Linear-Response Calculation of the Electron-Phonon Coupling in Doped $CaCuO_2$

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Using density-functional linear-response theory, we calculate the electron-phonon interaction for s- and d-wave pairing in the 0.24 hole doped infinite-layer compound $CaCuO_2$. We find $\lambda_{x^2-y^2} \sim 0.3$ to be positive and only slightly smaller than $\lambda_s \sim 0.4$. This suggests that the electron-phonon mechanism *alone* is insufficient to explain the high T_c but could *enhance* another d-wave pairing mechanism. Results of calculated lattice dynamics and transport properties are also presented and discussed. Out-of-plane distortions are found essential for the stability. [S0031-9007(96)01660-2]

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Despite enormous theoretical and experimental effort, the mechanism of high-temperature superconductivity in the hole-doped cuprates is still unclear [1]. The symmetry of the paired state seems to be d, with the lobes in the CuO bond direction, and this points to an electronic mechanism [2]. However, theoretical calculations for the Hubbard and t-J models with realistic parameter values leaves one with the suspicion that something more than the Coulomb repulsion is needed [2]. Experimentally, superconductivity-induced phonon renormalizations [3], Fano line shapes [3], a large isotope effect away from optimal doping [4], and phonon-related features in the tunneling spectra [5] indicate that the electron-phonon interaction (EPI) is substantial, but, usually, it would support only s pairing.

A large amount of theoretical work has been done to estimate the EPI and the strength λ_s for s-wave pairing in the cuprates. The first density-functional [local density approximation (LDA)] calculations used the rigid-muffin-tin approximation and gave quite small λ_s values ($\sim$0.1) [6]. Recent tight-binding (TB) studies of $YBa_2Cu_3O_7$, on the other hand, gave $\lambda_s \sim 2$ [7]. For this compound, frozen-phonon LDA calculations, which include the screening self-consistently, yield $\lambda_s \sim 1$ [8,9], but their accuracy is uncertain due to the crude sampling over merely a high-symmetry subset of phonons. Numerous attempts to deduce the strength of the EPI from the resistivity, optical conductivity, and other measurements lead to no firm conclusion either [10].

In the present Letter we report LDA *linear-response* calculations of the phonon spectrum and the EPI. In contrast to the frozen-phonon method, the linear-response approach allows the treatment of *arbitrary* phonon wave vectors $\mathbf{q}$. We used a newly developed linear-response full-potential linear-muffin-tin-orbital (LMTO) method [11] whose accuracy was proven on lattice-dynamical, superconducting, and transport properties of a large variety of metals [12]. It therefore seems that, with this method, we can obtain reliable estimates of λ_s and λ_d for high-T_c superconductors.

Since our new method does not yet allow us to treat large unit cells and, hence, a well-characterized stoichiometric, nearly optimally doped high-temperature superconductor such as $YBa_2Cu_3O_7$, we considered the compound $(Ca_{1-x}Sr_x)_{1-y}CuO_2$ (where $x \sim 0.7$ and $y \sim 0.1$) with $T_c = 110$ K [13] whose simple infinite-layer structure (space group P4/mmm) makes it unique for theoretical studies. It is generally agreed that high-temperature superconductivity does occur in this compound in CuO_2 planes. It is not clear, however, what the microscopic structure of the doping defect layers is, whether all or only the CuO_2 planes neighboring these layers superconduct, and what the doping level is of the superconducting planes [14]. Our calculations were performed for $CaCuO_2$ doped by holes in a uniform, neutralizing background charge. The doping was chosen to what we believe is nearly optimal, that is, such that the Fermi level is just above the uppermost van Hove singularity (the three-dimensional saddle point at R). This corresponds to doping level of 0.24 holes per unit cell. Since it turned out that, for the *calculated equilibrium* structure of $CaCuO_2$, our band structure and high-symmetry mode λ_s's are quite similar to those found in the previous LDA frozen-phonon calculations for $YBa_2Cu_3O_7$ [9,15], we believe that our results for $CaCuO_2$ are generic for high-temperature superconductors (HTSCs) near optimal doping.

