Giant Defect-Enhanced Electron-Phonon Interactions in Ternary Copper Oxide Superconductors

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A microscopic but schematic model is discussed for defects (such as oxygen vacancies $O^{\square}$) in compounds such as $YBa_2Cu_3O_{7+\delta}O^{\square}_{2-\delta}$ and $La_{3-x}Ba_{3+x}Cu_6O_{14+\delta}O^{\square}_{4-\delta}$ in relation to the superconductive properties of these materials. The discussion shows in detail how T_c can reach its maximum value at or near the metal-semiconductor transition T_{ms}. It introduces a new mechanism for enhancement of electron-phonon interactions that is separate from, and empirically superior to, Fermi-surface nesting.

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Microscopic theoretical discussions of superconductivity in ternary copper oxides have so far been of two types: conventional one-electron band calculations[1-3] or general mechanisms which are often claimed to differ significantly from the BCS theory[4] which has been so successful in explaining superconductivity in metallic alloys and compounds. Here I wish to continue my earlier discussion[5] of the behavior of defective crystalline materials vicinal to a mechanical instability which generates superstrong electron-phonon interactions.[4] In compounds with the highest transition temperatures ($T_c \gtrsim 50$ K), a large number of defects (mostly oxygen vacancies, $O^{\square}$) are always present, and variations in $[O^{\square}]$ can effect T_c drastically. I discuss a microscopic model which connects the mechanical effects of varying $[O^{\square}]$, or other alloy stoichiometries on the atomic structure, as well as on the electronic properties near the Fermi energy, both in the ranges $T < T_c$ and $T > T_c$. Because of the complexity of this problem my discussion is only schematic. It is, however, much more specific chemically than most other discussions, and the chief mechanism which emerges appears to be in good agreement with experiment. Specifically, my mechanism explains why $T_c(x,\delta)$ reaches its maximum value in $La_{3-x}Ba_{3+x}Cu_6O_{14+\delta}O^{\square}_{4-\delta}$ alloys for the values of x and δ such that the metal-semiconductor transition temperature $T_{ms}(x,\delta) = T_c$, as observed in a recent elegant experiment.[6] The detailed discussion here buttresses my earlier conclusions[5] supporting the validity of the BCS theory in general and the Bardeen-Fröhlich attractive electron-phonon interaction as the basic mechanism responsible for high-T_c superconductivity.

The schematic model in its simplest form begins with a simple-cubic lattice with s-state electrons only and nearest-neighbor overlap $(ss)_1$ only. The lattice is unstable against shear. More generally, it has coordination number (N_C) equal to 6, and with nearest-neighbor α forces only in three dimensions the number of cyclical $(\omega^2 = 0)$ vibration modes[7] is proportional to $6 - \langle N_C \rangle$. To stabilize the lattice against shear we add a very weak second-neighbor force γ [generated by second-neighbor electronic overlap $(ss)_2$] with $\gamma \lesssim 0.1\alpha$. [Typically $\gamma \gtrsim 0.2\alpha$, but I assume here that γ is small because $E_d(\mathrm{Cu}) = E_p(\mathrm{O})$, as suggested by band calculations.[1] Certainly such second-neighbor forces would be weakest with $E_d(\mathrm{Cu}) = E_p(\mathrm{O})$, and this condition in this model explains why Cu and O are special.]

Now we begin to reduce $\langle N_C \rangle$ by removing atoms. With $\gamma = 0$ cyclical modes appear in proportion to the vacancy concentration $[\square]$. With $(ss)_2$ and $\gamma > 0$, there are no true cyclical modes, but there is a large lattice relaxation and/or reconstruction associated with quasicyclical modes. We can imagine calculating this relaxation in two ways, quantum mechanically or classically. The simplest quantum method,[8] in the spirit of Hückel theory, utilizes a core repulsion (such as $e^{-\lambda r^2}/r^2$) together with attractive covalent interactions obtained by summing one-electron eigenvalues [with $(ss)_1$ and $(ss)_2$ proportional to e^{-ar_1} and e^{-ar_2}] over a partially filled band. This approach can be made entirely classical by calculating elastic constants from the quantum model for $[\square] = 0$, and then fitting these with classical spring constants α and γ and classical interatomic potentials, such as Morse potentials. By a judicious choice of parameters,[9] the relaxed configurations for $[\square] > 0$ obtained by the classical method may closely resemble those obtained quantum mechanically, at least when $6 - \langle N_C \rangle$ is small.

