Theoretical Determination of Strong Electron-Phonon Coupling in $YBa_2Cu_3O_7$

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(Received 29 January 1990)

Large nonlocal contributions to the electron-phonon interaction in $YBa_2Cu_3O_7$ are found using the linearized-augmented-plane-wave method with the frozen-phonon technique. These nonlocal effects greatly increase the electron-phonon coupling strength and lower the expected isotope effect for oxygen by increasing the coupling strength of the heavy ions. We find large anharmonicity of chain-oxygen motions, which can also enhance the superconducting transition temperature and decrease the isotope effect. Excellent overall agreement with experiment is found for the fifteen Raman-active-mode frequencies.

PACS numbers: 74.70.Vy, 63.20.Dj, 71.45.Nt

Despite considerable international effort, there is still no consensus about the mechanism of high-temperature superconductivity in the copper oxides. Experimental studies strongly suggest that the electron-phonon interaction is responsible for superconductivity in $(Ba,K)BiO_3$,[1] and calculations suggest that the electron-phonon interaction in metallic hydrogen can lead to T_c's as high as 250 K.[2] Many experimental studies suggest an intimate relationship between phonons and the superconducting transition in the high-T_c oxides. For example, Raman frequencies and linewidths,[3] elastic constants,[4] and the thermal conductivity[5] all show changes around T_c. Nevertheless, there is not a well-developed theoretical understanding of how the phonons are related to T_c.

Previous estimates of the electron-phonon coupling in $YBa_2Cu_3O_7$ are based on the rigid-muffin-tin or related rigid-atom approximations (RAA) that include only local, short-range, changes in the potential when atoms are displaced, and give electron-phonon coupling strengths which are too small.[6,7] In the RAA atoms that do not lie in the metallic Cu-O planes or chains do not contribute significantly to T_c. There are several studies that suggest that the lack of good metallic screening in the high-T_c oxides leads to nonlocal ionic contributions to the electron-phonon coupling.[8-10] Results from linearized-augmented-plane-wave[11] (LAPW) frozen-phonon calculations for La_2CuO_4 demonstrate that band theory within the local-density approximation (LDA) gives excellent agreement with experiment for structural and vibrational properties, indicate the presence of strongly anharmonic modes, and reveal large ionic contributions to the electron-phonon coupling strength.[9,12] Here we demonstrate that enhancements primarily due to non-RAA corrections are large enough to give strong electron-phonon coupling in $YBa_2Cu_3O_7$.

We have studied all fifteen Raman-active modes and one zone-boundary mode using the frozen-phonon technique and the LAPW method. The five A_g modes involve motion of the Ba, planar Cu(2), planar O(2) and O(3), and the out-of-plane O(4) atoms in the c direction; these motions can be obtained by varying the internal structural parameters. The B_{2g} (B_{3g}) modes involve motions of these same atoms in the a (b) direction. For the A_g modes, experimental structural parameters were used as the equilibrium structure:[13] $a=3.817$ Å, $b=3.883$ Å, $c=11.67$ Å, $Ba(z)=0.185$, $Cu(2)_z=0.3552$, $O(2)_z=O(3)_z=0.378$, and $O(4)_z=0.158$. The minimum-energy positions when each atom is displaced separately are $Ba(z)=0.182$, $Cu(2)_z=0.353$, $O(2)_z=0.379$, $O(3)_z=0.378$, and $O(4)_z=0.161$, which are very close to the assumed structure parameters. The latter positions were used as the equilibrium positions for the B_{2g} and B_{3g} modes.

The diagonal elements of the A_g, B_{2g}, and B_{3g} blocks of the dynamical matrix were found from quadratic coefficients of the energies versus displacements. The calculated energies for the A_g and B_{2g} modes were fitted well by parabolas; thus the Raman modes are at least diagonally harmonic. All of the off-diagonal elements were found by performing additional total-energy calculations for displacements of two types of atoms simultaneously. Table I shows the resulting frequencies and eigenvectors. The calculated A_g frequencies compare rather well with the experimental values.[14] The only significant discrepancy is for the 440-cm^{-1} mode, which we find about 20% low at 361 cm^{-1}. This mode involves

TABLE I. Calculated phonon eigenfrequencies (cm^{-1}) and eigenvectors for the A_g modes in $YBa_2Cu_3O_7$.