First, we discuss our results for the electronic and crystalline structure. Published LDA band structures for the compounds with $y = 0$ and $x = 0$, 0.7, and 1.0 exhibit little x dependence [16,17]. Our band structure for $y = 0$ and $x = 0$ is in accord with these, and (keeping the planes flat) it hardly changes upon doping by 0.24 holes, except for a shift of E_F to slightly above the (uppermost) van Hove singularity. Like for all CuO_2 superconductors, the bands near E_F are the antibonding $pd\sigma$ band (O_x-$Cu_{x^2-y^2}$-O_y) and the lower-lying two antibonding $pd\pi$ bands (O_z-Cu_{xz}-O_z and O_z-Cu_{yz}-O_z). Also the interplane hopping integrals are similar to those in bilayer compounds such as $YBa_2Cu_3O_7$. However, since, in $CaCuO_2$, each CuO_2 plane has two rather than one neighbor CuO_2 plane, the $k_\perp$ dispersions in $CaCuO_2$ are *twice* the interplane splittings in $YBa_2Cu_3O_7$, and this, together with the fact that the σ and π bands disperse *oppositely* with $k_\perp$, leads to the *unusual feature* that,

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in $CaCuO_2$, the maxima at $(0, \pi/a, 0)$ and $(\pi/a, 0, 0)$ (X-point) of the π bands reach *above the* σ band. Hence, for $k_\perp = 0$, the saddle points are π-like, while, for $k_\perp = \pi/c$ (at R), they have the usual σ character [15]. (Away from these high-symmetry points, the σ and π bands hybridize via interplane hopping.) The two corresponding (three-dimensional) van Hove singularities are almost degenerate so that EPI results based on this band structure could hardly be said to be typical for high-temperature superconductors.

However, our calculation predicts that the optical $\mathbf{q} = 0$ out-of-phase oxygen dimpling mode is unstable. For the *un*doped compound (which in our LDA calculation is a metal rather than an antiferromagnetic insulator), *all* calculated $\mathbf{q} = 0$ phonons are stable, and their frequencies agree both with previous calculations [17] and with infrared reflectivity measurements [18]. But for doping by 0.24 holes, the Fermi level has moved down into states with considerable π character, and here we find the B_{2u} out-of-plane and out-of-phase oxygen mode to be unstable with $\omega = 3.6i$ THz. The corresponding frozen-phonon analysis exhibits *a double-well potential* with minimum at a dimpling angle of 5°–7°, depending on the c/a ratio used in the calculation. (5° is obtained using the experimental values $a = 7.297$ a.u. and $c/a = 0.829$, whereas 7° is found for the theoretically determined values: $a = 7.112$ a.u. and $c/a = 0.895$.) This instability comes about because moving the oxygens out of the copper planes decreases the $pd\pi$ hopping integral faster than the $pd\sigma$ integral, whereby the top of the antibonding π bands decreases below the saddle points at X of the antibonding σ band, thus allowing the energy to be lowered. For the stable structure, our bands are now very similar to those of other HTSCs with a Fermi surface (FS) whose σ character dominates everywhere. The FS shown in Fig. 1 is holelike, centered at $\mathbf{k}_\parallel = (\pi, \pi)/a$, and has rounded-square cross sections which are (11) oriented for $k_\perp$ near $\frac{\pi}{c}$ and (10) oriented elsewhere. The $k_\perp = \frac{2\pi}{3c}$ cross section resembles the odd FS sheet for an underdoped bilayer material, while the $k_\perp = \frac{\pi}{3c}$ cross section resembles the even sheet of such a material. Experimentally and theoretically, $YBa_2Cu_3O_7$ has a static 7° in-phase dimple which induces sufficient intraplane $\sigma\pi$ coupling so as to cause the saddle points of the LDA plane bands to bifurcate [15]. In our 0.24 hole doped $CaCuO_2$, the saddle point at $R(\frac{\pi}{a}, 0, \frac{\pi}{c})$, which is just below the Fermi level, is not yet bifurcated, while the one at $X(\frac{\pi}{a}, 0, 0)$, which is 0.4 eV below E_F, *is* bifurcated. This FS with squarish cross sections, which are (10) oriented for most $k_\perp$'s, exhibits strong nesting for $\mathbf{q} \propto (1, 0, 0)$ and some nesting for $\mathbf{q} \propto (1, 1, 0)$.

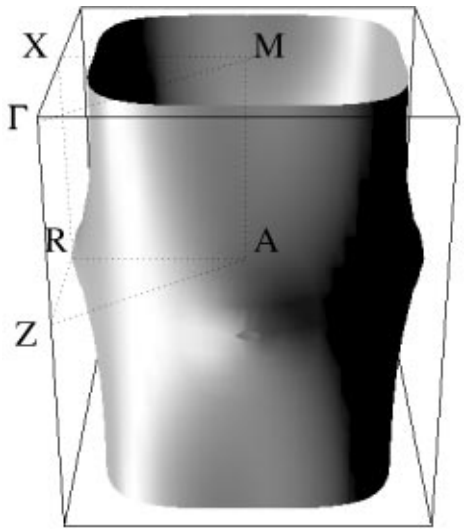

FIG. 1. Calculated Fermi surface of doped $CaCuO_2$.

