Anharmonic phonons and the isotope effect in superconductivity

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Anharmonic interionic potentials are examined in an Einstein model to study the unusual isotope-effect exponents for the high-T_c oxides. The mass dependences of the electron-phonon coupling constant λ and the average phonon frequency $\sqrt{\langle\omega^2\rangle}$ are computed from weighted sums over the oscillator levels. The isotope-effect exponent is depressed below $\frac{1}{2}$ by either a double-well potential or a potential with positive quadratic and quartic parts. Numerical solutions of Schrödinger's equation for double-well potentials produce λ's in the range 1.5–4 for a material with a vanishing isotope-effect parameter α. However, low phonon frequencies limit T_c to roughly 15 K. A negative quartic perturbation to a harmonic well can increase α above $\frac{1}{2}$. In the extreme-strong-coupling limit, α is $\frac{1}{2}$, regardless of anharmonicity.

I. INTRODUCTION

The small, but nonvanishing isotope effect[1] in Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O and other high-temperature superconductors (HTS) suggests an important and unusual role for phonons in the pairing mechanism. Frozen-phonon calculations yield strong anharmonicity, in the form of a double-well potential, for O(1) motions in Y-Ba-Cu-O.[2] Recent theoretical work[3] suggests that such a double-well ionic potential could produce extremely large values of the electron-phonon coupling parameter λ. We wish to study the influence of anharmonicity on both the transition temperature and the isotope effect to determine if such a mechanism is consistent with the properties of the high-T_c oxides. We have used three approaches in our study of anharmonic superconductors. Double-well potentials are studied via numerical solution of Schrödinger's equation. Strongly quartic potentials are considered using a simple scaling argument. Small anharmonicities are studied with perturbation theory. The weakly anharmonic well is also examined numerically to confirm and extend the analytic results.

In all cases we assume the validity of the standard formulas for the transition temperature T_c in terms of λ, the Coulomb repulsion μ^*, and the average phonon frequency $(\langle\omega^2\rangle)^{1/2}$. Although the Eliashberg equations are assumed to be applicable,[4] there is no rigorous justification for extending the scope of the harmonic T_c equations.

Anharmonicity affects superconductivity in three ways: a shift in the phonon frequencies, the introduction of Debye-Waller factors in the ionic potential, and multiphonon processes. These processes are all second order in the ratio of ionic displacement to lattice constant.[4] We concentrate on the modified phonon frequencies, ignoring the Debye-Waller factors and multiphonon processes. In the double-well problem, the modification of phonon frequencies is quite dramatic, suggesting that the other processes can be ignored in a first approximation.

With these caveats in mind, we explore the qualitative effects of anharmonicity. Section II describes the effect of a general anharmonicity. Section III presents the numerical calculations for the double-well potential. Section IV describes the pertubative results.

II. EFFECT OF AN ARBITRARY ANHARMONICITY ON THE ISOTOPE PARAMETER

The isotope parameter α is determined by calculating the mass dependence of λ and $\langle\omega^2\rangle$. We begin with the formula for λ introduced by Hui and Allen,[5]

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

which allows coupling between the lattice ground state $|0\rangle$ and excited states $|n\rangle$ with energy E_n in a one-dimensional Einstein oscillator at zero temperature. $N(0)$ is the electronic density of states at the Fermi energy and the sum over electronic states is limited to states on the Fermi surface. The electron-phonon matrix element $M_{kk'}$ is given by

$$M_{kk'} = \langle k'|[V(r - R_0 - \delta R) - V(r - R_0)]|k\rangle, \tag{2}$$

where V is the ionic potential, $|k\rangle$ and $|k'\rangle$ are electronic states, and δR is the ionic displacement from the equilibrium position R_0. For harmonic superconductivity calculations, the assumption of an Einstein spectrum should not introduce qualitative errors, since an Einstein model produces values of T_c reasonably close to those given by more realistic phonon spectra.[6] Dispersion of the anharmonic mode could qualitatively change the results. Unfortunately, the calculation of the dispersion relation for a strongly anharmonic phonon is problematic. In addition, the strong coupling between bare double-well

phonons of different **q** presents a difficult exercise in frequency renormalization. For the present discussion we limit ourselves to the Einstein model. Following McMillan,[7] we factorize (1) to obtain a computationally convenient form,

