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Anharmonic phonons and the anomalous isotope effect in $La_{2-x}Sr_xCuO_4$

Vincent H. Crespi and Marvin L. Cohen
Department of Physics, University of California at Berkeley, Berkeley, California 94720
and Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
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A model for the variation of an interionic potential near the orthorhombic to low-temperature-tetragonal structural phase transition in La-Sr-Cu-O can explain variations both above and below 0.5 in the superconducting isotope-effect parameter α. In particular, we posit a quadrupolar potential in which the four outer wells deepen as the phase transition is approached. This model can reproduce the experimentally observed variations in both T_c and α.

I. INTRODUCTION

Recent measurements[1] of the isotope-effect exponent α in $La_{2-x}Sr_xCuO_4$ have yielded $\alpha > 0.5$ for x in the range 0.10–0.13 and $\alpha \approx 0.1$ for larger values of x. A model based on a van Hove singularity in the electronic density of states near the Fermi level has been proposed to account for this unusual behavior.[2] In contrast, Crawford *et al.*[1] have speculated that anharmonic phonons associated with an incipient phase transition from the orthorhombic to the low-temperature-tetragonal structure could produce these anomalous values of α. We have used a simplified model of the effects of anharmonicity on the isotope effect to flesh out this speculation. The application of this model to a single one-dimensional Einstein phonon mode is described in a previous publication.[3] The present work generalizes the treatment to study an arbitrary two-dimensional Einstein mode within the framework of the Eliashberg equations. A straightforward model for the evolution of the relevant interionic potential with increasing Sr concentration can explain the measured variations in T_c and α.

We begin with an expression for the electron-phonon coupling λ at zero temperature,

$$\lambda = N(0) \sum_{k,k'}^{(FS)} \sum_{n=1}^{\infty} \frac{|\langle n|M_{kk'}|0\rangle|^2}{E_n - E_0}, \tag{1}$$

which describes[4] coupling between the lattice ground state $|0\rangle$ and all excited states $|n\rangle$ with energy E_n. The density of states at the Fermi level is $N(0)$. The sum over electronic states is restricted to the Fermi surface. The electron-phonon matrix element $M_{kk'}$ is given by

$$M_{kk'} = \langle k'|(\nabla V \cdot \delta \mathbf{R})_{R_0}|k\rangle, \tag{2}$$

where $V(r)$ is the electron-ion potential, $|k\rangle$ and $|k'\rangle$ are electronic states, and $\delta\mathbf{R}$ is the ionic displacement from the equilibrium position R_0. Assuming a two-dimensional phonon mode with displacements in the x and y directions, we can recast Eq. (2) in the form

$$M_{kk'} = \langle k'|\frac{dV}{dx}x + \frac{dV}{dy}y|k\rangle. \tag{3}$$

Following McMillan,[5] we factorize Eq. (1) to obtain a computationally convenient form,

$$\lambda = \sum_{n=1}^{\infty} \left[\langle I_x^2\rangle \frac{|\langle n|x|0\rangle|^2}{E_n - E_0} + \langle I_x I_y\rangle \frac{|\langle n|x|0\rangle||\langle n|y|0\rangle|}{E_n - E_0} + \langle I_y^2\rangle \frac{|\langle n|y|0\rangle|^2}{E_n - E_0} \right], \tag{4}$$

where the prefactors $\langle I_x^2\rangle$, $\langle I_x I_y\rangle$, and $\langle I_y^2\rangle$ contain the electronic contributions and the summation involves matrix elements between phonon states. The $N(0)$ factor has been absorbed into the electronic prefactors. For the potentials considered, the cross term is negligible and will, therefore, be dropped. For simplicity, the other prefactors, $\langle I_x^2\rangle$ and $\langle I_y^2\rangle$, will be assumed to be equal. The case of unequal prefactors can be easily treated, but the interesting physics is contained in the simpler situation. In any case, the prefactors should be equal for any potential symmetric in x and y.