Our calculated instability towards out-of-phase dimpling for $CaCuO_2$, together with the known static in-phase dimpling in $YBa_2Cu_3O_7$, suggests that out-of-plane instability is a common feature of HTSCs near optimal doping. Such instabilities may be local as it was recently found in $La_{1.85}Sr_{0.15}CuO_4$ by extended x-ray absorption fine structure (EXAFS) measurements [19].

The depth of the double-well potential varies between 50 and 300 K, depending on whether we use the experimental or theoretical lattice constants in the frozen-phonon calculations. The shallowness of the well calculated with the experimental parameters casts serious doubts on the validity of the harmonic approximation, and we therefore used the theoretical lattice constants when calculating the EPI.

We now discuss our calculated phonon spectrum for doped $CaCuO_2$. We used a single-κ LMTO basis set, 30 $\mathbf{k}$-points for the Brillouin zone (BZ) integrals with the tetrahedron method, and generated the dynamical matrix at 30 $\mathbf{q}$-points in the irreducible BZ with $q_\perp = 0$ and π/c. [The mesh corresponds to $(8, 8, 2)$ reciprocal-lattice divisions and is much denser than that employed in the previous frozen-phonon studies [8,9].] The convergence of the dynamical matrix with respect to the internal parameters was checked for the $\mathbf{q} = 0$ point, and the error of the setup is estimated to be about 10%. The calculated phonon spectrum is presented in Fig. 2. We see first that the structure is stable. Second, we notice that a low-frequency (1.8 THz) mode exists near the M-point $(\pi, \pi, 0)/a$. This mode is quadrupolar with the oxygen squares rotated around the copper atoms. It is interesting to note that, for the structure with flat planes, the quadrupolar mode is unstable (at M, $\omega = 3.7i$ THz) so that, *for structural stability of this compound, out-of-plane distortion is required.*

For calculating the EPI we use a standard expression

$$\lambda_L(\mathbf{q}) \propto \sum_{\mathbf{k}\nu} Y_L(\mathbf{k} + \mathbf{q}) |g^{\mathbf{k}}_{\mathbf{q}\nu}|^2 Y_L(\mathbf{k}) \delta(E_{\mathbf{k}+\mathbf{q}}) \delta(E_{\mathbf{k}}) \quad (1)$$

for the coupling in the L channel. Note that we investigate the $\mathbf{q}$ dependence, but have summed over all phonon

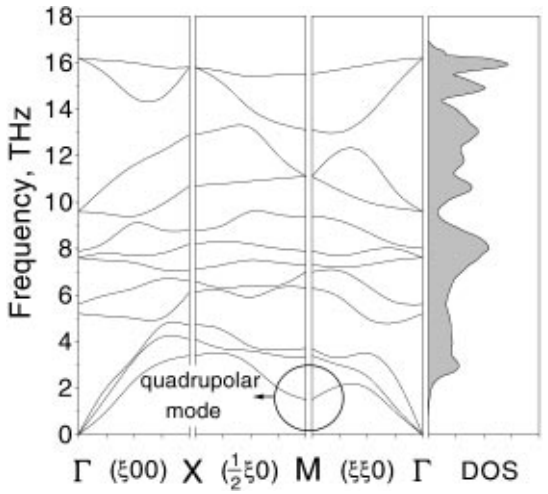

FIG. 2. Calculated phonon spectrum of doped $CaCuO_2$.

branches ν. $g^{\mathbf{k}}_{\mathbf{q}\nu}$ are the electron-phonon matrix elements found with our linear-response method [12]. Expression (1) must be normalized by $N_L(0) \propto \sum_{\mathbf{k}\nu} Y_L(\mathbf{k})^2 \delta(E_{\mathbf{k}})$. The coupling constant λ_L is the average of $\lambda_L(\mathbf{q})$ over the BZ. Two delta functions in (1) impose integration over the space curve resulting from the crossing of two Fermi surfaces separated by $\mathbf{q}$. For this integral we had to use as many as 1173 $\mathbf{k}$-points per irreducible BZ.

