Bond Asymmetry and High-T_c Superconductivity

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We propose a simple mechanism, anchored in weak-coupling BCS theory, which ties together the following facts: high T_c; quasi two dimensionality; orthorhombic distortion and/or disordered lines of oxygen; proximity to a metal-insulator transition; and anomalously small isotope effects.

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Any list of unusual features of high-T_c superconductors would have to include the following: (i) quasi two-dimensional electronic connectivity[1,2]; (ii) the importance of orthorhombic lattice distortion, coupled, in YBaCuO, with ordered lines of oxygen (*the symmetric phases of YBaCuO, LaSrCuO, and LaBaCuO show no evidence of superconductivity*[3]); (iii) proximity to a metal-insulator transition; (iv) anomalously small isotope effects[4]; and (v) the high T_c itself. Here we show that these features can all be understood in a conventional weak-coupling BCS framework—provided that an important, physically motivated *bond-asymmetry term* is included in the Hamiltonian, and that the chemical potential μ is properly tuned. Our mechanism is independent of the specific source of two-body attraction, and is compatible with a variety of tight-binding models, including the one suggested by band-structure calculations.[1,2]

The picture we start from is that of a 2D lattice (e.g., the top or bottom planes of the "triplet" of copper-oxygen planes in YBaCuO), with Cu on the vertices and O on both the horizontal (x) and vertical (y) links. The mechanism is illustrated most clearly in the "toy" model in which the charged carriers (holes in YBaCuO and LaSrCuO) are exclusively in the oxygen bands of the CuO_2 planes, i.e., on the links.[5] (An alternative tight-binding model[1,2] including the Cu atoms is discussed below.) Allowing only nearest-neighbor ($x \leftrightarrow y$) hopping, we have

$$H_{\rm hop}^{xy} = -\sum_{\mathbf{k}} \sum_{\sigma=\uparrow,\downarrow} t_{\mathbf{k}} [c_{x\sigma}^{\dagger}(\mathbf{k}) c_{y\sigma}(\mathbf{k}) + \text{H.c.}], \quad (1)$$

where $t_{\mathbf{k}} = 4t \cos\frac{1}{2}k_x \cos\frac{1}{2}k_y$, and $c_{x\sigma}^{\dagger}(\mathbf{k})$ $[c_{y\sigma}^{\dagger}(\mathbf{k})]$ creates an electron on an x (y) link of spin σ and momentum $\mathbf{k}$.

The second key ingredient is the "bond-asymmetry term,"

$$H_{\rm asym} = -\epsilon \textstyle\sum_{\mathbf{k},\sigma} [c_{x\sigma}^{\dagger}(\mathbf{k}) c_{x\sigma}(\mathbf{k}) - c_{y\sigma}^{\dagger}(\mathbf{k}) c_{y\sigma}(\mathbf{k})], \quad (2)$$

which favors occupation of x links, and in so doing opens a gap of width 2ϵ in the oxygen band. Such a term is naturally generated by the orthorhombic distortion present in high-T_c compounds, since the various potentials are no longer precisely equal on x and y bonds. An even larger source for $H_{\rm asym}$ in YBaCuO is the *electrostatic asymmetry,* present in the orthorhombic phase only, due to charged ordered lines of O's in the middle plane of the triplets, directly above or below just the y links in the CuO_2 planes.

The essence of our results lies in the following simple observation. Consider the familiar BCS formula

$$T_c \sim \omega_c \exp\{-1/\rho_0 g\}, \quad (3)$$

where g is the strength of an attractive two-body potential, ρ_0 is the average density of states (DOS) at the Fermi energy μ, and ω_c is some cutoff frequency. Typical low-T_c superconductors have $\rho_0 g \approx \frac{1}{3}$. In the presence of the asymmetry term (2), the electronic energies are $\pm(t_{\mathbf{k}}^2 + \epsilon^2)^{1/2}$. For $|\mu| > \epsilon$, one calculates

