Theory of High-T_c Superconductivity in Oxides

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It is shown that the properties of high-T_c oxide superconductors are consistent with a model in which the charge carriers are holes in the O($2p$) states and the pairing is mediated by strong coupling to local spin configurations on the Cu sites.

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The discovery that a number of superconducting oxides have remarkably high transition temperatures[1-3] has revived the discussion of unconventional pairing mechanisms in solids. Although phonon exchange[4] seems capable of producing transition temperatures above 30 K, as required[1] for doped La_2CuO_4, it is more difficult to imagine that it can be responsible for superconductivity above 90 K as attained[3] in $YBa_2Cu_3O_{9-\delta}$ and related materials. In this Letter, it will be shown that an analysis of the currently known properties of the oxides leads naturally to an alternative mechanism —strong coupling to local spin configurations— which can readily produce transition temperatures of the required magnitude. In some respects the mechanism resembles anisotropic pairing produced by exchange of spin fluctuations, proposed for organic superconductors[5] and heavy-fermion systems.[6] But the electronic and crystal structure of the oxides leads to a much stronger effect. The picture is quite different from Anderson's resonant-valence-bond model[7] and has an insulating limit which is antiferromagnetic (AF) rather than dimerized.

A common feature of the high-T_c oxides is the quasi two-dimensional motion of electrons within CuO_2 planes[8-11] which have a structure[12] shown in Fig. 1. It will be assumed that the Hamiltonian for a single plane is given by an extended Hubbard model,

$$H=\sum_{\mathbf{i},\mathbf{j},\sigma}\epsilon_{\mathbf{ij}}a^{\dagger}_{\mathbf{i}\sigma}a_{\mathbf{j}\sigma}+\frac{1}{2}\sum_{\substack{\mathbf{i},\mathbf{j}\\ \sigma',\sigma'}}U_{\mathbf{ij}}a^{\dagger}_{\mathbf{i}\sigma}a_{\mathbf{i}\sigma}a^{\dagger}_{\mathbf{j}\sigma'}a_{\mathbf{j}\sigma'}. \quad (1)$$

Here, $\mathbf{i}$ labels a copper or an oxygen site, and the vacuum consists of Cu^+ (all d states occupied) and O^{2-} (all p states occupied). The operators $a^{\dagger}_{\mathbf{i}\sigma}$ create holes with spin σ in the Cu($3d_{x^2-y^2}$), O($2p_x$), or O($2p_y$) states which are the ones most strongly hybridized by overlap integrals.[8-10] The site-diagonal terms ($\epsilon_{\mathbf{ii}},U_{\mathbf{ii}}$) are ($\epsilon_p,U_p$) and ($\epsilon_d,U_d$) for O($2p$) and Cu($3d$) states, respectively, and the only other nonvanishing terms are hopping integrals $\epsilon_{\mathbf{ij}}=\pm t$ and an interaction $U_{\mathbf{ij}}=V$ between neighboring sites (Cu and O). The parameters are not well known but, to fix ideas, it will be assumed that $t=1.3$–1.5 eV, $\epsilon\equiv\epsilon_p-\epsilon_d=1$ eV, $U_p=2$–3 eV, $U_d=5$–6 eV, and $V=1$–2 eV. ($\epsilon>0$ since ϵ_p and ϵ_d are hole energies.) These values are consistent with Mattheiss's effective tight-binding model,[9] regarded as equivalent to applying mean-field theory to H. [The mean-field hopping integral has a contribution from V, and site energies are equal if $\epsilon=(2U_d-U_p)/8$.]

Much of the discussion will be concerned with doped La_2CuO_4, whose properties are best known at the present time—application of the model to the higher-T_c materials will be considered at the end. The number of holes per Cu site will be denoted by $1\pm\delta$, where δ is determined by doping, oxygen defects, and the states of atoms outside the CuO_2 planes. According to electronic band-structure calculations,[9,10] La_2CuO_4 has a half-filled band ($\delta=0$) and an almost perfectly nested Fermi surface —which is quite difficult to reconcile with the observation that La_2CuO_4 is a superconductor.[13] A possible explanation is that, contrary to Refs. 9 and 10, the La($5d$) band actually dips below the Fermi level, thereby removing electrons from the CuO_2 planes and making $\delta>0$ in undoped stoichiometric La_2CuO_4. Then doping with divalent elements such as Sr or Ba would remove electrons from the La($5d$) band and increase δ, whereas oxygen defects would have the opposite effect. This view is consistent with studies of the La L_3 edge[14] which revealed that doping produced a systematic increase in the density of unoccupied states having d symmetry with respect to the La site. The strong pressure dependence[2] of T_c might also be produced by variations in the occupancy of

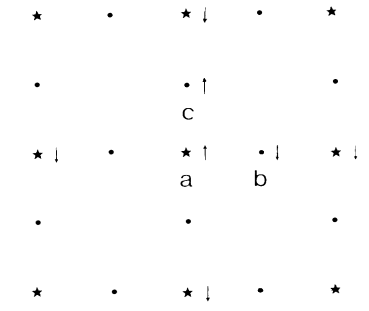

FIG. 1. The structure of the CuO_2 planes. The stars indicate Cu sites and the dots oxygen sites. The particular configuration of spins is discussed in the text.

the La($5d$) band.

