

Evidence of conventional superconductivity in La-Ba-Cu-O compounds

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First-principles methods are applied to investigate the electronic structure and electron-phonon coupling in the end-point members ($x=0$ and $x=1$) of the new high-transition-temperature (T_c) superconductor $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and their counterpart cubic perovskites $\text{La}_{1-x}\text{Ba}_x\text{CuO}_3$. Alloying with Ba ($x=1$) induces non-rigid-band changes in the Cu and O density of states, but the Cu charge state changes rather little. The calculated McMillan-Hopfield parameter η coupled with soft phonon modes provides a strong electron-phonon interaction $\lambda \sim 2.5$ that can account for the high T_c of ~ 30 – 40 K in these systems.

Within the last few months a new class of superconductors has been discovered. Bednorz and Müller¹ first reported the occurrence of an apparent superconducting transition at 30 K in the oxide material $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$, with $x=0.15$ and $y>0$ (probably small) which has the tetragonal layer-perovskite K_2NiF_4 structure. This result has since been reproduced and improved by alloying with Sr instead of Ba.²⁻⁶ In this paper we report results of first-principles band-structure calculations which assess the relative contributions of the oxygen, copper, and other metal atoms to the states which drive the superconductivity as well as identifying changes in ionicity and other effects of alloying. We also investigate the importance of the perovskite substructure in these materials, especially on the electron-phonon coupling strength. It is found that T_c in these layer perovskites can be explained by conventional phonon-mediated superconductivity in which soft phonon modes due to the vibrations of the light O atoms play the main role.

Our primary interest in these materials is in understanding what interaction between electrons is responsible for producing the superconducting state. Conventional superconductors utilize the electron-phonon interaction (EPI), which is normally enhanced by a large electronic density of states (DOS) at the Fermi level and by a strong electron-ion scattering.⁷ These new alloys, however, are oxides and not at all usual metals, with resistivities above T_c which are more than an order of magnitude larger than the resistivities of conventional superconductors, i.e., they might be semimetals. Since they are not good metals in the usual sense, the pairing interaction may be different from the conventional one. Suggestions include electrons coupled by two-dimensional plasmons, polarons, or bipolarons, although a novel kind of EPI is also a reasonable guess. In this paper we provide an accurate description of the electronic structure of pure La_2CuO_4 and LaBaCuO_4 (i.e., replacement of one of the La atoms in the unit cell by a Ba atom) in order to elucidate the effects of alloying.

We also investigate the role of the perovskite-type layers by performing parallel calculations for the perovskite compounds LaCuO_3 and BaCuO_3 . For purposes of comparison, the lattice parameter for the perovskites was chosen by taking a weighted average of the in-plane short Cu—O bond and the long Cu—O bond along the normal direction.

The calculations for La_2CuO_4 and LaBaCuO_4 were carried out with the self-consistent linearized-augmented-plane-wave (LAPW) method⁸ within the framework of the local-density-functional approximation using the Hedin-Lundqvist exchange-correlation potential. This method employs shape-unrestricted charge densities and potentials and basis sets of 500–600 LAPW's. Two "energy windows"⁸ were used so that the "semicore" O(2s) and La,Ba(5p) states could also be treated variationally. Similar calculations were performed using the APW method (in the muffin-tin approximation) for the perovskite LaCuO_3 and BaCuO_3 compounds with the same treatment of semicore levels and exchange correlation as in the LAPW calculations. Self-consistency in the LAPW calculations was achieved using a mesh of 16 special k points in the $\frac{1}{16}$ th irreducible Brillouin zone (IBZ), and three special k points for the semicore states. In the final iteration, energies and wave functions were calculated at 135 equally spaced k points in the IBZ for further analysis. A Fourier-series spline fit,⁹ which is constrained to pass smoothly through all 135 points, was then used to generate 542 points in the IBZ to calculate the density of states (DOS) using the linear analytic tetrahedron method. The APW DOS was calculated in a similar manner using another scheme¹⁰ to generate energy bands at 165 k points from 35 first-principles APW points in the $\frac{1}{48}$ zone. For the layer perovskites, the lattice parameters were taken to be $a=7.1622$ and $c=24.964$ a.u. The out-of-plane O distance was taken as $z=4.543$ a.u. and that of the La (Ba) atom was taken as $z=3.445$ a.u. The muffin-tin sphere radii are given in Table I. The cubic-perovskite

TABLE I. Sphere radii (a.u.) and valence-electron charge inside the various spheres. The $5p$ semicore electron charge is also given for the La and Ba spheres.