Figure 3 shows our result for $\lambda_s(\mathbf{q}_\parallel, q_\perp = 0)$. It is seen to be strongly enhanced along ΓX, where it almost reaches the value 3. This is caused by *nesting* corresponding to the *sliding* of a nearly flat, $(0, 1, 0)$-oriented FS sheet. Nesting will also occur for the wave vectors connecting opposite FS faces which in our case occurs for $\mathbf{q} \sim (\frac{\pi}{3a}, 0, 0)$ (see Fig. 1). This kind of nesting enhancement is well known in the theory of HTSC [20]. In all other points of the BZ, λ_s is seen to be small. It is almost zero around the X-point and, going towards M, it increases towards 0.3. This may be compared with the values $\lambda_s(X) = 0.7$ and

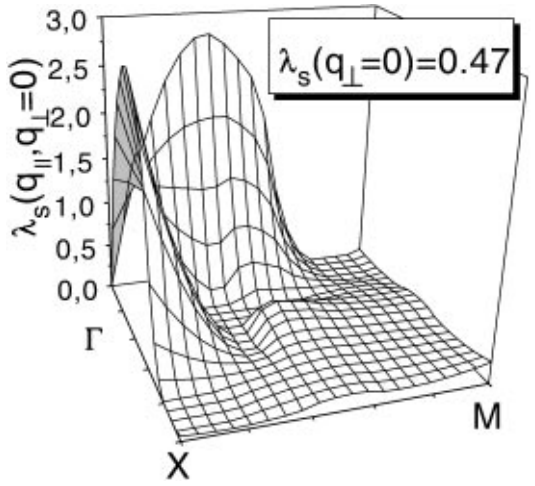

FIG. 3. Calculated $\mathbf{q}$ dependence of the electron-phonon coupling in the ΓXM plane for doped $CaCuO_2$.

$\lambda_s(S) = 0.6$ obtained for $YBa_2Cu_3O_7$ [9]. For $CaCuO_2$ we find similarly small values *throughout* the $\mathbf{q} = (\mathbf{q}_\parallel, \frac{\pi}{c})$ plane, for which there is no nesting. Averaging over $\mathbf{q}_\parallel$ now gives $\lambda_s(q_\perp = 0) = 0.47$ and $\lambda_s(q_\perp = \frac{\pi}{c}) = 0.21$. These values are upper and lower bounds for λ_s averaged over all $\mathbf{q}$. We conclude that the value $\lambda_s \sim 0.4$ *is too small to account for the high-temperature superconductivity in the* Ca-Sr-Cu-O *system.*

This conclusion is supported by the calculation of the electron-phonon contribution to such transport properties as electrical and thermal resistivities. The $\mathbf{q}$-dependent transport constant $\lambda_{\text{tr}}(\mathbf{q})$ is given by Eq. (1) if $Y_L(\mathbf{k} + \mathbf{q})Y_L(\mathbf{k})$ is replaced by the electronic velocity factor $(v_{\mathbf{k}} - v_{\mathbf{k}+\mathbf{q}})^2$. Our calculations exhibit no large values of $\lambda_{\text{tr}}(\mathbf{q})$, neither in the $q_\perp = 0$ nor in the $q_\perp = \frac{\pi}{c}$ planes. The enhancement due to nesting does not occur here due to the velocity factor. We find $\lambda_{\text{tr}}(\mathbf{q})$ to vary between 0 and 0.5 and obtain $\lambda_{\text{tr}}(q_\perp = 0) = 0.22$ and $\lambda_{\text{tr}}(q_\perp = \frac{\pi}{c}) = 0.14$, which are upper and lower bounds for λ_{tr}. Our calculated temperature dependence of the electrical resistivity displays a standard Bloch-Grüneisen behavior, and, above $T \sim 100$ K, it looks linear. Using the calculated value of the bare plasma frequency $\omega_p = 4.6$ eV in the ab plane, our estimated electrical resistivity is $\rho_{ab}(T = 300\ \text{K}) = 8\ \mu\Omega$ cm. This is evidently too low compared with the characteristic resistivity values in HTSCs which are always above 100 $\mu\Omega$ cm at room temperature. This 1-order-of-magnitude disagreement is also found when we compare calculated and experimental thermal resistivities, although it must be noted that, in addition, a large lattice contribution to the thermal current ought to be considered. One might argue that the plasma frequency used in these estimates is too large and should be substituted by a 2–3 times lower value. However, this would, first of all, be inconsistent because then the renormalization of the electronic velocities should also be included in the expression for $\lambda_{\text{tr}}(\mathbf{q})$, and, second, it will not help to get agreement for ρ_{ab}. We thus conclude that *the unusually large values of the electrical resistivities in HTSC are not due to electron phonon scattering* but are most likely due to spin fluctuations. Finally, we report on our calculation of the d-channel EPI. Currently, much interest is devoted to the possible $d_{x^2-y^2}$ symmetry of the gap in connection with the electronic mechanisms of superconductivity [2]. The EPI should also contribute to the d pairing. Using Eq. (1) for general L, we have analyzed all symmetry-allowed channels of superconductivity. We came to the conclusion that, *together with the s channel, relatively large values of* λ_L *are obtained for the symmetry* $d_{x^2-y^2}$; the calculated values of λ_L in the other channels are either negligibly small or negative. We have found that the $\mathbf{q}_\parallel$ dependence of $\lambda_{x^2-y^2}(\mathbf{q}_\parallel, 0)$ is very similar to that of $\lambda_s(\mathbf{q}_\parallel, 0)$ shown in Fig. 3, with the exception that λ_d becomes negative near -0.5 for $\mathbf{q}$ near the M-point. However, due to the large nesting enhancement, the average over $\mathbf{q}_\parallel$ becomes positive: $\lambda_{x^2-y^2}(q_\perp = 0) = 0.36$. This value is just slightly