Calc.	Expt.[a]	Ba	Cu(2)	O(2)	O(3)	O(4)
105	118	0.81	0.59	0.02	0.02	−0.02
127	145	0.59	−0.80	−0.07	−0.02	0.05
312	335	−0.02	0.03	−0.54	0.78	0.32
361	440	−0.01	0.05	−0.81	−0.40	−0.43
513	500	0.01	−0.07	0.20	0.49	−0.84

[a]Reference 14.

primarily the in-phase motion of the planar O(2) and O(3) ions. The discrepancy for this mode may be due to nonadiabatic effects, which can shift the Raman frequencies of strongly interacting modes,[15] or may be due to off-diagonal anharmonicity, which we did not investigate. The calculated phonon eigenvectors agree qualitatively with those obtained by either empirical lattice-dynamical models[16] or oxygen-isotope substitution.[17] [The displacements patterns are pictured in Refs. 14(b) and 16.] There are some important new features, however. We find that the Cu and Ba motions are strongly hybridized, and that the O(4) motion is strongly hybridized with the O(2) and O(3) modes. Since the O(4) mode couples strongly with Fermi-surface states (see below), this hybridization increases the electron-phonon coupling constant λ by transferring coupling to lower frequency. The hybridization of the Cu and Ba likewise increases λ.

Table II shows the B_{2g} and B_{3g} eigenfrequencies, which only recently have been observed in detwinned crystals by Raman scattering.[18] The observation of the $B_{2,3g}$ 340-cm^{-1} mode by Gasparov *et al.*[19] is questioned in Ref. 18 due to the probability of "polarization leakage" from the 335-cm^{-1} A_g mode, but our calculations indeed give $B_{2,3g}$ modes at 340 cm^{-1}. The calculated frequencies also agree fairly well with those derived from inelastic neutron-scattering studies on twinned crystals, which give "average" B_{2g}-B_{3g} frequencies of 60 and 150 cm^{-1} for the two lowest "modes" of these symmetries.[20]

The satisfying correspondence between calculated and observed frequencies strongly implies that LDA band theory is an excellent approximation for the charge density, total energies, and static density response in $YBa_2Cu_3O_7$. The discrepancies from experiment are comparable to those found in other, much simpler, materials.

For La_2CuO_4, it was found that a nonempirical ionic model, the potential-induced breathing (PIB) model, predicted which modes were likely to be strongly anharmonic. Modes that were found to be harmonically unstable, i.e., have imaginary frequencies, in the PIB model[8] were found to be very anharmonic, if not unstable, when self-consistent calculations were performed using the LAPW method.[12] For $YBa_2Cu_3O_7$, the PIB model also predicts some modes to be harmonically unstable.[21] One of the unstable modes involves motions of the O(1) chain oxygens out of the chain. At Γ this motion is a polar mode, whereas at the Y point the mode has inversion symmetry and can be pictured as a zigzag motion of the chain oxygens in the a direction. We have performed eight calculations for the Y-point "zigzag" mode, and find a wide, double well with a depth of greater than 1 mRy (for the 26-atom supercell) and a width of 0.5 Å between minima. The calculated points are fitted with an rms error of 4 meV by

$$\Delta E[(1\text{ meV})/(26\text{ atoms})] = -361d(\text{Å})^2 + 2920d^4.$$

This anharmonicity may be important because the chain atoms have large weight at the Fermi level,[7] *and thus there may be unusually large coupling between this distortion and Fermi-surface states.* A strongly anharmonic mode such as this buckled chain will, in general, couple to numerous other modes throughout the Brillouin zone, thus providing some support for anharmonic mechanisms for high T_c.[22] The effect of anharmonicity on the isotope effect is complex, but can be large and negative,[23] and the presence of such modes suggests caution in interpreting small isotope effects to rule out a phonon contribution to superconductivity in $YBa_2Cu_3O_7$.

All methods that have been used to estimate the electron-phonon interaction from first principles that give accurate averages over the phonon Brillouin zone neglect long-range contributions. The frozen-phonon method can be used to evaluate the electron-phonon coupling for individual modes self-consistently. Figure 1 shows the change in the self-consistent potential when the Ba atoms are displaced in an A_g symmetry mode. This mode has a *negligible contribution* to the electron-phonon coupling λ *within the RAA,* because there is no weight at the Ba site at the Fermi level. However, we find there are *large nonlocal changes* in the potential, including changes on the Cu-O planes and chains, which have the greatest weight at the Fermi level. Consider-

TABLE II. B_{2g} and B_{3g} frequencies (cm^{-1}) in $YBa_2Cu_3O_7$.