$$\rho_0 \sim |\mu/t| (\mu^2 - \epsilon^2)^{1/2} \ln[t^2 (\mu^2 - \epsilon^2)^{-1}], \quad (4)$$

and hence

$$T_c(\mu) \sim \omega_c \exp\left\{ -\frac{t(\mu^2 - \epsilon^2)^{1/2}}{g|\mu| \ln[t^2/(\mu^2 - \epsilon^2)]} f(\mu, \epsilon) \right\}, \quad (5)$$

where the function f depends on details of the potential. Clearly, if $|\mu|$ and ϵ are tuned experimentally to be close to one another, e.g., by a variation of the chemical composition or the percentage of oxygen defects, T_c can be hugely enhanced.[6]

The logarithmic singularity in Eq. (4) is well known. Note that it survives in the symmetry-restoring limit $\epsilon \to 0$. The square-root singularity—which does not—is the new feature.

In principle, a square-root singularity in the DOS is

not peculiar to two dimensions, but can occur in d dimensions as well, most easily if the Fermi surface at a band edge is a d-dimensional cube. [Equation (4) is an example of this: The Fermi surface at $\mu=\pm\epsilon$ is the square defined by k_x or $k_y=\pm\pi$.] To understand the crucial role of quasi two dimensionality, consider the inevitable perturbations by next-nearest-neighbor (nnn) hopping terms, which restore curvature to surfaces of constant energy. Conventional, *round* Fermi surfaces near a band edge at ϵ are characterized by $\rho_{\text{round}} \sim (|\mu|-\epsilon)^{d/2-1}$, which is constant in 2D but gives a square-root *suppression* at the band edge in 3D. One therefore expects nnn terms, which typically interpolate between the singular ρ_0 and ρ_{round}, to have a *much less deleterious effect* on T_c in 2D than in 3D. (In fact, in 2D it is even possible for T_c to be *enhanced* by a judicious admixture of nnn hopping.[7]) This might account for the comparatively low T_c's of the oxide superconductors Ba(Pb,Bi)O, which have a 3D structure.

The bond-asymmetry mechanism works in an altogether different way in the 2D tight-binding model that Mattheiss posits as an excellent approximation to his fully 3D band-structure calculations.[1,8] In this model, the hopping is strictly from Cu to nearest-neighbor coplanar O and *vice versa*:

$$H_{\text{hop}}^{\text{CuO}} = -2t\sum_{\mathbf{k},\sigma}\sum_{a=x,y}[\cos(\tfrac{1}{2}k_a)c_{a\sigma}^{\dagger}(\mathbf{k})d_{\sigma}(\mathbf{k})+\text{H.c.}]+\sum_{\mathbf{k},\sigma}E_d d_{\sigma}^{\dagger}(\mathbf{k})d_{\sigma}(\mathbf{k}), \tag{6}$$

where d destroys an electron on the Cu d shell, and E_d is the energy of the Cu level measured from that of the O. One finds two hybridized Cu-O bands with energies

$$\tfrac{1}{2}E_d \pm \tfrac{1}{2}(E_d^2+16t^2\cos^2\tfrac{1}{2}k_x+16t^2\cos^2\tfrac{1}{2}k_y)^{1/2},$$

plus an infinitely narrow band at zero energy corresponding to localized states on the oxygen atoms. To leading order in ϵ/t, inclusion of the asymmetry term (2) gives the latter band a width 2ϵ, and a dispersion $E_{\mathbf{k}}=\epsilon(1-r^2)/(1+r^2)$, with $r=\cos(\frac{1}{2}k_y)/\cos(\frac{1}{2}k_x)$. This yields

$$\rho_0 \sim \epsilon(\epsilon^2-\mu^2)^{-1}\ln\{|\mu|^{-1}[\epsilon+(\epsilon^2-\mu^2)^{1/2}]\}, \tag{7}$$

which has a square-root divergence as before when $\mu \to \pm\epsilon$.