	R_S	La_2CuO_4 (q)	LaBaCuO_4 (a.u.)
La	2.90	1.263	1.240
La($5p$)	2.90	5.599	5.616
Ba	2.90	...	1.208
Ba($5p$)	2.90	...	5.058
Cu	1.95	9.180	9.058
O_{xy}	1.55	3.460	3.378
$\text{O}_{z,\text{La}}$	1.55	3.349	3.272
$\text{O}_{z,\text{Ba}}$	1.55	3.349	3.267

lattice parameter was set equal to $a = 7.8234$ a.u. and the sphere radii were 3.576 a.u. for La and 1.956 a.u. for Cu and O.

An overview of the electronic structure can be seen in the DOS. The DOS of the layer-perovskite compounds are shown in Fig. 1 and that of the cubic perovskites in Fig. 2. In both Figs. 1 and 2 the Fermi energy (E_F) moves to lower energy upon replacement of La by Ba, and as seen in Table II the DOS at E_F , $N(E_F)$, increases. Matheiss¹¹ and Yu and Freeman¹² have also obtained the La_2CuO_4 band structure with the LAPW method. The DOS in Fig. 1(a) is very similar to that given by Matheiss.¹¹ It is immediately apparent that while one might have expected simple rigid-band behavior in going to the 50% Ba compound, this is not at all the case *in general*. One prominent change is the shift in spectral weight on the Cu atom from higher to lower energy. This is also seen in the perovskite compounds in Fig. 2, and represents primarily a rearrangement of t_{2g} spectral weight. It is also interesting that the Cu t_{2g} contribution to the DOS at E_F is zero. In both structures Cu-O $dp\sigma$ -type bands cross E_F .

While the in-plane O_{xy} DOS in the layer compound is changed relatively little by the addition of Ba, there is a significant change in the O_z DOS. The 50% Ba compound

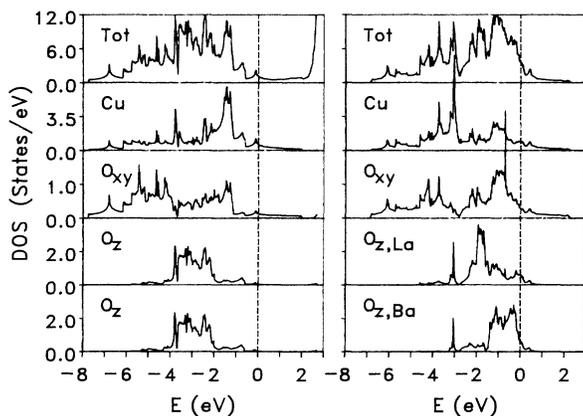


FIG. 1. Total and projected DOS per atom for La_2CuO_4 (left panel) and LaBaCuO_4 (right panel). The dashed line indicates E_F .

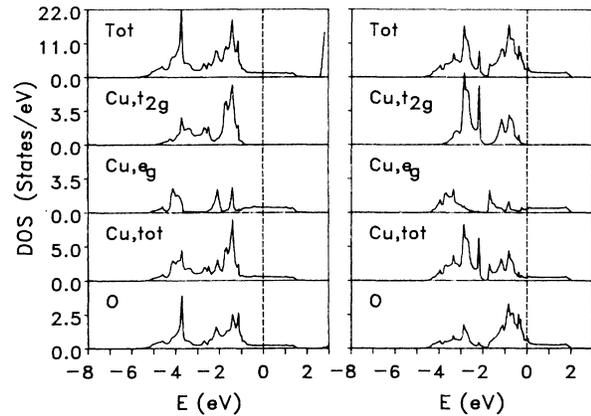


FIG. 2. Total and projected DOS (per atom) for LaCuO_3 (left panel) and BaCuO_3 (right panel).