smaller than that of $\lambda_s(q_\perp = 0)$. We furthermore find $\lambda_{x^2-y^2}(q_\perp = \frac{\pi}{c}) = 0.16$. Since we find that $\lambda_d \sim \lambda_s$, *the electron-phonon scattering is highly anisotropic* in this material and probably in all HTSCs near optimal doping. We can directly observe the anisotropy of the EPI matrix elements if we average $|g^{\mathbf{k}}_{\mathbf{q}\nu}|^2$ over all possible $\mathbf{k}$ and sum over ν. This is done by calculating the susceptibility function $\chi''_L(\mathbf{q}) \sim \sum_{\mathbf{k}} Y_L(\mathbf{k}+\mathbf{q}) Y_L(\mathbf{k}) \delta(E_{\mathbf{k}+\mathbf{q}}) \delta(E_{\mathbf{k}})$ and then the dispersion of the average matrix element from $|\bar{g}(\mathbf{q})|^2 = \{\lambda_L(\mathbf{q})/\chi''_L(\mathbf{q})\}_{L-av}$. As a result, we find that $|\bar{g}(\mathbf{q}_\parallel, 0)|^2$ behaves the same as $\lambda_s(\mathbf{q}_\parallel, 0)$ as shown in Fig. 3, i.e., $|\bar{g}(\mathbf{q})|^2$ is large ($\sim$0.05 Ry* cell) for the nesting wave vectors and is small ($\sim$0.01 Ry* cell) at all other $\mathbf{q}$ points. Such behavior is very unusual since the band structure factor $\delta(E_{\mathbf{k}+\mathbf{q}})\delta(E_{\mathbf{k}})$ enters both $\lambda_L(\mathbf{q})$ and $\chi''_L(\mathbf{q})$, and thus cancels. It must be directly related to the behavior of the self-consistent potential screening the nuclei displacements of given $\mathbf{q}$ or, equivalently, to the inverse dielectric matrix $\epsilon^{-1}_{\mathbf{q}}(\mathbf{r}, \mathbf{r}')$ of the crystal (these exact quantities are evaluated by our linear-response method). The $\mathbf{q}$ dependence of those are indirectly influenced by nesting. In addition, from the analytical results in Ref. [15] we have found that also $|g(\mathbf{q})|^2$ for the oxygen dimpling mode has a $\mathbf{q}$ dependence similar to the one shown in Fig. 3 [21]. Exactly this kind of electron-phonon interaction, i.e., attractive for $\mathbf{q}$ along (1,0) or $\mathbf{q}$ small, and negligible for $\mathbf{q}$ near (1,1), is what is required to support the $3d$-$3d$ electron-electron interaction, which is repulsive for large $\mathbf{q}$ along (1,1), in causing $d_{x^2-y^2}$-wave pairing.

In conclusion, we have found that the electron-phonon interaction alone cannot explain high values of T_c in the Ca-Sr-Cu-O system and, most likely, in all other cuprate superconductors. On the other hand, we found that $\lambda_d \sim \lambda_s \sim 0.3$, and this suggests that the electron-phonon scattering may support d-wave superconductivity based, for example, on the spin-fluctuation mechanism. Many questions remain unresolved, however. (i) If the Fermi surface is predicted correctly by LDA, can the LDA electronic velocities be used in the expressions for λ? (ii) Are these expressions for λ, based on Migdal's theorem, valid if the energy bands are narrowed due to Coulomb correlations? (iii) To what degree will the lattice instabilities influence the superconductivity through the anharmonic effects? Attempts to answer these and further questions clearly requires much further work.

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