Charge-transfer mechanisms for high-T_c superconductivity

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We report results from a Bardeen-Cooper-Schrieffer analysis of the Weber *d-d* exciton model of the high-temperature superconductors. The pairing between oxygen holes is mediated by localized intrasite charge-transfer excitations between the $d_{x^2-y^2}$ and the $d_{3z^2-r^2}$ Cu orbitals. For reasonable oxygen on-site Coulomb energies, we find *s*-wave superconductivity for low filling fraction (<0.44), and *d*-wave superconductivity for larger filling. The same symmetry analysis applies to a localized version of the intersite Cu-O charge-transfer model of Varma, Schmitt-Rink, and Abrahams. We explore the limitations imposed by the Weber model symmetry, and interpret optical data based upon the *d-d* exciton picture. We briefly discuss the suppression of antiferromagnetism of the Cu moments by the Ruderman-Kittel-Kasuya-Yoshida interaction in the metallic limit.

Recently, Weber proposed an intrasite (Cu *d-d* exciton) charge-transfer mechanism[1] for the high-temperature superconductors. In this paper we will explore some of the properties of this mechanism, and the related intersite (Cu-O *p-d*) charge-transfer resonance mechanism proposed by Varma, Schmitt-Rink, and Abrahams.[2]

The basis for Weber's mechanism is the three-band extended Hubbard model for the superconducting CuO_2 planes[2,3] (see Fig. 1). The Cu site Coulomb energies are assumed to be much larger than the charge-transfer energy for putting holes on the O sites. Thus, as hole doping increases, the first hole per site goes onto the Cu, and the excess is assumed to go onto the O σ orbitals.[4] Cu-O hybridization is strongly inhibited by the large local Coulomb interactions on the Cu sites, the charge-transfer gap for putting holes on the oxygen atoms, and the extended Cu-O Coulomb interaction. Hence, conduction is mediated by direct hole hybridization between the planar oxygen atoms.

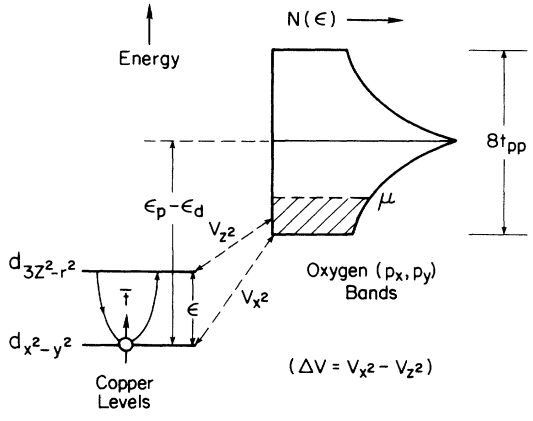

FIG. 1. Model energy-level diagram. The O bands form through direct hybridization of holes between the σ-bonded p_x and p_y orbitals, with density-of-state profile $N(E)$. The peak in $N(E)$ separates the empty upper band from the partially filled lower hole band. The copper *d* bands are treated as localized; the lowest copper levels have hybridization $\bar{t}$, and crystal-field splitting ε. Oxygen holes interact with the Cu levels through Cu-O Coulomb interactions, V_{z^2} and V_{x^2}, causing a charge transfer between the two Cu levels.

Weber proposes that the Cu sites act as excitonic centers, with a charge transfer from the $d_{x^2-y^2}$ orbital in the Cu-O plane, to the $d_{3z^2-r^2}$ orbital pointing out of the plane. As the conduction holes jump from O to O, they cause the holes on the adjacent Cu sites to move from the in-plane orbital to the out-of-plane orbital, leaving a region of negative charge. A second hole is then drawn toward this region of negative charge, yielding an attractive interaction between the pair. In contrast to conventional phonon-mediated pairing, this interaction operates on a much higher energy scale.

We have explored this model within the weak-coupling Bardeen-Cooper-Schrieffer (BCS) formalism, and we find that it can give rise to superconducting transitions even if the Coulomb interaction on the O sites is as large as the attractive interaction mediated by the charge transfer. We find *s*-wave superconductivity for low filling ($<44\%$) of the lower O band (see Fig. 1), and *d*-wave superconductivity for higher fillings.