There are two interesting regimes in which the BCS weak-coupling formula for T_c, with ρ_0 square-root enhanced as in (4) or (7), breaks down. For μ relatively close to ϵ, the nature of the asymptotic expansion of the BCS gap equation for large βt changes completely. Instead, because of the rapidly varying DOS, one finds power-law behavior, with limiting cases

$$T_c \sim \begin{cases}(g/t)(\epsilon\omega_c)^{1/2}, & \omega_c/2T_c \ll 1,\\ \epsilon(g/t)^2[\text{const}+(g/t)(\epsilon/\omega_c)^{1/2}]^{-2}, & \omega_c/2T_c \gg 1.\end{cases} \tag{8}$$

Numerically, as we shall see in Fig. 1, the changeover from the exponential regime (5) to the power-law regime (8) actually cuts off the steep rise in T_c as $|\mu| \to \epsilon$, preventing it from reaching its "natural" scale of ω_c. Another consequence of power-law behavior is a *much smaller isotope effect*; for example, in the model worked out below, $T_c^{\max}$ effectively scales like $(\omega_c)^{0.26}$. Experimentalists should take note that, for fixed g, increasing ϵ increases T_c, so long as $|\mu|$ tracks ϵ (see Fig. 1).

The second regime occurs when μ passes through ϵ into the gap. Here one finds that the BCS gap equation can no longer be satisfied, and T_c falls abruptly to zero. As μ enters this regime, our model superconductor makes a sudden transition to a semiconductor—a surprising feature heretofore observed only in the laboratory.

Many experimentalists have remarked on the inhomogeneous nature of high-T_c superconductivity. From our theoretical perspective, it is conceivable that in equilibrium, inhomogeneous phases develop so as to accommodate a given supply of carriers.[9] Thus a fraction p of the material may have $\epsilon \lesssim |\mu|$ for optimal superconductivity, while the remaining $1-p$ has $\epsilon > |\mu|$, and hence

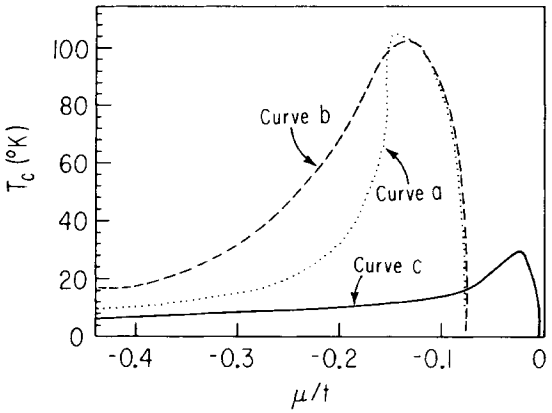

FIG. 1. T_c vs μ. Curve a corresponds to the phonon-exchange model, with $\epsilon=0.1t$, $\omega_c=0.05t$, and $V_0=3.6t$. Curves b and c give the analogous result for the static model, with $U_1=8t$, $U_2=2t$, and, respectively, $\epsilon=0.1t$ or $\epsilon=0.01t$. We take $t=5000$ K throughout, for a bandwidth $8t=40000$ K. In both models, the coupling constants are sufficiently weak that the corresponding curves for $\epsilon=0$ would be *hardly visible on this scale.*

semiconducting properties, in such a way that μ is constant throughout the sample. In contrast to the usual granular superconductors, the values of ϵ and p and the geometry and size of individual domains are not given *a priori,* but are to be adjusted for optimal free energy.

We next examine the bond-asymmetry mechanism in two specific models, both based (for simplicity) on $H_{\rm hop}^{xy}$, but with quite different potentials: the first a variant of the usual phonon-mediated weak-coupling BCS theory, and the second relying on attractive static forces of arbitrary origin. We find surprisingly similar, but not identical, results in both models.