has two inequivalent O_z atoms, one which is nearly coplanar with the La atoms while the other lies in a Ba layer. Although La (Ba) may not be fully trivalent (divalent), nevertheless the La sphere is essentially one unit more ionic than Ba. [Since the La and (especially) Ba $5p$ core states are quite extended, we have used rather large spheres and treated the $5p$ states variationally in a separate window. As a result of the large sphere radius, the valence charge (see Table I) in the sphere is 1.24 for La and 1.21 for Ba, approximately one electron of which can be attributed to overlapping oxygen states.] Due to the unit difference in ionic charge between Ba and La the $\text{O}_{z,\text{Ba}}$ atoms experience a less attractive electrostatic potential than do the $\text{O}_{z,\text{La}}$ atoms, which accounts for the $\text{O}_{z,\text{Ba}}$ DOS being nearer E_F than the $\text{O}_{z,\text{La}}$ DOS. For the $\text{O}_{z,\text{Ba}}$ atom, $N(E_F)$ is also about 10% larger than for the $\text{O}_{z,\text{La}}$ atom. In addition, there is more spectral weight above E_F on both O_z atoms compared to Fig. 1(a), i.e., adding Ba causes the originally $2-$ O_z ions to become partially metallic.

Rigid-band behavior does appear to hold near E_F , however, where only the broad $d_{x^2-y^2}-p_x(y)$ band contributes to $N(E)$. From Figs. 1(a) and 1(b) it is evident that there is similar structure in $N(E)$ in the region of $E_F(\text{La}_2\text{CuO}_4)$, with the prominent feature being the van Hove peak 0.1 eV below E_F in Fig. 1(a) which occurs at a concentration $x = x_{\text{cr}} \approx 0.14$ of Ba. This peak is of similar height in the two calculations, and x_{cr} , defined from the La_2CuO_4 DOS, lies within about 0.03 eV of the peak in LaBaCuO_4 . Thus using the rigid-band model for $x \lesssim 0.2$ should be realistic.

The van Hove peak, which defines x_{cr} , occurs very near the concentration of Ba (and Sr) where T_c is highest. The peak results from a saddle point in the $d_{x^2-y^2}-p_x(y)$ band slightly beyond the zone boundary along the x (and y) axis, which lies midway between the nearly touching corners of the La_2CuO_4 Fermi surface (see Fig. 3 of Matheiss¹¹). At $x = x_{\text{cr}}$ the Fermi surface transforms from distorted holelike cylinders along the z axis centered at the X ("corner") point to distorted electron cylinders centered at Γ . Many transport and thermodynamic prop-

TABLE II. Total DOS at E_F (states/eV) and the McMillan-Hopfield parameter η per atom ($\text{eV}/\text{\AA}^2$).

	La_2CuO_4	LaBaCuO_4	LaCuO_3	BaCuO_3
$N(E_F)$	1.24	3.69	1.42	2.70
η_{La}	0.00	0.08	0.00	...
η_{Ba}	...	0.16	...	0.012
η_{Cu}	0.62	1.08	0.89	1.65
$\eta_{\text{O}_{x,y}}$	0.72	0.32	0.48	0.60
$\eta_{\text{O}_{z,\text{La}}}$	0.04	0.15		
$\eta_{\text{O}_{z,\text{Ba}}}$	0.04	0.33		

erties can be extremely x dependent¹⁴ near $x \approx x_{\text{cr}}$.

Whether T_c in these compounds arises from EPI is a question of fundamental interest. To investigate this question, the Fermi-surface-averaged electron-ion matrix elements were evaluated using the rigid muffin-tin approximation (RMTA) of Gaspari and Gyorffy.¹⁴ Quantities entering the calculation of the McMillan-Hopfield constant η are presented in Table II. The main features of the calculations of η are the following. The La and Ba atoms always have very small η 's within RMTA. The Cu atoms have moderately sized values of η which are enhanced by the replacement of La by Ba. The O_z atoms have very small η 's in La_2CuO_4 but are moderate in size in LaBaCuO_4 . The O_{xy} η is larger than for O_z but is reduced in LaBaCuO_4 . The contributions to η come predominantly from the $\text{Cu}(d)\text{-O}(p)$ interaction. While replacement of La by Ba triples $N(E_F)$, the η 's do not increase proportionally. It is interesting to note the approximate transferability of the η values, that is, those in La_2CuO_4 are comparable to those of LaCuO_3 : $\eta_{\text{Cu}}=0.62$ (respectively, 0.89), $\eta_{\text{O}_{\text{total}}}=1.52$ (respectively, 1.44) $\text{eV}/\text{\AA}^2$. This suggests that the cubic-perovskite structure, if stable, might also provide high- T_c materials. Because the η 's are significantly smaller than those of typical high-temperature superconductors (e.g., A_{15} compounds, NbN) it appears likely that the layered perovskites possess soft phonon modes as found by Weber.¹⁵

