

Electron-Phonon Interaction in the New Superconductors $\text{La}_{2-x}(\text{Ba,Sr})_x\text{CuO}_4$

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A realistic tight-binding theory, based on first-principles energy-band results of Mattheiss, is used to study the electron-phonon interaction in the new high- T_c superconductors $\text{La}_{2-x}(\text{Ba,Sr})_x\text{CuO}_4$. The calculated results include the phonon dispersion curves, phonon linewidths, the Eliashberg function $\alpha^2(\omega)F(\omega)$, and the interaction constant λ . A very strong coupling of specific O phonons to the conduction electrons is found ($\lambda \geq 2$), leading—because of the light oxygen mass—to T_c values of $\sim 30\text{--}40$ K.

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Superconducting transition temperatures T_c in the range of 30–40 K have been observed recently by Bednorz and Müller¹ and others^{2–5} for bulk $\text{La}_{2-x}(\text{Ba,Sr})_x\text{CuO}_4$, of the tetragonal K_2NiF_4 -type structure, with the divalent dopant Ba or Sr in the range $0.1 < x < 0.2$. Under pressure, even larger values of T_c have been reported.⁴

The results of first-principles energy-band calculations by Mattheiss⁶ for pure La_2CuO_4 suggest the occurrence of a strong Peierls-type Fermi-surface instability involving breathing-type displacements of the oxygen atoms O(2) in the basal plane of the K_2NiF_4 structure, where the arrangement of the Cu and O(2) atoms is the same as in a cubic perovskite basal plane. In this Letter I summarize the results of calculations of the electron-phonon (e-ph) interaction for these materials carried out in the framework of the nonorthogonal tight-binding (NTB) theory of lattice dynamics, and based on the energy-band results of Ref. 6.

The principal result is that for divalent-dopant concentrations beyond ≈ 0.1 the static Peierls distortions are suppressed. However, gigantic Kohn anomalies exist near the Brillouin-zone (BZ) boundary, involving the O(2)-bond-stretching vibrations of breathing type. These phonons usually have a very high frequency, but are now very strongly renormalized and exhibit an enormous coupling to the conduction electrons—one that is sufficient to explain the observed high T_c values.

In the NTB theory of lattice dynamics,^{7,8} the phonon dynamical matrix $D(q) = D_b + D_2$ is divided into D_b , a contribution representing the “bare” phonon frequencies, and into D_2 , the renormalization due to the conduction electrons. Using common notation we have

$$D_2(\kappa\alpha, \kappa'\beta | q) = - \sum_{\substack{k\mu\mu' \\ k'=k+q}} \frac{f_{k'\mu'} - f_{k\mu}}{\epsilon_{k\mu} - \epsilon_{k'\mu'}} g_{k\mu, k'\mu'}^{\kappa\alpha} g_{k'\mu', k\mu}^{\kappa'\beta} \quad (1)$$

The electron-ion form factors $g^{\kappa\alpha}$ (κ , particle; α , Cartesian index) contain first-order gradients of the NTB integrals with respect to atomic displacements. When one

takes the form factors so that $g^2=1$, the right-hand side of Eq. (1) is usually called the bare susceptibility χ_0 . The imaginary part $\Gamma(q)$ of the renormalization can be represented as a Fermi-surface integral involving the same form factors $g^{\kappa\alpha}$ and is the essential ingredient of the phonon linewidths γ_{qj} . The latter enter the expression of the Eliashberg function for the strong-coupling theory of superconductivity,⁹

$$\alpha^2 F(\omega) = [hN(E_F)]^{-1} \sum_{qj} \left(\frac{\gamma_{qj}}{\omega_{qj}} \right) \delta(\omega - \omega_{qj}), \quad (2)$$

where ω_{qj} are the phonon frequencies. The e-ph coupling parameter is $\lambda = 2 \int d\omega \alpha^2(\omega) F(\omega) / \omega$.