B_{2g}		B_{3g}	
Calc.	Expt.[a]	Calc.	Expt.[a]
57	70	72	83
133	142	133	140
185	210	257	303
365	340	335	340
568	579	524	526

[a]Reference 18; 340-cm^{-1} mode, Ref. 19.

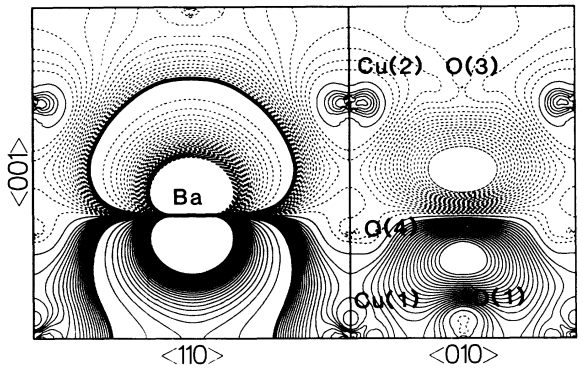

FIG. 1. Change in the self-consistent potential for the Ba A_g symmetry mode for a displacement of 0.047 Å. The contour intervals are 10 mRy near the Ba atom, inside the thick curve, and 0.5 mRy elsewhere. The dashed contours are negative. Note the potential changes on the metallic planes [Cu(2)-O(3)] and chains [Cu(1)-O(1)].

able nonlocal changes in the potential, which arise from the Madelung contributions, are found for all of the A_g symmetry modes.

There are actually two types of long-range contributions that are ignored in RAA but that we find important in the high-T_c oxides. The first is the change of potential on other atoms when a given atom is displaced, as discussed above. There are also changes in the on-site ($l=0$) potential on the displaced atom. We find the on-site potential derivative to be 0.7 eV/Å for A_g displacements of the Cu(2), 0.2 eV/Å for the O(2), and 0.1 eV/Å for the O(3).

In ordinary superconductors with large metallic screening, the RAA works fairly well, in general, and the potential changes appear to be rather local, but the high-T_c oxides are ionic metals, and the motions of the ions lead to large nonlocal changes in the potential. We find the nonlocal changes to be smaller for the B_{2g} and B_{3g} modes, due to the vanishing of the monopole contributions for these symmetries. Nevertheless, the dipole contributions to the potential changes are evident for some motions; for example, motion of the Cu(2) in the x direction causes a dipole to form in the O(2) atomic sphere. Motions parallel to the x-y plane for nonzero q vectors are likely to have greater nonlocal contributions, because the Madelung ionic contributions no longer vanish.

In order to make a quantitative estimate of the electron-phonon matrix elements, we have examined the deformation potentials at the k points which were used in the self-consistent calculations. The deformation potential $D_{kij}=\langle\psi_{ik}|\Delta V/\Delta d_j|\psi_{ik}\rangle$, for k-point k and electronic state i when atom type j is displaced a distance Δd, is the shift in the band eigenvalue ϵ_{ki} (relative to the Fermi energy) resulting from atomic displacements.[24] ΔV is the change in the self-consistent potential and ψ is the wave function for the undistorted crystal. The deformation potentials around the Fermi level are 0.2 eV/Å for the Ba A_g symmetry mode, 0.4 eV/Å for the Cu(2), and 0.3 eV/Å for each oxygen.

For the sake of obtaining an estimate of the coupling strength λ_ν for mode ν, we suppose that the coupling of modes at Γ is indicative of the coupling throughout the zone. By assuming a constant effective matrix element $V_{\nu,\mathrm{eff}}$, where

$$V_{\nu,\mathrm{eff}}^2\rho^2(E_F)=\sum_{k,q}\langle\psi_k|\Delta V_\nu|\psi_{k+q}\rangle^2\delta(\epsilon_k)\delta(\epsilon_{k+q}), \tag{1}$$

and no optical-phonon dispersion, we obtain

$$\lambda_\nu=3N_a\rho(E_F)\frac{V_{\nu,\mathrm{eff}}^2}{\sum_\alpha 2M_\alpha\omega_\nu^2\Delta d_{\nu\alpha}^2}, \tag{2}$$

where N_a is the number of atoms in the primitive cell, $\rho(E_F)$ is the density of states for both spins at the Fermi level, M_α is the mass of atom α, and ω_ν is the frequency of phonon branch ν. With this definition, $\lambda=(1/3N_a)\sum_\nu\lambda_\nu$.