The quantity which characterizes the contribution to the electron-phonon interaction strength λ from a given type of atom is⁷

$$\lambda_i = \eta_i / (M_i \Omega^2), \quad (1)$$

where Ω is an rms vibrational frequency. We propose an EPI mechanism for superconductivity with the transition temperature given by the Allen-Dynes equation¹⁶ $T_c = T_c^{\text{AD}}(\eta_i, \mu^*, \Omega)$, where $\mu^* = 0.1$ is the Coulomb pseudopotential.

In the absence of experimental information on the phonon spectrum, we use for the spectral function $\alpha^2 F$ a two-peak Einstein model with frequencies Ω_{Cu} and Ω_0 . Since the important vibrations are expected to involve Cu-O bond stretching¹⁵ and since each Cu-O force constant contributes equally to $M \Omega^2$ projected onto each of the atoms, we assume $M_{\text{Cu}} \Omega_{\text{Cu}}^2 = M_0 \Omega_0^2$ and study the effect on T_c of varying Ω_0 . Using the rigid-band model discussed above for $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ for $x = x_{\text{cr}} = 0.14$, we find $\eta_{\text{Cu}} = 0.74$ and $\eta_{\text{O}_{\text{total}}} = 2.2 \text{ eV}/\text{\AA}^2$. In Fig. 3 we show

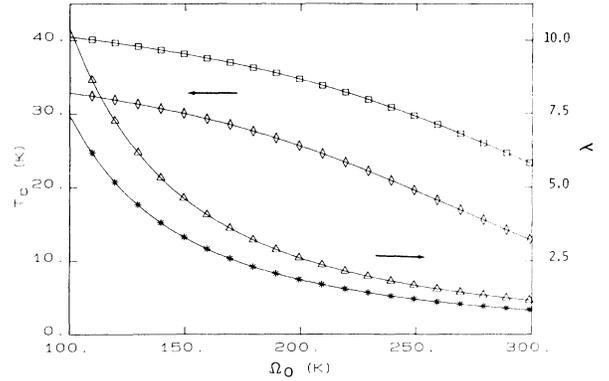


FIG. 3. Values of λ and T_c (from the Allen-Dynes equation) as a function of Ω_0 . The bottom curve in each case corresponds to La_2CuO_4 (stars and diamonds), while the top curves (triangles and squares) correspond to $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, $x = 0.14$, in the rigid-band picture.

T_c and λ as a function of Ω_0 for both $x = 0.0$ and $x = x_{\text{cr}}$. These results indicate that for mean oxygen frequencies of about 200 K, λ is about 2.6 and T_c exceeds 34 K in the case $x = x_{\text{cr}}$. Experimental values of T_c are sample dependent but lie in the range 30–40 K and peak near $x = x_{\text{cr}}$. (Note that for $\lambda > 2$ it is important to include the prefactors f_1, f_2 in the Allen-Dynes equation¹⁶ for T_c .) These conclusions are in agreement with those of Weber.¹⁵ Our results also indicate that, were it not for the electronically driven structural transition^{11,12} for $x = 0.0$, the pure compound would also be a superconductor with a somewhat lower T_c , within the same frequency range for Ω_0 . On the other hand, Weber expects additional softening as x is decreased from 0.15 which would raise T_c , contrary to experimental evidence. Both analyses give strong support to the assertion that soft phonon modes due to the vibrations of the light O atoms are the main cause of superconductivity in these compounds. This is reminiscent of the situation¹⁷ in PdH, where the hydrogen optic-phonon modes play a key role in the occurrence of superconductivity.

To summarize, we have shown that replacement of La by Ba in La-Cu-O compounds leads to large changes in the Cu and O spectral density without inducing large changes in their charge state. Although these compounds display an unusual mixture of ionic and metallic character not seen in other high- T_c superconductors, calculation of the EPI strength indicates that it may be of the magnitude necessary to account for the high- T_c values in these systems.

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