In contrast to our previous work, we will not make use of an expression for the average phonon frequency $\langle\omega^2\rangle$. Instead, the various energy-level differences $(E_n - E_0)$ and their contributions to λ are used to create an expression for α^2F,

$$\alpha^2F(\omega) = \sum_{n=1}^{\infty} \lambda_n \omega_n \delta(\omega - \omega_n), \tag{5}$$

where

$$\lambda_n = \langle I_x^2\rangle \left[\frac{|\langle n|x|0\rangle|^2}{E_n - E_0} + \frac{|\langle n|y|0\rangle|^2}{E_n - E_0} \right] \tag{6}$$

and

$$\omega_n = E_n - E_0. \tag{7}$$

This strategy avoids the inherent inaccuracies in reducing the phonon frequency distribution to a single moment such as $\langle\omega^2\rangle$ or $\langle\omega_{\log}\rangle$. In any case, the potentials examined will be dominated by the transition between the ground state and the first excited state, so that this energy difference will closely approximate the average phonon frequency.

The two-dimensional Schrödinger equation is solved by expansion with a basis of solutions to the harmonic oscillator. For each energy level, we calculate the mass dependence of ω_n and λ_n and solve the Eliashberg equations nu-

merically to obtain T_c and α.

The theoretical model has several shortcomings. It does not include phonon dispersion, multiphonon processes, or quadratic terms in the expansion of the electron-ion potential. In addition, the Eliashberg equations are of questionable accuracy in the anharmonic regime. A more complete discussion of these weaknesses is given in a previous publication.[3]

II. APPLICATION TO $La_{2-x}Sr_xCuO_4$

Preliminary numerical study of one-dimensional modes indicated that a triple well potential with weak outer minima could produce $\alpha > 0.5$, while a triple well with stronger outer minima could produce $\alpha < 0.5$. These results suggest a simple explanation for the variation in α with Sr concentration. As the Sr concentration is increased, the system approaches a phase transition to the low-temperature-tetragonal phase. Frozen-phonon calculations[6] suggest that a quadrupolar interionic potential is associated with the orthorhombic to high-temperature-tetragonal transition. We will assume a similar form of potential for the orthorhombic to low-temperature-tetragonal transition. The potential examined should not be considered a quantitative prediction, but rather a representative model of a phase transition. Related multiple well potentials have yielded similar results, as will be discussed in a future publication.

In the present work we consider potentials of the form

$$V(r,\theta) = ar^2 + cr^6 + br^4\cos 2\theta . \tag{8}$$

When $b < 0$, the last term produces triple wells for $\theta = \pi/4, 3\pi/4$. In the case $a < 0$, the first term is also multiplied by the cosine factor to produce double wells at these angles. To ensure convergence, we used from 22 to 28 basis functions in the x and y directions. We model a structural phase transition by considering a series of potentials with the outer wells increasing in strength. A plot of the r dependence of these potentials for $\theta = \pi/4$ is given in Fig. 1. The outer minima are located at ± 0.18 Å, in accord with the frozen-phonon calculations.[6]

The difficulty of defining normal modes in a strongly anharmonic system clouds the choice of effective oscillator mass. We assume an oscillator mass equal to the mass of an oxygen atom. The relevance of the linear term in the electron-phonon coupling for the phonon mode governing the orthorhombic to low-temperature tetragonal transition has been questioned within the context of a tight-binding model.[7,8] However, this model ignores long-range nonrigid-ion contributions, which are quite important in the cuprate materials.[9] In addition, the strong anharmonicity of the system complicates any considerations based on the symmetry of a harmonically defined normal mode. We will assume that the linear term dominates the interaction.

To calculate T_c and α, we need a value for λ to set the scale for α^2F. The formalism provides only the ionic part of λ, without the electronic prefactor. This ionic part of λ increases with decreasing phonon frequency, which corresponds to increasing Sr concentration. However, one cannot assume that the electronic prefactor will remain constant as the Sr concentration changes. For each potential, λ is adjusted to fit both α and T_c. Note that the coefficients a, b, and c of Eq. (8) were not adjusted in order to better match the data, but merely chosen to produce a smooth evolution in the shape of the potential. We take $\mu^* = 0.10$ for each potential. The results for T_c, α, and λ are plotted in Figs. 2–4, along with the data of Crawford *et al.*[1] The theoretical results are not particularly sensitive to the value of μ^*.