Phonon exchange model.—Consider the Hamiltonian

$$H_{\rm PEM}=H_{\rm phonon}+H_{\rm hop}^{xy}+H_{\rm asym}-\mu\hat{N}, \tag{9}$$

where $\hat{N}$ is total electron number. As the charged carriers in this idealized model are assumed to live exclusively on the O's,[5] their hopping should be primarily correlated with the vibrations of the nearby Cu atoms, just as Weber argued for the reverse case.[10] We can model the vibrations of the Cu sublattice by taking[11]

$$H_{\rm phonon}=\sum_{n,m}\left\{\frac{\mathbf{p}_{nm}^2}{2M_{\rm Cu}}+\frac{K}{2}\left[(x_{n,m+1}-x_{nm})^2+\left(x_{n+1,m}-x_{nm}+d\sum_\sigma c_{x\sigma}^\dagger(n+\tfrac{1}{2},m)c_{x\sigma}(n+\tfrac{1}{2},m)\right)^2\right.\right.$$
$$\left.\left.+(y_{n+1,m}-y_{nm})^2+\left(y_{n,m+1}-y_{nm}+d\sum_\sigma c_{y\sigma}^\dagger(n,m+\tfrac{1}{2})c_{y\sigma}(n,m+\tfrac{1}{2})\right)^2\right]\right\}. \tag{10}$$

The electron-phonon coupling in (10) is designed to reduce the equilibrium distance between adjacent Cu's by an amount d in the presence of an electron on the intervening O atom.

If one rotates to a basis defined by operators

$$c_{\pm,\sigma}(\mathbf{k})=\pm\rho_\pm c_{x,\sigma}(\mathbf{k})+\rho_\mp c_{y,\sigma}(\mathbf{k}), \tag{11}$$

with $\rho_\pm(\mathbf{k})=[(E_\mathbf{k}\pm\epsilon)/2E_\mathbf{k}]^{1/2}$ and $E_\mathbf{k}=(t_\mathbf{k}^2+\epsilon^2)^{1/2}$, the last three terms in (9) diagonalize as

$$\textstyle\sum_{\mathbf{k}\sigma}[(-E_\mathbf{k}-\mu)c_{+\sigma}^\dagger(\mathbf{k})c_{+\sigma}(\mathbf{k})+(E_\mathbf{k}-\mu)c_{-\sigma}^\dagger(\mathbf{k})c_{-\sigma}(\mathbf{k})]. \tag{12}$$

Clearly, for $\mu<0$, it is then legitimate to ignore the "−" states entirely for temperatures $T\ll 2\epsilon$, and we shall do so. In second order in d, the cross terms in Eq. (10) allow an electron in the "+" band, of energy $-E_\mathbf{k}$ slightly below μ, to emit and absorb a phonon and scatter to an energy $-E_{\mathbf{k}'}>\mu$. Following BCS theory, we model the effect of the resulting energy denominator D by restricting $E_\mathbf{k}$ and $E_{\mathbf{k}'}$ individually to be within some cutoff frequency ω_c of $|\mu|$; in this region D is simply replaced by a negative constant. The net result is an effective interaction term in this region of the form

$$N^{-1}\sum_{\mathbf{k}\mathbf{k}'}V_{\mathbf{k}\mathbf{k}'}c_{+\uparrow}^\dagger(\mathbf{k}')c_{+\downarrow}^\dagger(-\mathbf{k}')c_{+\downarrow}(-\mathbf{k})c_{+\uparrow}(\mathbf{k}), \tag{13}$$

where

$$V_{\mathbf{k}\mathbf{k}'}=-V_0\sum_{\alpha=x,y}[\sin\tfrac{1}{2}(k_\alpha-k_\alpha')\rho_\pm(\mathbf{k})\rho_\pm(\mathbf{k}')]^2, \tag{14}$$

adopting the convention that ρ_+ is associated with $\alpha=x$ and ρ_- with $\alpha=y$. We have discarded all terms that vanish in the BCS ground state, and have grouped together all the constants into V_0.