We now have arrived at the central point. Although the two methods *seem* similar, I expect a crucial difference to occur when $0 < (6 - \langle N_C \rangle)/6 \lesssim \gamma/\alpha$. The classical method derives the spring constants α and γ by averaging over all the occupied electronic states in the *unrelaxed* configuration. The Hückel method sums over these explicitly for *each* atomic configuration. As is well known,[10] the frontier electrons (the π electrons for aromatic hydrocarbons) determine chemical reactions and polarizational configurational relaxation. What this means here is that the quasicyclic modes associated with inadequately constrained[5,7] nearest-neighbor rearrangements will couple very strongly to electrons of energy E in the frontier range $E_F - \Sigma < E < E_F + \Sigma$, where $\Sigma = |\delta r\, d(ss)_2/dr|$ and δr is a typical relaxation distance. This is because polarizing these frontier electrons costs less energy than the average energy used to define

γ. For equal polarization energies, δr derived quantum mechanically will exceed δr derived classically. On phase-space grounds this means that the former relaxation modes will configurationally dominate the latter. Quantum-mechanical relaxation via frontier electron polarization will remove states with E near E_F and place them near $E_F \pm \Sigma$. Put more physically, in the frontier energy range a pseudogap or reduction in the density of states $N(E)$ will be generated by defect relaxation for E near E_F, and peaks in $N(E)$ will appear near $E = E_F \pm \Sigma$. This process is shown in Fig. 1. This pseudogap can be regarded as the result of forming defect-defect bonding and antibonding states. The elastic strain energy associated with the formation of these bonds is only of order γ, not α, because the lattice is underconstrained. Hence we expect the maximum electron-phonon coupling strength λ for the frontier electrons near the Fermi energy to be of order $\alpha\lambda_0/\gamma$, where $\lambda_0 \simeq 1$ is the electron-phonon coupling for the remaining valence electrons, and is similar to that found in simple metals such as Al. Note that this superstrong coupling need not generate further lattice instabilities and reconstruction, because the frontier electrons are only a fraction Σ/W of all the valence electrons, where W is the valence-band width. Thus another upper limit for λ is $W\lambda_0/\Sigma$; both limits correspond to $\lambda \simeq 10$–20.

Several comments can be made here. I expect that 2Σ should be comparable to kT_a, where T_a is the oxidation annealing temperature (typically between 750 and 1250 K),[6] since oxygen diffuses by utilizing the "soft" pathways with deformation energies of order 2Σ. Next I have drawn $N(E)$ in Fig. 1 in the frontier interval $E_F - \Sigma < E < E_F + \Sigma$ much as one would expect to find it in glassy amorphous semiconductors, i.e., with Urbach (exponential) tails,[11] because I believe similar kinds of relaxation occur because both kinds of materials are vicinal to constraint thresholds.[7] Also there is some similarity of the present model to the Tauc-Nagel model of metallic glasses.[12] However, I believe the dip in $N(E)$ discussed here depends crucially on $0 < (6 - \langle CN \rangle) \ll 6$, a condition which is not satisfied in metallic glasses, which are formed kinetically near a deep eutectic by rapid quenching. Thus the dip is much more likely to occur for the present materials, which are nearly in equilibrium.

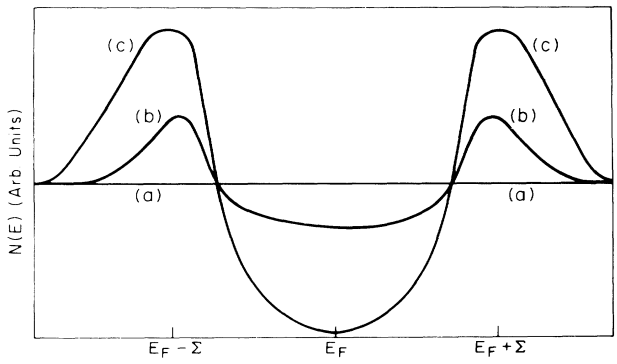

FIG. 1. Effect of dates on $N(E)$ for E near E_F: (curve a) defect density $\rho = 0$, $T_{sm} = 0$; (curve b) defect density at average value such that $T_{sm} = T_c$, and (curve c) large defect density, $T_{sm} \gg T_c$.

The striking part of Fig. 1 is that 2Σ is close to (or nearly resonant with) an optical phonon energy $\hbar\omega_0$ of order[3] 600–700 cm^{-1}, which is of order 1000 K. Thus the optical-phonon transition rate, which is roughly proportional to $N(E_F - \Sigma)N(E_F + \Sigma)$, is maximized by defect relaxation and the formation of defect-defect bonds, providing γ/α is small enough to make 2Σ nearly equal to $\hbar\omega_0$.