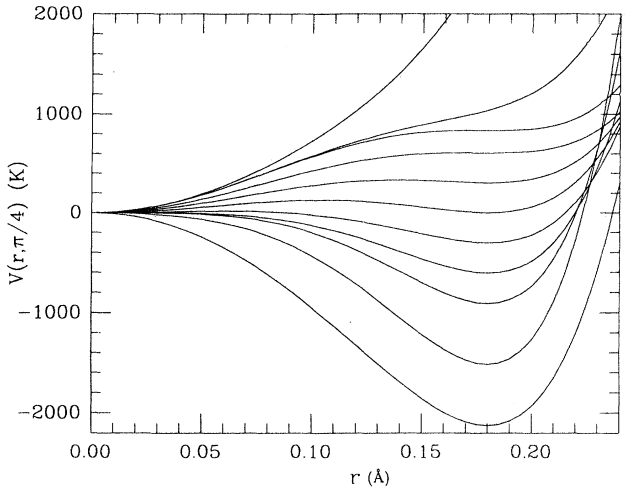

FIG. 1. The r dependence of the various quadrupolar potentials studied, plotted for $\theta = \pi/4$. Sr concentration increases with increasing depth.

Note that the horizontal scale of the theoretical results is arbitrary, since we do not have a quantitative relation between Sr concentration and the particular potentials chosen. The ordering of the potentials is fixed, but the horizontal scale is chosen to match the experimental data.

The proposed variation in potentials can produce an isotope parameter that starts near 0.5, increases, and then

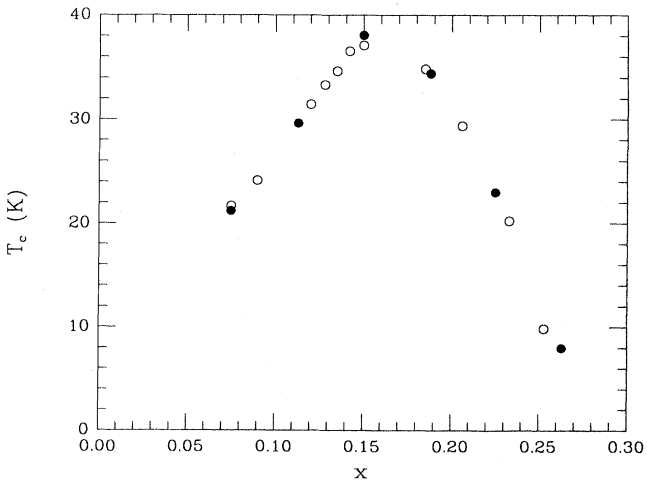

FIG. 2. T_c vs x in $La_{2-x}Sr_xCuO_4$ for the interionic potentials shown in Fig. 1. The depth of the potentials increases with increasing Sr concentration. Solid circles are the data of Crawford *et al.* (Ref. 1). Open circles are the theoretical results.

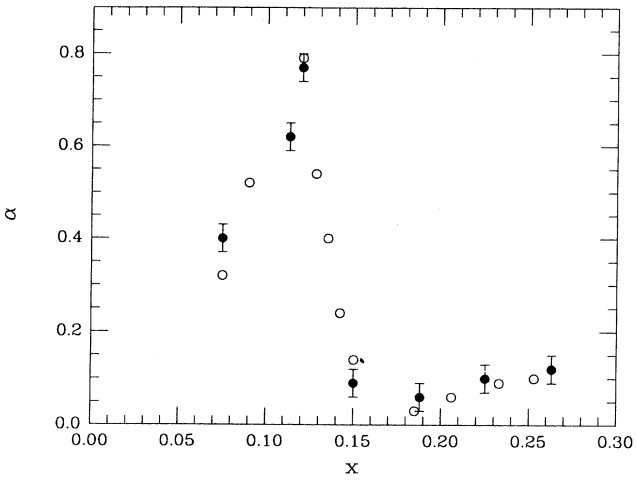

FIG. 3. The isotope exponent α vs x in $La_{2-x}Sr_xCuO_4$ for the interionic potentials shown in Fig. 1. Solid circles are the data of Crawford *et al.* (Ref. 1). Open circles are the theoretical results.