For the Weber mechanism, the same arguments used for conventional excitonic mechanisms[5,6] yield an attractive interaction between the O holes of the form

$$\sum_{\mathbf{R}} V_{\rm eff}(\tau-\tau')\bar{n}_{\mathbf{R}}(\tau)\bar{n}_{\mathbf{R}}(\tau') . \tag{1}$$

Here $\bar{n}_{\mathbf{R}}$ is the *sum* of the hole occupancies on the four oxygen atoms surrounding a Cu site at $\mathbf{R}$. $V_{\rm eff}$ is given by

$$V_{\rm eff}(i\omega_n) = \frac{(2\Delta V\bar{t})^2}{\Omega((i\omega_n)^2-4\Omega^2)} , \tag{2}$$

where ΔV is the difference between the extended Hubbard interactions of an O hole with the two Cu orbitals. The net excitonic splitting is $\Omega=(\varepsilon^2+\bar{t}^2)^{1/2}$, where ε and $\bar{t}$, respectively, are the crystal-field splitting and hybridization between the two Cu orbitals.

Direct hybridization between the Cu $d_{x^2-y^2}$ and the $d_{3z^2-r^2}$ orbitals is forbidden by symmetry; however, there

is an indirect one since both of these orbitals hybridize with the neighboring in-plane O orbitals. Hence $\bar{t}$ is given by $\bar{t}=\sqrt{3}[(t_{pd}^a)^2-(t_{pd}^b)^2]/(\varepsilon_d-\varepsilon_p)$, where ε_d and ε_p are the Cu and O site energies, respectively; and t_{pd}^a and t_{pd}^b are the hybridizations between the $d_{x^2-y^2}$ orbital and the O p_x and p_y orbitals in the a and b directions, respectively. If the crystal has tetragonal symmetry, then $\bar{t}=0$; however, at least in the $Y_1Ba_2Cu_3O_{7-y}$ material, $t_{pd}^a \neq t_{pd}^b$ due to the orthorhombic distortion and $\bar{t}$ can be substantial. In a muffin-tin-orbital approximation t_{pd} varies with the Cu-O distance r like $1/r^4$.[7] For an orthorhombic distortion of 1.5%,[8]

$$t \approx 0.12\sqrt{3}(t_{pd}^a)^2/(\varepsilon_d-\varepsilon_p) .$$

Different estimates of t_{pd}^a and $\varepsilon_p-\varepsilon_d$ have been published,[1,9,10] which yield values of $\bar{t}$ ranging from 0.15 to 0.30 eV.

Our preliminary calculations indicate that in the parameter regime that we are discussing Cu-O intersite charge-transfer resonance excitations[2] will also give rise to an attractive interaction with a component of the same form as in Eq. (2), but with different retardation effects. The idea here is that an O hole can push a Cu hole away from the $d_{x^2-y^2}$ orbital, into the O band, and a second O hole will be attracted to the negative charge left behind. This mechanism does not suffer from the limitations imposed by symmetry that the d-d charge-transfer mechanism does; therefore, it may mediate a larger attractive interaction.

Hence we explore the consequences of an interaction of the form of Eq. (1) with a BCS approximation,[11] replacing the interaction with a constant in an energy shell of width $2\omega_c \approx 2\ \Omega$ around the Fermi surface. If we choose our energy scale such that $\varepsilon_p=0$, then the O hole-band energies are $\pm|t_{\mathbf{k}}|$, where

$$t_{\mathbf{k}}=-4t_{pp}\sin(k_x/2)\sin(k_y/2) ,$$

and the density of states is relatively flat except for a logarithmic Van Hove singularity at the boundary between the upper and lower band. Since the filling of the O band is small, the oxygen-hole Fermi surface falls within the lower band (see Fig. 1).

The exciton will scatter the O-hole quasiparticles within a shell of width $\sim 2\omega_c$ around this Fermi surface. Since this scattering shell is far from the upper band, and the temperature is much less than $|\mu|$, we may ignore the upper band completely.