The BCS gap equation follows in the usual way:

$$\Delta(\mathbf{k})=-\tfrac{1}{2}N^{-1}\sum_{\mathbf{k}'}V_{\mathbf{k}\mathbf{k}'}\Delta(\mathbf{k}')\mathcal{E}_{\mathbf{k}'}^{-1}\tanh(\tfrac{1}{2}\beta\mathcal{E}_{\mathbf{k}'}), \tag{15}$$

where $\mathcal{E}_\mathbf{k}=[(E_\mathbf{k}+\mu)^2+\epsilon^2]^{1/2}$. $V_{\mathbf{k}\mathbf{k}'}$ is separable, since

$$\sin^2\tfrac{1}{2}(k_\alpha-k_\alpha')=\tfrac{1}{2}(1-\cos k_\alpha\cos k_\alpha'-\sin k_\alpha\sin k_\alpha').$$

Every solution $\Delta(\mathbf{k})$ must therefore be of the form

$$\sum_{\alpha=x,y}\rho_\pm(\mathbf{k})^2(\delta_{\alpha1}+\delta_{\alpha2}\cos k_\alpha+\delta_{\alpha3}\sin k_\alpha), \tag{16}$$

where the δ's depend only on β. Thus $\Delta(\mathbf{k})$ indeed varies with $\mathbf{k}$, and contains a mixture of partial waves.

Equation (15) simplifies at T_c, where the even and odd pieces of $\Delta(\mathbf{k})$ decouple. In fact, since $V_0>0$, the odd sector has no nontrivial solution: $\delta_{x3}(\beta)=\delta_{y3}(\beta)\equiv 0$. The remaining four δ's satisfy four linear homogeneous equations, and T_c can be extracted by our requiring the determinant to vanish. Our numerical results are as follows. Figure 1 plots T_c vs μ for parameters chosen to give $T_c^{\max}\gtrsim 100$ K. The various regimes discussed earlier are apparent: As μ increases, the rise in T_c is of the general shape predicted by Eq. (5), until $\mu\approx-1.4\epsilon$, at which point power-law behavior sets in and the curve levels off. There follows a rapid drop into the semiconductor phase at $\mu\approx-0.75\epsilon$, where (15) no longer has a (nontrivial) solution. Significantly, at the point of maximum T_c, μ is far enough from the band edge at $-\epsilon$ that (i) there is a sufficient number of carriers to accommodate a high supercurrent density, and (ii) ρ_0 is not overly large. In the high-T_c region, $\delta_{x2}/\delta_{x1}\approx 0.4$, while δ_{y1}/δ_{x1} and $\delta_{y2}/\delta_{x1}<0.1$. Thus the Cooper pairs are primarily s waves with a d-wave admixture; the fact that $\delta_{y2}<\delta_{x2}$ implies anisotropy within the basal plane.

In Eq. (10), ω_c explicitly depends only on Cu mass, not on O mass. For the parameters chosen in Fig. 1, in the region of $T_c^{\max}$, we have calculated $T_c\propto(\omega_c)^{0.26}$;

hence we expect a very small Cu isotope effect, as compared with $T_c \propto \omega_c$ for μ far from ϵ. Note, though, that the value of the exponent is highly parameter dependent.

Static model.—We now turn to a general class of models characterized by a static potential connecting only x (y) carriers to x (y) carriers:

$$H = H_{\text{static}} + H_{\text{hop}}^{xy} + H_{\text{asym}} - \mu \hat{N}, \tag{17}$$

where

$$H_{\text{static}} = N^{-1} \sum_{\mathbf{k},\mathbf{k}'} \sum_{\alpha=x,y} V_{\mathbf{k}\mathbf{k}'}^{\alpha} c_{\alpha\uparrow}^{\dagger}(\mathbf{k}') c_{\alpha\downarrow}^{\dagger}(-\mathbf{k}') c_{\alpha\downarrow}(-\mathbf{k}) c_{\alpha\uparrow}(\mathbf{k}). \tag{18}$$