Table III shows the minimum, maximum, and average values, with respect to the k points, of λ_ν for the A_g modes, including only those states within 0.1 eV of the Fermi level. Large values of λ_ν are found, even for the high-frequency modes, and there are individual electronic states that are particularly strongly coupled to particular phonons.

The relative importance of a mode for T_c is given not simply by λ_ν, which can be greatly enhanced by low frequencies, but rather by a quantity between $\omega_\nu\lambda_\nu$ and $\omega_\nu^2\lambda_\nu$, and phonons with frequencies at about $2\pi T_c$ ($\sim$400 cm^{-1} in $YBa_2Cu_3O_7$) are most effective.[25] Simple calculations based on the Allen-Dynes equation show that λ between 1.5 and 2 is sufficient to give $T_c=90$ K for phonon frequencies of 400 cm^{-1}.[26] The present calculations thus show that an electron-phonon mechanism is plausible, though accurate averages over both the Fermi surface and over phonons throughout the zone are clearly needed to make a strong case for an electron-phonon mechanism.

Although the A_g modes are strongly coupled, the B_{2g} and B_{3g} modes have negligible coupling strength for most electronic states, though a few states with λ_ν up to 0.6 are found. As mentioned above, we expect the matrix elements for displacements in the x and y directions to be larger elsewhere in the Brillouin zone, because there are no Madelung contributions at $q=0$ to the $B_{2,3g}$ modes, and such contributions are present elsewhere in the zone. Also, small-q LO phonons, which we have not studied, are expected to contain particularly strong electrostatic contributions.

Here we have shown that nonlocal contributions, neglected in earlier estimates of the electron-phonon coupling strength and T_c, are *quantitatively important for many modes* in the high-T_c oxides. Even the Ba motion, which has zero contribution within rigid-ion-like models, and heretofore has been neglected, contributes strongly to λ. This has some consequences for the isotope effect as well, because only the sum over all atoms of the isotope exponents is expected to be of the order of one-half. If one simply assumes all of the ions to couple approximately to the same degree in $YBa_2Cu_3O_7$, one expects

TABLE III. Electron-phonon coupling strength λ_ν for the A_g modes.

A_g mode (cm^{-1})	Min.	Max.	Avg.
105	0.2	3.6	1.9
127	1.1	2.1	1.7
312	0.1	3.5	1.0
361	0.3	1.2	0.8
513	0.0	0.5	0.2

$\alpha_O = 0.3$ and $\alpha_{Cu} = 0.1$. However, we find that modes with primarily Cu and Ba weight have large coupling constants. The Coulomb pseudopotential, indirect effects such as structural changes with ion mass, and anharmonicity, as well as electronic mechanisms, can change the total α from one-half. The lack of a substantial isotope effect in $YBa_2Cu_3O_7$ is by no means conclusive, and even the smallness of α_O is contradicted by some studies.[27]

In summary, we have computed the phonon eigenmodes and deformation potentials for all fifteen Raman-active modes in $YBa_2Cu_3O_7$. We find these to be harmonic, but to contain large nonlocal contributions to the electron-phonon coupling. We also find an anharmonic "double-well" mode at the Y point that involves buckling of the chains, consistent with earlier model calculations, which could enhance the electron-phonon coupling. We have studied only 15 of the 36 optic branches, and all of the modes we have studied would not couple strongly according to the conventional wisdom that breathing-type motions that modulate Cu-O bond lengths should be the strongest coupling modes. We expect such modes to couple even more strongly than those we have examined; since such motions require supercell calculations and are thus even more computationally intensive they have not yet been performed for $YBa_2Cu_3O_7$, but we calculate the breathing mode in La_2CuO_4 to indeed have a huge electron-phonon coupling strength.[9]

Computations were performed on the Cray 2 computer at the National Center for Supercomputing Applications at the University of Illinois and were supported by the National Science Foundation. H.K. was supported by NSF Grant No. DMR-8719535 and acknowledges computing support from the Cornell National Supercomputer Facility. We would like to thank B. M. Klein, D. Singh, J. Serene, P. B. Allen, J. Hardy, L. L. Boyer, W. Reichardt, L. Pintschovius, K. F. McCarty, K. L. Cohen, and L. F. Mattheiss for helpful discussions. We especially thank Howard Lu for providing technical and computational support.

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