In terms of the lower-band O-hole operators the attractive interaction can be expressed in the separable form

$$V_{\mathbf{k},\mathbf{k}'}=\begin{cases} -\sum_i \phi_i(\mathbf{k})\phi_i(\mathbf{k}') & \text{if } E_{\mathbf{k}-\mu}, E_{\mathbf{k}'-\mu} < \omega_c, \\ 0 & \text{otherwise.} \end{cases} \tag{3}$$

The functions $\phi_i(\mathbf{k})$ are the gap harmonics. There is no strong experimental evidence to suggest triplet pairing in either class of high-temperature superconducting material. Thus in this paper we restrict our discussion to spin-singlet pairing. The corresponding gap harmonics are

$$\phi_1(\mathbf{k})=\sqrt{-V_{\text{eff}}-U_p^*} , \tag{4}$$

$$\phi_2(\mathbf{k})=\sqrt{-2V_{\text{eff}}-V_p^*}\sin(k_x/2)\sin(k_y/2)\text{sgn}(k_xk_y) , \tag{5}$$

$$\phi_3(\mathbf{k})=\sqrt{-V_{\text{eff}}/4}[\cos(k_x)+\cos(k_y)] , \tag{6}$$

$$\phi_4(\mathbf{k})=\sqrt{-2V_{\text{eff}}-V_p^*}\cos(k_x/2)\cos(k_y/2)\text{sgn}(k_xk_y) , \tag{7}$$

$$\phi_5(\mathbf{k})=\sqrt{-V_{\text{eff}}/4}[\cos(k_x)-\cos(k_y)] . \tag{8}$$

Here V_{eff} is the zero-frequency limit of the excitonic interaction, and we have included the effect of oxygen Coulomb interactions via U_p^* and V_p^*, the local and extended Coulomb pseudopotentials,[12] respectively.

The first three gap harmonics have s-wave symmetry. ϕ_1 corresponds to on-site pairing, ϕ_2 to pairing between adjacent oxygens, and ϕ_3 to pairing between oxygen atoms separated by an intermediate Cu. The last two gap harmonics have d-wave symmetry. ϕ_4 corresponds to d-wave pairing between adjacent oxygen atoms, and ϕ_5 to that between oxygen atoms separated by an intermediate Cu.

We may determine the symmetry of the gap by solving the BCS gap equation in the standard way.[13] As the gap harmonics are linearly independent, they form a basis in which the gap function $\Delta(\mathbf{k})$ may be expanded as $\Delta(\mathbf{k})=\sum_i b_i\phi_i(\mathbf{k})$. Then the gap equation at the transition temperature reduces to the linear system $b_i=B_{ij}b_j$, where

$$B_{ij}=\frac{1}{2N}\sum_{\mathbf{k}'}\phi_i(\mathbf{k}')\phi_j(\mathbf{k}')\frac{\tanh[\frac{1}{2}\beta(|t_{\mathbf{k}'}|+\mu)]}{(|t_{\mathbf{k}'}|+\mu)} . \tag{9}$$

As the temperature is lowered, the first nontrivial solution to the linear system occurs at T_c, which is signaled by the growth of the largest eigenvalue of B_{ij} to unity. The elements of the corresponding eigenvector determine the composition of the gap function.

Using units of energy such that $t_{pp}=1$, we choose $V_{\text{eff}}=-1.8$ and our cutoff frequency $\omega_c \sim 0.1$, so as to achieve reasonable transition temperatures while remaining within the parameter region treatable with the BCS approximation. For the ceramic superconductors the cutoff frequency will be much larger and the effective interaction smaller. For most band fillings the density of states at the Fermi surface is relatively flat and $N(\varepsilon_F) \sim 0.25$. With this choice of parameters we have studied the solution of the gap equation for a range of values of U_p^*, V_p^* and the band filling.