In the present e-ph calculations, I have used a NTB Hamiltonian with a 27-orbital basis (Cu, La d , O p) obtained by a least-squares fit to the first-principles energy bands of Ref. 6. The fit included all 17 occupied (Cu d , O p) valence bands as well as the lower portion of the unoccupied La d bands. As was indicated in Ref. 6, the only partially filled energy band at the Fermi energy E_F in La_2CuO_4 is one involving antibonding combinations of Cu $d(x^2 - y^2)$ orbitals with neighboring O(2) $2p$ orbitals that are directed along the (short) Cu—O(2) bond axes in the x - y plane. Its width is determined mainly by the energy-transfer integral ($pd\sigma$) of ~ -1.6 eV (with an overlap integral [$pd\sigma$] of 0.09 and orbital energies $E_d \sim E_p \sim 3$ eV below E_F). I note that the present Fermi surface agrees very well with that of Ref. 6, i.e., the small band dispersion along k_z is included, so that there is no singularity in the electronic density of states at E_F for $x=0.0$.

The dominant NTB gradient for the e-ph calculations is $\beta = (pd\sigma)^{-1} d(pd\sigma)/dr$. By fitting the results of a further band calculation¹⁰ involving slightly reduced (3%) lattice constants, I have determined $\beta \approx -1.6 \pm 0.1 \text{ \AA}^{-1}$. This value is very close to a corresponding one found earlier for refractory compounds.⁸

As limited phonon data are available presently for La_2CuO_4 , I have used a Born-von Kármán force-constant model derived from neutron-scattering data¹¹ for the perovskite-type material $\text{Ba}(\text{Pb-Bi})\text{O}_3$ for the

bare phonon part D_b . Some obvious changes for the values of the Cu-O(1) and the first-nearest-neighbor La-O(1) force constants have been estimated. Of great importance is the magnitude of the Cu-O(2) force constant f_2 , as discussed below.

The 21-dimensional matrices $D_2(q)$ and $\Gamma(q)$ have been calculated with use of a mesh of ~ 400 k points in the irreducible part of the BZ. I limit the summation in D_2 to the one conduction band and treat the effect of divalent-atom doping at the La sites as a rigid-band lowering of E_F . An evaluation of $D(q)$ then yields ω_{qj} and—with utilization of $\Gamma(q)$ — γ_{qj} . For the evaluation of the Eliashberg function $\alpha^2(\omega)F(\omega)$, a q mesh of 45 phonons in the irreducible BZ was used except in the vicinity of the X point, where a q mesh was chosen as fine as the (electron) k mesh. Finally, a standard program was used to calculate T_c from the Eliashberg equations in the “dirty limit” approximation, employing the “canonical” μ^* value of 0.13.

Figure 1(a) shows the q dependence of the bare susceptibility χ_0 along some BZ directions and as a function of dopant concentration x . For $x=0.0$ an enormous Kohn anomaly is found at the X point, indicating an almost one-dimensional behavior of χ_0 . This is caused by very flat pieces of the Fermi surface, which nearly has the shape of a quadratic prism.⁶ With doping, the Kohn anomaly rapidly gets weaker and shifts away from X . Along the line X - D - X parallel to the c direction, the dispersion is very small, indicating the planar nature of the e-ph coupling.

In the D_2 results of Fig. 1(b) the Kohn anomaly is further enhanced by the q dependence of the form factors $g^{k\alpha}$. Yet the $g^{k\alpha}$ single out the contributions from bond-stretching displacements of Cu and O(2) atoms in the basal plane. This is caused by the modulation of the ($pd\sigma$) integral that occurs only when the Cu—O(2) bond length is changed. The biggest components of D_2 are breathing-type displacements of the O(2) atoms. For simple structural reasons these components also have a maximum at X . Yet a quadrupolar deformation of the O(2) square shows very little coupling, as the contributions of neighbor bonds to the form factors $g^{k\alpha}$ add up destructively for the quadrupolar deformation, but constructively in the breathing case.

As a Fermi-surface quantity, the linewidth matrix $\Gamma(q)$ varies even more dramatically with the dopant x than either D_2 or χ_0 [see Fig. 1(c)], and has some q dependence along the line D for $x=0.0$. For $x > 0.2$ it vanishes around X .