Introducing gap functions Δ_x and Δ_y, we find

$$H = \sum_{\mathbf{k}} \left[\sum_{\alpha=x,y} \Delta_{\alpha}(\mathbf{k}) \langle c_{\alpha\uparrow}^{\dagger}(\mathbf{k}) c_{\alpha\downarrow}^{\dagger}(-\mathbf{k}) \rangle - 2\mu \right] + \sum_{\mathbf{k}} \Psi \begin{pmatrix} -\mu-\epsilon & 0 & -t_{\mathbf{k}} & -\Delta_x(\mathbf{k}) \\ 0 & \mu-\epsilon & -\Delta_y^*(\mathbf{k}) & t_{\mathbf{k}} \\ -t_{\mathbf{k}} & -\Delta_y(\mathbf{k}) & -\mu+\epsilon & 0 \\ -\Delta_x^*(\mathbf{k}) & t_{\mathbf{k}} & 0 & \mu+\epsilon \end{pmatrix} \Psi^{\dagger}, \tag{19}$$

with

$$\Psi = (c_{x\uparrow}^{\dagger}(\mathbf{k}), c_{y\downarrow}(-\mathbf{k}), c_{y\uparrow}^{\dagger}(\mathbf{k}), c_{x\downarrow}(-\mathbf{k})).$$

Using Feynman's theorem, we obtain the coupled gap equations

$$\Delta_{\alpha}(\mathbf{k}) = -N^{-1} \sum_{\mathbf{k}'} \sum_{\tau=\pm 1} V_{\mathbf{k}\mathbf{k}'}^{\alpha} (\partial \mathcal{E}_{\mathbf{k}}^{\tau} / \partial \Delta_{\alpha}^*) \tanh(\tfrac{1}{2} \beta \mathcal{E}_{\mathbf{k}'}^{\tau}), \tag{20}$$

$\alpha = x,y$, where $\{\mathcal{E}_{\mathbf{k}}^{\pm}, -\mathcal{E}_{\mathbf{k}}^{\pm}\}$ are the eigenvalues of the matrix in (19).

For concreteness, we have examined

$$V_{\mathbf{k}\mathbf{k}'}^{\alpha} = U_1 - U_2 \cos(k_{\alpha} - k_{\alpha}'), \quad U_i > 0, \tag{21}$$

with U_1 representing Coulomb repulsion. $\Delta_{\alpha}(\mathbf{k})$ is then of the form $\delta_{\alpha 1} + \delta_{\alpha 2} \cos k_{\alpha} + \delta_{\alpha 3} \sin k_{\alpha}$. In this model, there *is* an odd solution, since $U_2 > 0$. However, for all ranges of parameters that we have considered, the even solution has the higher T_c, and hence lower free energy, at least for T's near T_c. We therefore set $\delta_{x3} = \delta_{y3} \equiv 0$, although we should mention the intriguing possibility of a new phase transition at a lower temperature in which these components, associated with p-wave spin-1 Cooper pairs, "turn on," perhaps discontinuously.

Figure 1 depicts T_c vs μ for the even solution, again with a choice of parameters that gives $T_c^{\max} \gtrsim 100$ K. The surprising feature of the curve is that, despite the radically different potential, it is quite similar to its counterpart in the phonon-exchange model. Now, however, the Cooper pairs are primarily d wave rather than s wave: $\delta_{x1}/\delta_{x2} \approx 0.5$, $\delta_{y1}/\delta_{x2} \approx -0.15$, and $\delta_{y2}/\delta_{x2} \approx -0.1$ near $T_c^{\max}$.

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Note added.—A recent experiment by Horn *et al.*[12] finds an anomalous jump in orthorhombic distortion as T is lowered through T_c. This provides direct evidence of an asymmetry-driven electron-lattice coupling mechanism, such as forms the basis of the present theory.

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