Figure 2 is the phase diagram when $V_p^*=0$, as a function of U_p^* and the filling of the lower band. When U_p^* is small, $U_p^* \ll |V_{\text{eff}}|$, the gap is predominantly on-site s-wave for all the fillings we have studied. Increasing U_p^* will suppress on-site s-wave pairing. For finite U_p^* and small filling, the gap is a linear combination of s-wave harmonics, dominated by ϕ_2. In the intermediate filling regime, the gap is dominated by the on-site s-wave harmonic ϕ_1. This region shrinks as U_p^* increases, and finally vanishes when $U_p^* \sim |V_{\text{eff}}|$. For larger fillings we find that the gap is proportional to ϕ_4, the extended d-wave

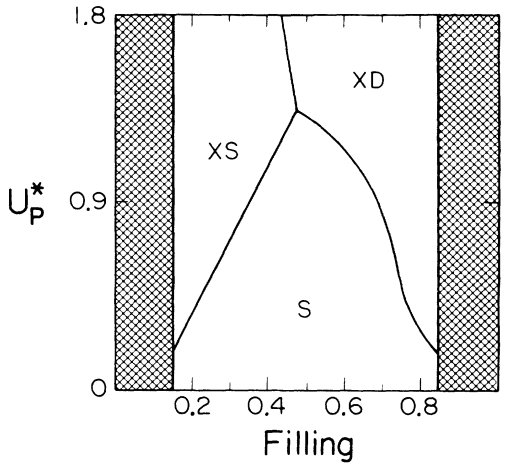

FIG. 2. Superconducting phase diagram as a function of filling and U_p^* when $V_p^*=0$. In both the extended-s dominated region and the s-wave dominated region, the gap function is a linear combination of all the isotropic s-wave harmonics (ϕ_1, ϕ_2, and ϕ_3); whereas in the extended-d region the gap function is proportional to the extended-d wave harmonic, ϕ_4. Results are not given in the cross-hatched region due to the invalidity of the calculation there.

harmonic.

The effect of V_p^* is to inhibit the extended s- and d-wave pairing (ϕ_2 and ϕ_4, respectively). When $U_p^*=|V_{\text{eff}}|$ and V_p^* finite, the phase diagram is similar to that found when $V_p^*=0$ and U_p^* is large; however, the transition temperatures are lower.

We can understand why the gap symmetry changes from s to d wave by examining the functional form of the gap harmonics and the Fermi surface. When we introduce holes on the oxygen σ orbitals, the Fermi surface first appears at the corners of the Brillouin zone $(\pm\pi,\pm\pi)$, and moves toward the center of the zone as the band is filled. The extended s-wave gap harmonic,

$$\phi_2 \sim \sin(k_x/2)\sin(k_y/2)\mathrm{sgn}(k_x k_y)\ ,$$

is largest at the corners of the zone, whereas the extended d-wave gap harmonics,

$$\phi_4 \sim \cos(k_x/2)\cos(k_y/2)\mathrm{sgn}(k_x k_y)\ ,$$

is largest at the center of the zone. The on-site s-wave harmonic ϕ_1 is constant over the zone. Thus, the location of the Fermi surface in the Brillouin zone determines the symmetry of the gap.

Figure 3 is a plot of the transition temperature versus filling when $U_p^*=0.9$ and $V_p^*=0.0$. The transition temperature is lowest when the lower band is about half full. This is true, in general, for all values of the pseudopotentials.

How relevant is this picture and these mechanisms to the ceramic high-T_c materials? In this context we discuss high-energy spectra, optical spectra, and the observed magnetic properties of the materials.

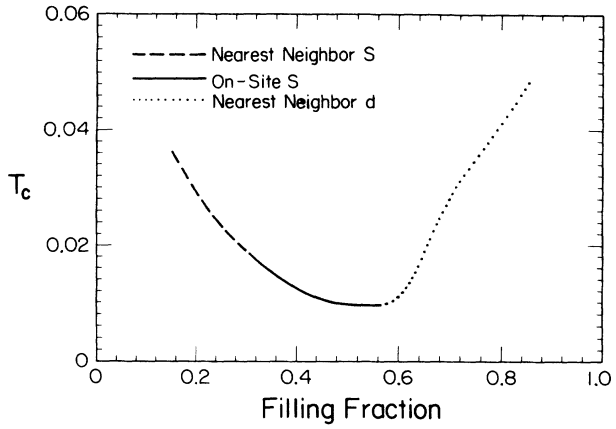

FIG. 3. The superconducting transition temperature as a function of filling when $U_p^*=0.9$ and $V_p^*=0.0$.