$$\lambda = N(0)\langle I^2\rangle \sum_{n=1}^{\infty} \frac{|\langle n|\delta R|0\rangle|^2}{E_n - E_0}, \tag{3}$$

where the prefactor $\langle I^2\rangle$ contains the electronic contributions and the summation involves matrix elements between phonon states. The electron-ion interaction has been approximated by the linear term in the Taylor series. This approximation is of questionable validity for the large ionic excursions in the double-well system. Inclusion of higher-order terms necessitates the calculation of the electronic prefactors so that the higher-order terms are included with the proper relative weight. By concentrating on the linear term, we avoid this problem, at the risk of a loss in accuracy.

Assuming that $\langle I^2\rangle$ is independent of the ionic mass, the mass dependence of λ can be calculated from the mass dependence of the dipole matrix elements and the oscillator levels, as obtained from a numerical solution of Schrödinger's equation.

An expression similar to (3) can be written for the average squared phonon frequency

$$\langle\omega^2\rangle = \frac{N(0)}{\lambda}\langle I^2\rangle \sum_{n=1}^{\infty} |\langle n|\delta R|0\rangle|^2 (E_n - E_0). \tag{4}$$

The summation has the form of a sum rule with value $\hbar^2/2M$, where M is the ionic mass. Using this information,

$$\langle\omega^2\rangle = \left[\frac{N(0)\hbar^2\langle I^2\rangle}{2}\right]\frac{1}{M\lambda}. \tag{5}$$

The anharmonic λ and $\langle\omega^2\rangle$ are related in the same manner as in the harmonic case. We define separate isotopic exponents for λ and $(\langle\omega^2\rangle)^{1/2}$ in the form

$$\lambda_M = \frac{M}{\lambda}\frac{d\lambda}{dM}, \tag{6}$$

$$\omega_M = \frac{M}{(\langle\omega^2\rangle)^{1/2}}\frac{d(\langle\omega^2\rangle)^{1/2}}{dM}, \tag{7}$$

with the relationship

$$\omega_M = -\frac{\lambda_M + 1}{2}. \tag{8}$$

for a pure harmonic potential, $\omega_M = -\frac{1}{2}$, so that $\lambda_M = 0$, as expected.

Having elucidated the mass dependence of λ and $\langle\omega^2\rangle$, we determine α from the Kresin-Barbee-Cohen T_c equation,[8,9]

$$T_c = 0.26\frac{(\langle\omega^2\rangle)^{1/2}}{(e^{2/\lambda}-1)^{1/2}}, \tag{9}$$

where we have assumed that the Coulomb repulsion parameter $\mu^* = 0$. The double-well calculations will produce λ in the range from 1.5 to 4, so that the Kresin-Barbee-Cohen equation should be applicable. For these strong coupling λ's the $\mu^* = 0$ approximation should be reasonable. A simple calculation yields

$$\alpha = \tfrac{1}{2} - \lambda_M\left[\frac{e^{2/\lambda}}{(e^{2/\lambda}-1)\lambda} - \tfrac{1}{2}\right]. \tag{10}$$

The term multiplying λ_M is positive for all values of λ, so that the direction of deviation of α from $\frac{1}{2}$ will be determined by the sign of λ_M. In the strong-coupling limit, we obtain

$$\alpha = \tfrac{1}{2} - \frac{\lambda_M}{2\lambda}. \tag{11}$$

The extreme-strong-coupling limit of α is one-half, regardless of anharmonicity. To study the effect of finite μ^*, we have solved the Eliashberg equations. As μ^* ranges from 0.05 to 0.25, the strong-coupling limit of α varies from 0.5 to 0.4. We introduce a finite Coulomb repulsion in the weak-coupling case to obtain

$$\alpha = \frac{1}{2}\left[1 - \left[\frac{\mu^*}{\lambda^* - \mu^*}\right]^2\right](1+\lambda_M) - \frac{\lambda_M}{\lambda}\left[\frac{\lambda^*}{\lambda^* - \mu^*}\right]^2. \tag{12}$$

For positive λ_M, the introduction of μ^* will decrease α, as in the harmonic case. However, for negative λ_M, the effect of μ^* depends on the value of λ_M. For sufficiently large negative λ_M, a positive μ^* can actually increase α. Calculations using the Eliashberg equations extend this result to the strong-coupling regime.