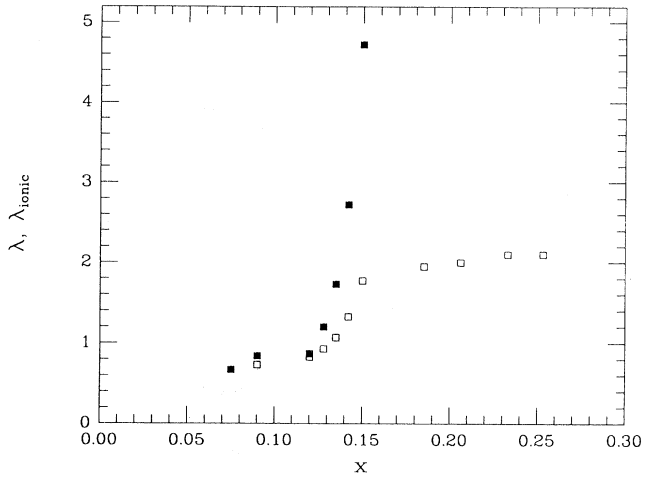

FIG. 4. Electron-phonon coupling λ vs x in $La_{2-x}Sr_xCuO_4$ for the quadrupolar potentials shown in Fig. 1. Open squares are the λ used to determine T_c and α. Solid squares are the ionic part of λ, scaled so that the first point coincides with the value of λ used in the calculations of T_c and α. The value of λ_{ionic} continues to increase for higher Sr concentrations, with values of 6.4, 7.9, 12.1, and 36.6 for the higher Sr concentrations considered.

falls to a constant value below 0.5, with T_c peaking just after α has dropped. For each potential we have one free parameter, λ, with which to fit both T_c and α. This fit produces λ's which increase with increasing Sr concentration, as does the calculated ionic part of λ alone, as shown in Fig. 4. The ionic contribution has been scaled so that the first points of either curve coincide.

It is not surprising that the ionic part of λ increases much more quickly than the total λ since the variations in the electronic contributions to λ have not been taken into account. In fact, a comparison of the fitted values of λ with the ionic contributions to λ provides a measure of the variation in the electronic prefactor $\langle I_x^2 \rangle$. The electronic prefactor begins to fall steeply at the same point that α decreases, possibly indicating a drop in the density of states at the Fermi level, or a significant change in the character of the electronic wave functions. Such a change could be associated with a structural phase transition.

The present model has one outstanding weakness: The quadratic part of the potentials with $\alpha > 0.5$ is rather large, producing a phonon frequency of roughly 500 K. The tetragonal to orthorhombic soft phonon mode is experimentally observed at roughly 50–100 K.[10,11] One might expect the low-temperature-tetragonal mode to have a similar frequency. If the quadratic parts of the relevant potentials are decreased in order to lower the phonon frequency, then the central minima are no longer deep enough to produce ionic wave functions that yield $\alpha > 0.5$. However, phonon modes with smaller $\mathbf{q}$ than the mode driving the orthorhombic to low-temperature-tetragonal transition could have higher frequencies, since these modes do not involve rigid motion of Cu-O octahedra. Such modes might also be described by quadrupolar potentials, or possibly a different multiple well potential. Other buckling motions of the oxygen atoms out of the Cu-O plane could also produce higher frequency multiple well modes. In addition, a more thorough study of the possible potentials for the orthorhombic to low-temperature-tetragonal transition, going beyond the somewhat restrictive form of Eq. (8), may yield a more physically plausible phonon frequency. We would expect a lower-frequency potential to produce less pronounced variations in λ than that exhibited in Fig. 4.

Numerous theories for high T_c can explain an anomalously weak isotope effect. However, few can explain strong variations in α both above and below 0.5. A quadrupolar anharmonic potential appears to be a likely candidate for a phonon-mediated mechanism for such a variation, although related potentials give similar results. A reproducible measurement of $\alpha > 0.5$ in $La_{2-x}Sr_xCuO_4$ would put significant constraints on possible theories of high-temperature superconductivity.

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