High-energy spectra

There is some experimental evidence that can be interpreted as suggesting that single Cu holes form localized magnetic degrees of freedom, and the O holes form the conducting degrees of freedom. In particular, valence-band x-ray photoemission (XPS) studies show very little change with doping in the structure of what is commonly interpreted as the Cu^{2+} or d^9 peak.[14] Core-level XPS (Ref. 15) and x-ray absorption measurements[16] also provide strong evidence for the placement of holes on the O sites (and for the absence of trivalent Cu ions).

Optical spectra

Geserich *et al.*[17] have interpreted optical spectra as showing evidence for the d-d excitations. Since there are no direct dipole matrix elements between the crystal-field split d levels, and since the intensities for magnetic dipole and electric quadrupole transitions are very weak, this interpretation requires the mixing of the O orbitals with the Cu orbitals. The selection rules for the optically allowed transitions in the presence of Cu-O hybridization may be worked out within a localized molecular-orbital picture. We find for the Cu-O geometry of the $YBa_2Cu_3O_{7-\delta}$ structure that the dipole-allowed transitions for polarization in the xy plane are from $d_{x^2-y^2}\rightarrow d_{xz},d_{yz}$ ($T1$) and from $d_{z^2}\rightarrow d_{xz},d_{yz}$ ($T2$). $T1$ and $T2$ should show up as two distinct transitions because the xz and yz orbitals are essentially degenerate. The $T1$ transition vanishes without the buckling of the planar oxygens, and the $T2$ transition intensity is proportional to the weight of d_{z^2} in the ground state and hence upon $\bar{t}^2$. The splitting between $T1$ and $T2$ gives the excitonic splitting Ω. Finally, the transition between $d_{x^2-y^2}$ and d_{z^2} is allowed only for polarization parallel to the c axis.

Hence, by examining the optical transmission spectra for oriented thin films (c axis normal to the film) with basal-plane polarization, we can estimate both $\bar{t}$ and Ω. The data of Geserich *et al.* show two low-lying features at 0.4 and 1.3 eV, which are interpreted as $T2$ and $T1$, respectively. Hence, we estimate $\Omega\approx 0.9$ eV. By making

reasonable assumptions about hybridization and dipole matrix element strengths, we obtain $\bar{t} \approx 0.3$ eV, consistent with our previous estimate. Thus both first-principles estimates and this semiempirical calculation yield surprisingly large values for $\bar{t}$. Obviously this interpretation should be tested by experiments which change $\bar{t}$ by sweeping the oxygen content, changing the symmetry from orthorhombic to tetragonal.

Magnetic properties

La_2CuO_4 and $Y_1Ba_2Cu_3O_6$ are insulating and antiferromagnetic. As these materials are doped, the antiferromagnetic order is diminished. Further doping causes the materials to become superconducting. Superconductivity and magnetism cannot coexist in these materials due to the short coherence length of the superconducting pairing. Thus an excitonic model requires an independent mechanism by which the magnetic order goes away as the materials are doped.

There are two ways in which this might happen within the three-band Hubbard model. First, it has been shown that at low doping an O hole localized between two adjacent Cu holes will cause the Cu holes to be ferromagnetically aligned.[18] At higher doping, when the O holes become itinerant, this effect evolves into a long-ranged oscillatory Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling which competes with the antiferromagnetic superexchange coupling. Calculation of the RKKY coupling indicates that from 0.5% to 20% doping of the O band the nearest-neighbor RKKY interaction is ferromagnetic and can easily dominate the superexchange.

The second mechanism by which magnetism can be destroyed is through delocalization of the Cu d holes by doping. If this happens, then the whole excitonic picture presented in this work will break down.

In conclusion, we believe that the picture and the mechanisms discussed here may provide a viable basis for understanding the high-T_c materials, and merit further detailed theoretical and experimental investigations.

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