The case of a pure quartic potential provides a simple application of Eq. (10). For such a well, a simple scaling arguement can be applied to the Schrödinger equation to obtain information about $(\langle\omega^2\rangle)^{1/2}$. To wit, a shift in the mass can be counteracted by changes in length scale and energy scale. The energy rescaling implies that

$$(\langle\omega^2\rangle)^{1/2} \propto M^{-2/3}, \tag{13}$$

so that

$$\lambda_M = \tfrac{1}{3}. \tag{14}$$

Since $\lambda_M > 0$, α is depressed below 0.5. Such an argument can be applied to any potential with only one length scale (e.g., pure sixth-order, etc), but only the quartic case is of physical interest.

In the extreme anharmonic limit of a square-well potential, elementary quantum mechanics yields

$$(\langle\omega^2\rangle)^{1/2} \propto M^{-1}, \tag{15}$$

so that

$$\lambda_M = 1. \tag{16}$$

The stronger anharmonicity produces a greater deviation from the harmonic case.

III. DOUBLE-WELL POTENTIAL

For the double well, we calculate λ_M and ω_M from numerical solutions of Schrödinger's equation for a variety of anharmonic potentials of the form

$$V(x)=Ax^2+Bx^4 \tag{17}$$

with well widths of 0.25, 0.35, and 0.5 Å and depths of 60, 150, and 300 K. The well width is defined as the distance from the origin to the zero of the potential. The potential calculated by Cohen *et al.*[2] corresponds most closely to a depth of 150 K and a width of 0.35 Å. The summations in (3) and (4) were carried over six levels, with the dominant contribution in all cases coming from the first term.

In addition to λ_M and ω_M, the numerical calculations provide $\langle\omega^2\rangle$ and the ionic part of λ (without the electronic prefactor). In accordance with the results of Hardy and Flocken,[3] the ionic part of λ increases 100-fold from the shallow, narrow wells to the deep, wide potentials. However, possible variations in the electronic prefactor for different potentials rule out a direct comparison between the λ calculations for different potentials. We circumvent this difficulty by exploiting the relationship between λ and α given by Eq. (10). Setting α equal to 0.02, the accepted value for Y-Ba-Cu-O, we obtain an estimate for λ. The transition temperature T_c is calculated from (9). Obviously, this technique will not produce a quantitative prediction for T_c, but the general trend may be relevant.

Imposing the $\alpha=0.02$ condition produces moderately strong coupling λ's. The largest λ's occur for wide, deep wells in which λ is most sensitive to M. This trend is elucidated by Eq. (11), which shows λ to be proportional to λ_M in the strong-coupling limit, under the condition $\alpha=0$. As noted above, the wide, deep wells also have the largest ionic contributions to the electron-phonon coupling, as computed directly from the numerical solutions of Schrödinger's equation, without imposing the $\alpha=0.02$ condition.

In the limit of an infinitely deep double well, the ground state and first excited state are degenerate, corresponding to linear combinations of the ground states of two uncoupled oscillators. For finite double wells the degeneracy is broken, but the energy difference remains small. This near degeneracy produces a very small average phonon frequency, which counteracts the large λ, limiting the critical temperature to roughly 15 K. For some potentials, the transition temperature is only 2 or 3 K. If λ is increased by hand to produce T_c on the order of 90 K, then α will approach the strong-coupling limit of one-half, at variance with experimental results. Note that a closely related calculation by Dreschler and Plakida[10] produces similar results for the variation of α with λ.

