are nearly rigid, and $|\mathbf{Q}|$ is similar for the two phases [4], the LTO-to-LTT transformation is characterized mainly by a change in the direction of tilt of the octahedrons, and an accompanying change in the direction of the displacement of the La or Ba cation (and loss of orthorhombic strain, of course).

The measured atomic displacements [11] for the LTO phase were used to generate the displacements for the LTT and $Pccn$ phases. The energies versus normal-mode (order-parameter) amplitude $Q=[N^{-1}\sum M_n \mathbf{u}_n^2]^{1/2}$, where $M_n$ and $\mathbf{u}_n$ are the mass and displacement of the $n$th atom and $N$ is the number of atoms in the supercell, are shown for each of the phases in Fig. 1. The LTO curve is similar to the earlier one [8], which included strain in an amount taken from structural data, indicat-

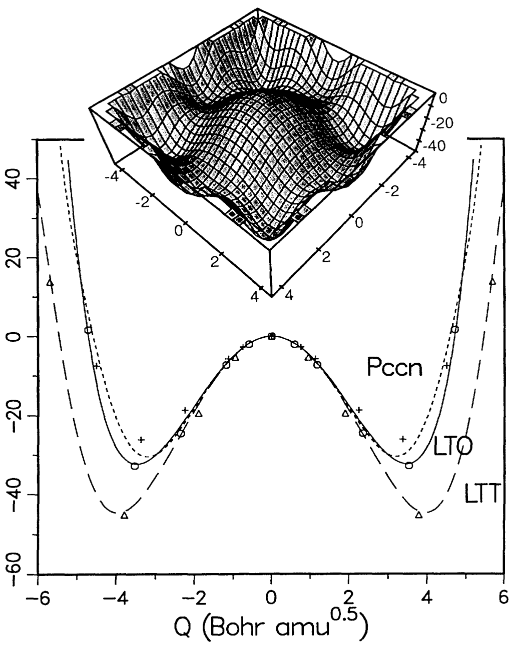

FIG. 1. Energy difference per primitive seven-atom cell of the LTO, LTT, and *Pccn* phases relative to the HTT structure, vs normal-mode magnitude $Q$. Lines result from a fit of the energy expansion in the text to all calculated energies (symbols). Inset (identical units): A surface plot of the resulting octuple-well energy surface for $X$-point tilts in the $(Q_1,Q_2)$ plane, with minimum along the diagonal (LTT phase).

ing that the strain contribution is secondary. The LTT distortion leads to the greatest gain in energy, consistent with this phase being the lowest-temperature one. The reference HTT structure is also unstable with respect to distortions of *Pccn* symmetry; in fact, the HTT point $Q=0$ is a *local maximum* in the energy surface.

The Landau free-energy analysis [12] of this system indicates that the energy ($T=0$ free energy) for this class of distortions must have square symmetry in the $(Q_1,Q_2)$ plane and can be expanded in the form

$$\Delta E(Q,\theta)=F_2(Q)+F_4(Q)\cos 4\theta+F_8(Q)\cos 8\theta+\cdots,$$

where only even powers of $Q$ occur in the functions $F_n$, and the subscript $n$ denotes the lowest power of $Q$ to appear in that function. This expression, for which $Q^{12}\cos 12\theta$ is the lowest-order correction, has been fitted to the calculated energies and leads to the octuple-well potential function shown in the inset of Fig. 1.

This potential surface accounts for many structural properties: (1) Such a system will assume the LTT phase at low temperature as long as the LTO strain energy is less than the LTO-LTT energy difference. (2) At high $T$ the system will rapidly pass from minimum to minimum among the eight minima, giving $\langle \mathbf{Q}\rangle=0$ (HTT phase) in spite of $\mathbf{Q}=0$ being a local maximum. (3) At intermediate $T$ the system may settle into an LTO minimum which will be stabilized both by orthorhombic strain and by the additional entropy of the one $X$-point soft mode that only hardens in the LTT phase. (4) The $\langle \mathbf{Q}\rangle=0$, $\langle \mathbf{Q}^2\rangle\neq 0$ result for LTT is consistent with the pancake ellipsoids that arise in the structural refinements [13], corresponding closely to this type of octahedron wobble. (5) The small energy difference ($\sim$15 meV$\sim$200 K per octahedron) between the LTO and LTT minima and the *Pccn* saddle point separating them is consistent with the observed transformation temperatures and with the types of fluctuating short-range order surmised from the modeling [2] of pair distribution functions. (6) Such local fluctuations should be very low in energy, and may be affected by the onset of the superconducting state, as suggested [2] for $Tl_2Ba_2CaCu_2O_8$. (7) This energy surface suggests anharmonic dynamics highly sensitive to the O mass, so the O isotope effect may be unusual, and be strongly affected by an incipient LTO-to-LTT instability [3]. (8) Since this energy surface indicates extreme anharmonicity of $X$ tilts, one would expect obvious effects of anharmonicity to show up in the neighborhood of the $X$ point, as is the case for the "extra mode" in the phonon dispersion curves of $La_{2-x}Sr_xCuO_4$ [14].