The drastic increase of D_2 around X is reflected in the phonon dispersion curves plotted in Fig. 1(d). At the Γ point of the BZ, with strictly zero renormalization, the (infrared active) in-plane O(2) bond-stretching modes have very high frequencies. Near X , where the mode character has changed to breathing type, these modes have been depressed by almost one order of magnitude,

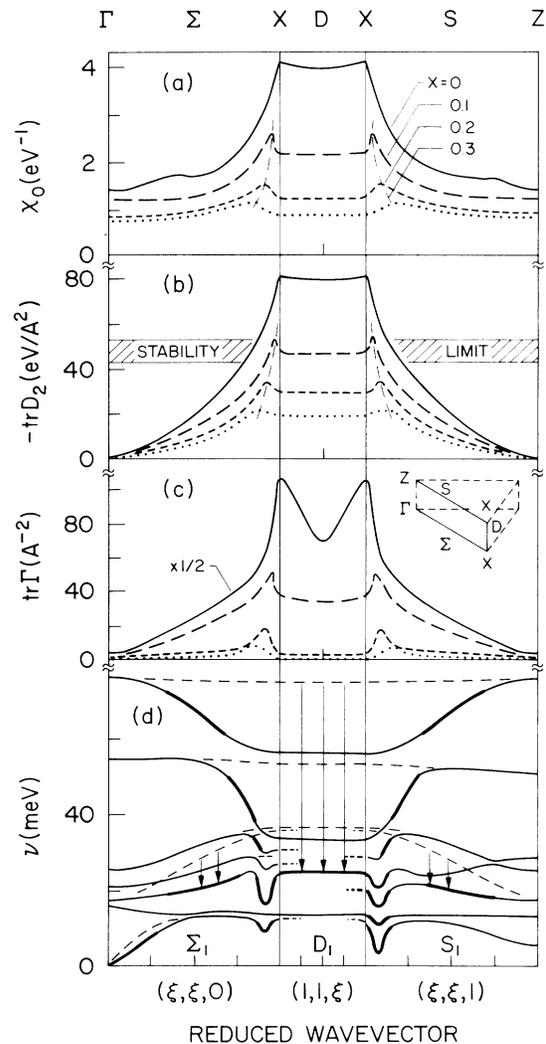


FIG. 1. Results of the electron-phonon calculations, as a function of wave vector q . (a) Bare susceptibility χ_0 for four different dopant concentrations x . (b) Corresponding curves for the phonon renormalization D_2 . Also indicated is the stability limit due to finite bare-phonon stiffness. (c) Linewidth Γ with its very rapid increase for small x (note the scale change). (d) Effect of the phonon renormalization on the dispersion curves (full lines, with D_2 ; dashed lines, without D_2). Results are for a calculation with $x=0.15$ and $f_2=7.8$ eV/Å². Only the fully symmetric Σ_1 and S_1 branches and some of the D_1 phonons are shown. The dispersion of the breathing-type branch is indicated by the strong solid lines.

thereby diving below all other phonon branches. Some other branches also show significant softening, including the longitudinal-acoustic branch away from the Γ point and a similar one away from Z . Yet none of the O(2) rotational modes nor any of the modes with a strong O(1) component, not to speak of the La modes, participate in the e-ph coupling. I thus arrive at the conclusion