In Fig. 1 the effective density of states is shown for fixed microscopic parameter ratios $(ss)_2/(ss)_1 \sim \gamma/\alpha \simeq 0.1$ as a function of the defect density ρ or of $u = (6 - \langle N_C \rangle)/6$. As u increases, coupling of quasicyclic relaxation modes to frontier electrons gradually opens a gap at $E = E_F$. One might think that the effects on T_c of the gain in the optical-phonon transition rate due to exciting defect-defect bonding $\rightarrow$ antibonding transitions would be offset by the reduction in electronic states at $E = E_F$. However, electrical conduction in an inhomogeneous medium is a percolative process. When the alloy parameters are such that the relaxed $N(E_F)$ is on the average reduced compared with the unrelaxed $N(E_F)$, as in Fig. 1, curve b, we will be near a metal-semiconductor transition in the normal state for $T > T_c$. The percolative metallic paths, as in Fig. 1, curve a, with low defect densities, however, will be embedded in a semiconductive medium, as in Fig. 1, curve c, with very strong electron-phonon interactions due to defect-defect bonding-antibonding optical-phonon transitions. (These far-infrared optic-mode transitions should not be confused with actual excitonic transitions in the near infrared.) This will resonantly enhance superconductivity in the conductive paths via the proximity effect.[13]

We now turn to the data shown in Fig. 3 of Ref. 6 which shows $\rho(T)$ for tetragonal (or slightly orthorhombic) $La_{3-x}Ba_{3+x}Cu_6O_{14+\delta}O^{\square}_{4-\delta}$ with $x = 0.75$. The sample was annealed at 450 °C for 24 h in various oxygen pressures. A metal-semiconductor transition at $T = T_{ms}$ is observed as a minimum in $\rho(T)$ and an onset T_c is also measured. The values of (T_{ms}, T_c) for various degrees of annealing to decrease $[O^{\square}]$ are (in kelvins): (120,45); (90,55), (85,85), and (<85,80). The highest T_c is observed for $T_{ms} = T_c$, consistent with the discussion of Fig. 1. Also consistent with the present discussion is the reduction in T_c which occurs in $YBa_2Cu_3O_{7-x}$ when the chains are interrupted by the rapid quenching[14,15] and/or increases in x.

The defect density $\rho = [O^{\square}]/([O] + [O^{\square}])$ may have a more decisive influence on T_c than other variables. In Fig. 2 I have plotted both dT_c/dP and T_c as a function of ρ for $La_{1.85}Sr_{0.15}CuO_4$ ($\rho = 0$); $La_{2.25}Ba_{3.75}Cu_6O_{16}O^{\square}_2$;

and $YBa_2Cu_3O_7O_2^{\square}$, assuming $\delta=2$. The point of the plot is the correlation between dT_c/dP and $dT_c/d\rho$, which suggests that $YBa_2Cu_3O_7O_2^{\square}$ is a local stationary point, at least for unstressed stable bulk phases. Similar behavior of T_c as a function of P or ρ has been predicted by Thorpe[16] and is important to my discussion of the isotope effect.[5] Note that this discussion not only explained the absence of the isotope shift, $\alpha=0$, in $YBa_2Cu_3O_7O_2^{\square}$, but it also *predicted* $\alpha\simeq 0.2$ in $La_{1.85}Sr_{0.15}CuO_4$, in good agreement with preliminary results of several workers.[17] The basis for these predictions was a correlation between dT_c/dP and dT_c/dm_0. Such correlations are not expected from interactions other than the electron-phonon interaction, and if these correlations persist for other alloys (such as $La_{2-x}Sr_xCuO_4$ with $x>0.15$) they may provide further evidence for the present model.[18]

When we compare the present global defect mechanism for giant electron-phonon interactions ($T_c\gtrsim 75$ K) with the Fermi-surface nesting mechanism[3] for strong electron-phonon interactions ($T_c\simeq 35$ K), we notice interesting similarities and differences. The two mechanisms are similar because both involve soft phonons, but they differ because the soft phonons are generated in different ways. Nesting is a geometrical condition in **k** space, but the global defect mechanism is made possible by a mechanical instability in configuration space. Defects make k fuzzy and are inimical to nesting, so the formation of vacancies suppresses T_c in $(La,Sr)_2CuO_4$ alloys. Vacancies are intrinsic to the global mechanism when the defect-free crystal is overconstrained, $\langle C_N\rangle>6$, and large concentrations of vacancies must be added to make $\langle C_N\rangle<6$ and thereby produce a high T_c. The present model empirically indicates that T_c will not exceed 50 K in perovskitelike crystals without large vacancy concentrations. It also shows how in metals even when nesting fails[19] to explain the high T_c in $YBa_2Cu_3O_7O_2^{\square}$, defect relaxation can succeed, because the atomic and molecular configurations of defects may have many special properties[20] which are definitely *not* "random." Here the defects have giant polarizabilities primarily because of proximity of the mechanical network to a stiffness threshold.[5,7]

I have benefited from discussions with M. F. Thorpe.