Since the $Q^2$ term in the Landau expansion is isotropic, the HTT phase is unstable to *all* of the LTO, LTT, and *Pccn* phases if it is unstable to any. Therefore we expect the energy surface of $La_{2-x}Sr_xCuO_4$ (LTO at low $T$) to be very similar to Fig. 1 even though the LTT phase never appears. Either the LTO curve is somewhat lower, or the coupling to orthorhombic strain is larger, to account for the lack of LTT phase. Our results are consistent with pair potential [15] and potential-induced breathing [16] studies which indicate that the instability is simply due to strong ionic forces, with the $O_z$-La interaction being dominant and the La displacement being essential. This strong ionic interaction also accounts for one other $X$-point instability we have found, involving an $O_z$-La pairing displacement that would be a $B_{2u}$-symmetry phonon in a harmonic crystal. In addition, we find that the $CuO_6$ rotational mode is extremely anharmonic [17], but no unstable, in the HTT phase.

An obvious but important consequence of our energy surface is that *some X-point phonons in the HTT phase are harmonically unstable,* and harmonic models based on the HTT phase [14] are bound to have strong limitations. The phonons in the HTT phase are only stabilized by strong anharmonic interactions and some vibrations may be librational in nature. Our energy surface also suggests an increased coupling of carriers to planar O and Cu displacements, since these atoms no longer lie on high-symmetry sites as they would in a harmonic HTT phase.

To address the electronic structure of the LTT phase, we show the band structure in Fig. 2 (top); band splitting *precisely* at $E_F(x=x_{\rm cr})$ occurs all along the zone edge $M$-$A$. This band splitting reflects the sensitivity of these Fermi surface states to the tilt and the deformation potential indicates strong coupling, particularly so in light

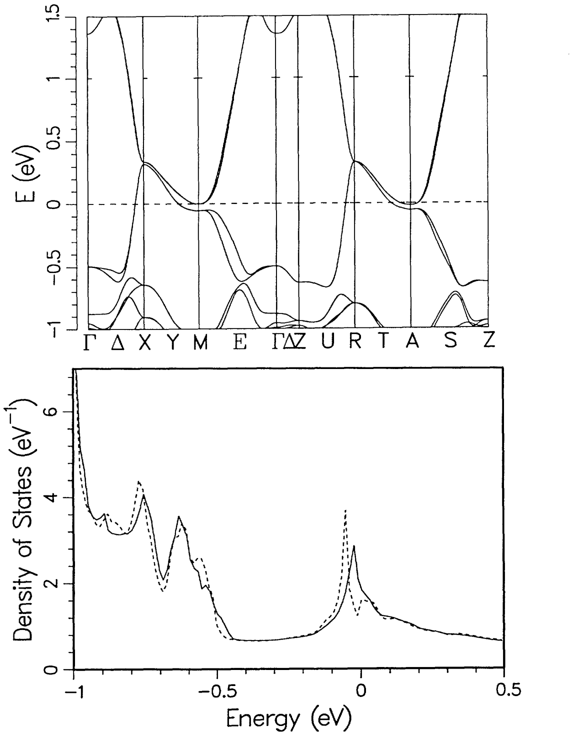

FIG. 2. Top: Energy bands in the LTT structure along high-symmetry directions. Note the gap opening along the $M$-$A$ zone edge at $E_F$. Bottom: Density of states near $E_F$, showing the decrease in $N(E_F)$ by one-half due to the LTT distortion. In both panels the zero of energy is placed at $E_F(x = x_{\rm cr})$.

of the very low frequency [14] of the tilt mode. Much of the Fermi surface is destroyed, and the effect on the density of states (DOS) is pictured in the lower panel of Fig. 2. The LTO to LTT transformation lowers $N(E_F)$ by as much as a factor of 2, but only in a region near $x = x_{\rm cr}$ (using the rigid-band picture). This is the right size to account for the factor-of-2 reduction in the linear specific-heat coefficient near $x \sim x_{\rm cr}$ measured by Okajima *et al.* [18]. Considering the decrease in $N(E)$, extending our calculations to an electron count corresponding to $x = x_{\rm cr}$ (via virtual crystal methods) and thereby accounting for Peierls-like contributions could lower $N(E_F)$ somewhat and further stabilize the LTT phase, along the lines suggested by Barisic and Zelenko [19]. However, we find that the instability is essentially of an ionic nature typical of perovskite compounds. The LTO distortion has a much milder effect (the van Hove singularity remains intact [8]) at least partly due to the symmetry requirement that bands "stick together" along certain zone edges [13].