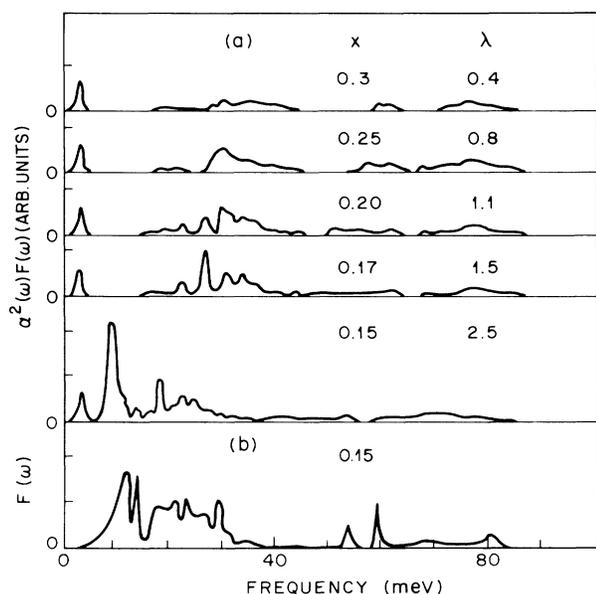


FIG. 2. Spectral functions. (a) $\alpha^2(\omega)F(\omega)$ curves for various values of x , all calculated with use of $f_2=9 \text{ eV/\AA}^2$. (b) Corresponding phonon density $F(\omega)$ for $x=0.15$.

that a relatively small number of phonon modes, specifically those in a very limited region near the X point of the BZ, show an extremely strong interaction with the conduction electrons.

Figure 2(a) shows typical spectral functions $\alpha^2(\omega) \times F(\omega)$ as a function of dopant concentration. As expected, $\alpha^2(\omega)F(\omega)$ increases in magnitude with decreasing x and also shifts more and more weight into the lower-frequency regions, as a result of the ever increasing Kohn anomaly. In all cases, the $\alpha^2(\omega)F(\omega)$ spectra exhibit little similarity to the phonon density of states $F(\omega)$ [Fig. 2(b)]. The latter is dominated first by oxygen rotational modes (up to ~ 15 meV) and then by a mixture of La, Cu, and O bond-bending modes. The peaks near 60 and 80 meV arise from the O(1) and the remaining high-frequency O(2) stretch modes, respectively.

The stability against the Peierls distortion depends on the strongest bond in this material, the planar Cu-O(2) bond-stretching force constant f_2 . For Ba(Pb-Bi)O₃ I have found $f_2 \approx 8.5 \text{ eV/\AA}^2$. Infrared data¹² for La₂CuO₄ give frequencies of the O stretch modes as 550 and 690 cm^{-1} , corresponding to f_2 values between ≈ 7.5 and $\approx 11 \text{ eV/\AA}^2$. Bond-length arguments suggest a rather large value of f_2 in La₂CuO₄. To determine the range of possible T_c values, I have carried out calculations for D_2 and Γ for selected x values between 0.3 and 0.1, and used values between 7.5 and 11 eV/\AA^2 for f_2 . For those cases where the lattice was stable, $\alpha^2(\omega)F(\omega)$ was calculated and then T_c .

The results of this procedure are shown in Fig. 3. A

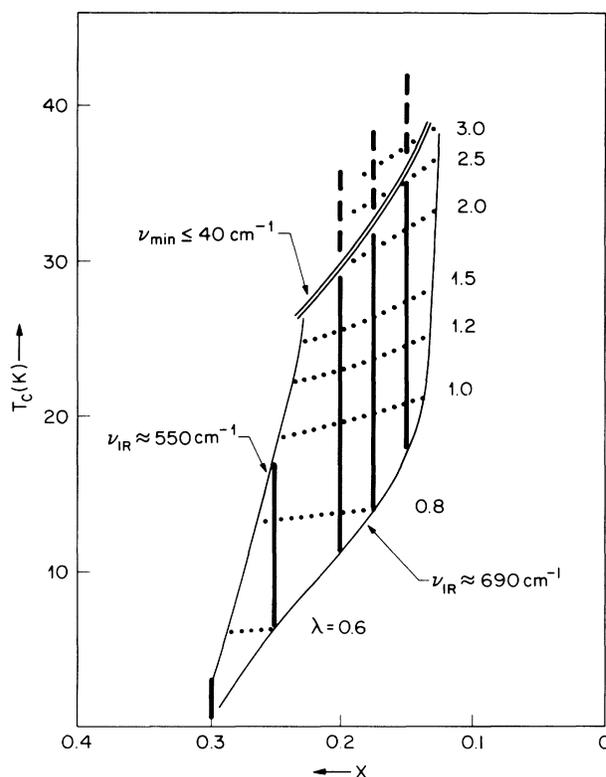


FIG. 3. Range of T_c values for various compositions x , and as a function of the Cu-O(2) force constant f_2 , with f_2 limits suggested by the infrared data of Ref. 12. The variation of λ is shown by the dotted lines. The double line marked ν_{\min} indicates an estimate of the minimum lattice stability.