In a two-dimensional double well, the angular-momentum term will break the near degeneracy of the lowest levels, increasing the average frequency. Such a situation could possibly increase T_c into the range of the HTS oxides. Since the O(1) atoms lie in chains, one could consider a two-dimensional anharmonic buckling motion out of the chain. The standard description of phonons would necessitate a separation of the two-dimensional mode into two coupled one-dimensional modes. The Einstein scheme avoids the problem of analyzing such strongly coupled modes. A preliminary analysis yields roughly a factor of 3 increase in the phonon frequency (and transition temperature) for a two-dimensional potential. A neutron powder diffraction study has measured large thermal ellipsoids for the O(1) atoms. The ellipsoids are pancake-shaped and oriented perpendicular to the Cu—O bond,[11] providing some support for the hypothesis of a two-dimensional anharmonicity. However, other diffraction studies have yielded a cigar-shaped thermal ellipsoid,[12,13] a result inconsistent with a soft two-dimensional double well. The average phonon frequency could also conceivably be increased by coupling of the double well to higher-frequency modes. A detailed discussion of the relevance of such coupling is beyond the scope of this paper. Finally, finite-temperature effects should increase the contributions of the higher-energy levels to the average phonon frequency. Of course, a nonzero temperature should also influence ω_M and λ_M.

The value of λ_M is positive for all double-well potentials, implying that α is always less than one-half. The date of Crawford *et al.*[14] with α for $La_{2-x}Sr_xCuO_4$ substantially above $\frac{1}{2}$ for certain strontium concentrations cannot be accounted for by a double-well potential, at least within our approximations. However, a negative quartic perturbation on a harmonic well may be able to explain the results, as will be discussed in Sec. IV.

IV. SMALL ANHARMONIC PERTURBATIONS

Here we present the results of an analytic calculation to determine the effect of small quartic anharmonicities on the isotope effect. The potential is of the form

$$V(x)=Ax^2+Bx^4. \tag{18}$$

The perturbation will shift the average phonon frequency to first order in the relevant expansion parameter, namely, the ratio of the energies contained in the quartic and quadratic parts of the oscillation,

$$(\langle\omega^2\rangle)^{1/2}=\sqrt{(2A)/M}\left[1+K\frac{B}{A^{3/2}M^{1/2}}\right]. \tag{19}$$

The order-unity prefactor K is initially left indeterminate. Equation (5) then determines the mass dependence of λ,

$$\lambda_M=K\frac{B}{A^{3/2}M^{1/2}}. \tag{20}$$

The prefactor K can be approximated by a perturbation calculation using using the first term in the sum for $\langle\omega^2\rangle$, which yields $K=1.06$. Numerical solutions of Schrödinger's equation for weakly anharmonic wells produce $K=1.05\pm0.01$, confirming the perturbative approach. These numerical studies also allow a rough evaluation of the coefficient of the next term in the perturbation expansion, producing

$$\lambda_M = 1.05\frac{B}{A^{3/2}M^{1/2}} - 5\frac{B^2}{A^3 M}. \quad (21)$$

We obtain a shift in α as expressed by Eq. (10). A positive quartic part will decrease the isotope effect, with the reduction most pronounced for light ions.

A negative quartic part, on the other hand, will produce $\lambda_M < 0$ and thereby increase α above $\frac{1}{2}$. In addition, a negative value of λ_M can result in μ^* increasing the isotope parameter, as discussed in reference to Eq. (12). Crawford *et al.*[14] discuss an incipient phase transition from orthorhombic to tetragonal in $La_{2-x}Sr_xCuO_4$, which appears to be correlated with values of α above $\frac{1}{2}$. This phase transition is associated with an optical tilt mode of the Cu-O octahedra. The form of the interionic potential for this mode in orthorhombic $La_{2-x}Sr_xCuO_4$ is not known.

A phonon mode which gains a strong negative quartic part as a function of Sr doping could explain $\alpha > \frac{1}{2}$. In addition, preliminary calculations indicate that certain forms of triple-well potentials could increase α. A detailed discussion of these possibilities will appear in a future publication wherein we will consider the effects of a phonon spectrum with more than one Einstein mode.

V. CONCLUSION

A simplified model of anharmonicity will usually produce isotope effect exponents from one-half to less than zero. The analysis yields a relationship between α and λ. Using this relationship, we obtain λ in the range from 1.5 to 4 for various double-well potentials. The specific double well suggested by frozen-phonon calculations on Y-Ba-Cu-O yields $\lambda = 2.2$. However, such wells produce phonon frequencies much too low to explain the high transition temperatures. Perhaps a two-dimensional phonon mode could increase the frequencies sufficiently. In addition, the anharmonic mode could be coupled strongly to higher-frequency modes. Isotope effects greater than one-half appear possible for both negative quartic perturbations and certain triple-well potentials.

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