Strong anharmonicity can affect the isotope shift of $T_c$ by making the average electronic structure dependent on mass; this has been one suggestion for the large inverse isotope effect [20] in PdH. A related anharmonic effect will occur in the present system. For very heavy masses a crystal with the energy surface we find would always be in the LTT phase. Finite masses (we consider specifically oxygen) allow the other structures with higher energy to become favored at higher temperatures. The extreme anharmonicity of this tilt surface suggests an explanation of the enhanced oxygen isotope shift $\alpha$ measured by Crawford *et al.* [3]. With $T_c = T_c(\Omega, \lambda, \mu^*)$, the *standard* isotope effect arises from the representative lattice frequency $\Omega$ ($\alpha_\Omega \sim 0.5$ if all masses are varied) and the Coulomb repulsion $\mu^*$ ($\alpha_\mu < 0$), since for harmonic crystals the coupling strength $\lambda$ is mass independent. Because of the extreme anharmonicity, the structure and therefore $\lambda$ can become mass dependent. Using $\lambda = N(E_F)\langle I\rangle^2/M\Omega^2$ (in standard, abbreviated notation), we have

$$\alpha_\lambda = -(d\ln T_c/d\ln\lambda)(d\ln\lambda/d\ln M)$$

$$\sim -2\{d\ln N(E_F) + d\ln(\langle I\rangle^2) - d\ln(M\Omega^2)\}/d\ln M\,,$$

where we have incorporated $d\ln T_c/d\ln\lambda \sim 2$ (Refs. [17 and 21]) for $\lambda \sim 1$ (consistent with $T_c \sim 25$ K). The tilt energy surface indicates that, near the LTO-to-LTT transition, replacing $^{16}$O with $^{18}$O (12.5% increase in mass) increases the tendency for small regions to assume an LTT structure, thereby halving $N(E_F)$ in those regions. If this replacement causes a fraction $\zeta$ of the sample to transform (perhaps locally and invisible to x rays), then the contribution to this anomalous isotope shift is $\alpha_\lambda = -2\zeta[\Delta N(E_F)/N(E_F)]M/\Delta M \sim 8\zeta$, so the local transformation of $\zeta = 5\%$ of the sample due to the increased mass would result in a positive isotope shift of 0.4. This is the right size to account for the measured shifts [3] as large as 0.7 (compared to the "normal" 0.1–0.2 value). A more detailed evaluation of this anharmonic contribution to the isotope shift would require accounting for the electronic structure in the *Pccn* phase as well as performing an appropriate thermal averaging. In addition, due to the hardening of the soft mode in the LTT phase, the (normally mass independent) $M\Omega^2$ will also give a positive shift, but we estimate it to be at least an order of magnitude smaller.

We have discussed the enhanced isotope shift in terms of an electron-phonon pairing mechanism. This origin [alteration of $N(E_F)$] for a nonstandard isotope shift is more general, however, applying to any mechanism that pairs carriers with coupling strength proportional to $N(E_F)$. Other anharmonic origins [22] of an anomalous isotope shift have been suggested, but these are based primarily on an effect via the $\langle I\rangle^2$ or $M\Omega^2$ terms in Eq. (2) rather than on the basic electronic structure. Very recently, Phillips and Rabe [23] have suggested an explanation based on ordering of the Ba ions and a two-Fermi-liquid model. To date, this ordering has not been seen, and our explanation in terms of the LDA band structure does not rely on such ordering.

In summary, we have presented an $X$-point tilt energy surface for the $\mathrm{La}_{2-x}\mathrm{Ba}_x\mathrm{CuO}_4$ system, $x \sim 0.12$, that accounts for much of the lattice behavior of this material. Two particularly intriguing aspects of electron-lattice coupling, the destruction of superconductivity by a small lattice distortion and the enhanced isotope shift, have been explained semiquantitatively.

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