rapid increase of T_c with decreasing x is evident, yielding possible T_c values of 30 K and above. For smaller f_2 values T_c rises more rapidly, but the lattice-instability limit is reached sooner (I defined this limit as a minimum frequency of ~ 5 meV, below which the linewidths γ usually exceeded the frequencies ω). When f_2 is stiffer, the advent of the Peierls instability can be delayed, allowing larger values of T_c . For $T_c \sim 30\text{--}35$ K, λ values are in the range of 2–2.5, similar to values found for $A15$ compounds. Thus, the high T_c is not caused by an unusually strong e-ph coupling but by the very light mass of the O, which allows the $\alpha^2(\omega)F(\omega)$ spectrum to extend to much higher frequencies than in a typical transition-metal compound. In fact, substituting the mass of Nb for that of O causes the T_c values to drop from 36 to 18 K in one test, and from 18 to 12 K in another.

In accordance with experimental observations, the present results suggest a strong positive T_c gradient with pressure, either external or "chemical" by use of smaller-size dopants.^{4,5} As f_2 is expected to vary with a high power of the bond length, pressure can push the

Peierls instability to smaller x values, thereby allowing larger T_c values. Very probably, the dopant concentration fluctuates in the samples, possibly as a result of onsets of spinodal decomposition waves, so that some parts of the samples always have smaller concentrations of x than the nominal one. Onsets of superconducting transition have been reported⁴ which exceed even 50 K. I speculate that under favorable conditions a very small fraction of the sample could maintain its metallic phase much closer towards $x \rightarrow 0.0$ than the bulk, and thereby take advantage of the even stronger and also more one-dimensional e-ph coupling.

In many of the superconducting samples, an orthorhombic distortion has been observed, even below T_c .¹³ This distortion corresponds to a warping of the basal-plane O(2) atoms^{12,14} and is caused by a specific rotation of the O octahedra. Its presence does not appear to reduce T_c , but to lower the amount of superconducting volume in the samples.¹³ As I find no coupling whatsoever to any rotational modes near E_F , I would exclude any direct effect of this rotational distortion on T_c . Hence I believe that it is not the Peierls distortion. Yet an indirect influence via the relaxation of the Cu—O(2) bond may exist, limiting the metallic regions via a weakening of f_2 .

The predicted very strong Peierls instability of breathing-type O distortions for pure La_2CuO_4 , similar to the one found in BaBiO_3 ,¹⁵ has, so far, not been verified experimentally. Because of the very small coupling along the c axis, there need not be any displacive coherence in neighbor planes, which would make the O distortions very difficult to detect by powder crystallography.¹⁴ It is conceivable that the Peierls distortion helps to induce the rotations in order to relieve strain from the compressed Cu—O(2) bonds, and thus the rotational distortion is present as long as the Peierls instability exists.

The present calculations ignore the very large anisotropy of the e-ph coupling, as the "dirty limit" approximation is used in the Eliashberg equations. In addition, the adiabatic approximation is losing its validity for the most strongly renormalized phonons. These effects appear to be larger than those found previously in refractory compounds or $A15$ materials,^{8,16} and should be further investigated, including the possibility of a real-space description of the pairing.¹⁷

In conclusion, the present study of the electron-phonon interaction in $\text{La}_{2-x}(\text{Sr,Ba})_x\text{CuO}_4$ strongly suggests

that the high T_c values are caused by conventional—yet very large—e-ph coupling in the vicinity of a Peierls instability. The coupling is mainly caused by O p orbitals of the conduction band involving specific O vibrations, and the light O mass is instrumental for reaching the high T_c values. Hence, this material may best be described as a chemical manifestation of metallic oxygen.

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