Note added.—More recent data obtained by tunneling on epitaxial films and nuclear quadrupole resonance relaxation independently give $E_g/kT_c=8.0(5)$ in $YBa_2Cu_3O_7$, which corresponds (J. C. Phillips, to be published) to $\lambda=8$. Thus the need for a superstrong interaction is evident. Strong circumstantial evidence for nonadiabatic selective coupling of Cooper pairs to displacive soft modes in $YBa_2Cu_3O_7$ is contained in temperature-dependent Debye-Waller factors[21] B which are much the largest for O(4) atoms, and for which B reaches a minimum near $T=T_c$. A similarly large and site-specific B is not seen for $La_{1.85}Sr_{0.15}CuO_4$, and no *detectable* anomaly is resolved[22] near T_c.

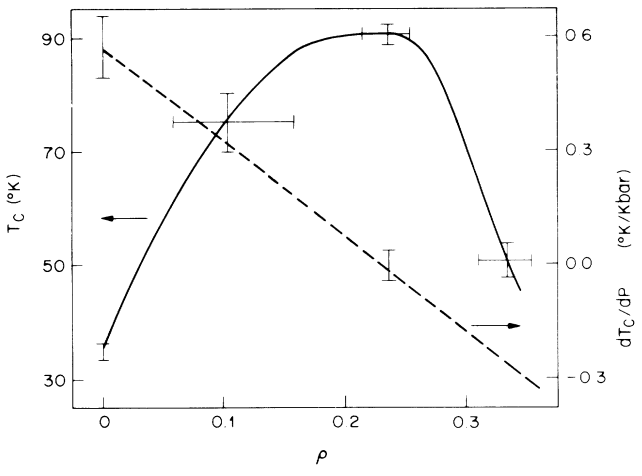

FIG. 2. T_c and dT_c/dP against ρ for three compounds: $La_{1.85}Sr_{0.15}CuO_4$ or $\rho=0$; $YBa_2Cu_3O_{6.9}$ or $\rho=0.22$, and $La_{2.25}Ba_{3.75}Cu_6O_{14+\delta}$, where the value of ρ shown is intended only to illustrate the general trend (a maximum in T_c at $\rho=0.22$). I have inferred that $\rho(La_{2.25}Ba_{3.75}Cu_6O_{14+\delta})<\rho(YBa_2CuO_{6.9})$ for two reasons: The improvement of T_c in the former with annealing at increased O_2 partial pressure, and the orthorhombic distortion of the latter by Cu(1) chains (Ref. 2). The datum point for T_c for $\rho=0.33$ corresponds to quenched $YBa_2Cu_3O_6$.

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which are higher. The low background stiffness level also is necessary for facile sample (de-)oxidation and annealing at temperatures as low as 450 °C, so that the observation of these processes itself is direct evidence for the present model. Note that facile oxygen diffusion requires small activation energies, and that these are the expected result in the presence of cyclic coordinates, which do not depend on the harmonic approximation and which exist quite generally regardless of the local bonding geometry. Also in metals exchange and correlation volume forces shift soft modes to short wavelengths. In the phonon density of states $N(\omega)$ for 100 $cm^{-1} \lesssim \omega \lesssim 200$ cm^{-1} (the quasicyclic or transverse acoustic range) progressive increases in strength for the sequence $BaPbO_3$, $Ba(Pb,Bi)O_3$, La_2CuO_4, $(La,Sr)_2CuO_4$, and $YBa_2Cu_3O_7$ with decreasing N_C and increasing T_c have been observed by inelastic neutron scattering [A Masaki *et al.*, Jpn. J. Appl. Phys. Pt. 2 **26**, L405 (1987); J. J. Rhyne *et al.*, Phys. Rev. B **36**, 2294 (1987)]. An intense soft mode at 150 cm^{-1} in $YBa_2Cu_3O_7$ is greatly reduced in $YBa_2Cu_3O_6$ ($T_c = 0$).

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