For $t=0$ and $\delta=0$, the ground state of H will have exactly one hole on each Cu site (Cu^{2+}). Hopping may be included by the elimination of the oxygen sites to give an effective Hamiltonian for motion on the Cu. To second order this is a simple Hubbard model with hopping integral $t_d=t^2/(\epsilon+V)$. Hirsch[15] has carried out an extensive Monte Carlo study of this model: The ground state is an AF insulator, and when the weak hopping between CuO_2 planes is taken into account there will be long-range AF order at finite temperature. Recently, it has been established[16,17] that there is indeed AF order in La_2CuO_4 samples which presumably have δ close to zero.

There is a gap Δ between the energies of occupied and unoccupied states of the Hubbard model for a half-filled band.[15] Consequently, any additional holes will go into the O($2p$) states if the site energy lies inside the gap. This will be the case for $t=0$ if $U_d>\epsilon+2V$, and it will persist for a finite range of values of t since $\Delta\approx U_d$ for intermediate coupling. Experiments on doped La_2CuO_4 fit well with this picture and it will be assumed to hold true. The most direct evidence comes from an x-ray-absorption near-edge study[14] of $La_{2-x}Ba_xCuO_4$ and $La_{2-x}Sr_xCuO_4$ which found that the copper remained in the Cu^{2+} state for all x in the range $0\le x\le 0.3$.

An effective Hamiltonian for the O($2p$) holes may be obtained by elimination of the available Cu($3d$) states. To second order in t the kinetic energy is given by

$$H_0=\sum_{\mathbf{k},\sigma} t^2 e_{\mathbf{k}} G_{\mathbf{k}}(\epsilon+2V-\mu) b^{\dagger}_{\mathbf{k}\sigma} b_{\mathbf{k}\sigma}, \tag{2}$$

where $G_k(\omega)$ is the one-particle Green's function and μ the chemical potential of the Cu($3d$) holes,

$$e_{\mathbf{k}}=2(2-\cos k_x a-\cos k_y a), \tag{3}$$

where a is the lattice spacing, and $b_{\mathbf{k}\sigma}$ is the Fourier transform of $a_{\mathbf{j}\sigma}$ for *all oxygen* states, divided by $e_{\mathbf{k}}^{1/2}$ for normalization. The energy spectrum is determined by the shape of $G_{\mathbf{k}}$: Even for an insulator, $G_{\mathbf{k}}$ may vary rapidly but without discontinuity in the neighborhood of the ideal Fermi surface S_F, on a scale determined by the mean free path or localization length. As a result, $e_k G_k$ would have a minimum just inside S_F. From Hirsch's Monte Carlo calculations,[15] it may be inferred that this picture is valid for intermediate coupling but, for very large U_d, $G_{\mathbf{k}}$ depends weakly on $\mathbf{k}$ and the minimum in the spectrum moves to the zone corners. Experiment supports the intermediate-coupling picture: The plasma frequency ω_p in doped La_2CuO_4 obtained directly[18] and from the London penetration depth[19] ($\lambda=c/\omega_p$, where c is the velocity of light) varies slowly with δ, which requires[18] that the Fermi surface be close to S_F. The values of $\hbar\omega_p$ (0.8 eV) and the density of states[20] ($\gamma=6$ mJ/mole-Cu K^2) may both be fitted with a spectrum $-\bar{t}e_{\mathbf{k}}$ with $\bar{t}=0.13$ eV, which is much smaller than the band-structure value[9] (1.6 eV) but is compatible with Eqs. (2) and (3) since t^2/Δ is about 0.5 eV and the density of states is increased by the factor $G_{\mathbf{k}}(\epsilon+2V-\mu)$. (There is also mass enhancement due to the interactions.) Thus, it is reasonable to have a picture in which the charge carriers, mainly on the oxygen atoms, have a narrow band $-\bar{t}e_{\mathbf{k}}$ and a number density $n_c=n\delta$, where $n=10^{22}$ cm^{-3} is the number density of the copper.

Elimination of the Cu sites will also produce an effective attractive coupling between the O($2p$) holes which is responsible for superconductivity. The essential point, and the reason for high T_c, is that the coupling is strong because O($2p$)-Cu($3d$) exchange interactions are larger than Cu($3d$)-Cu($3d$) exchange. (This is why AF order is destroyed for relatively small δ.) Consider the situation shown in Fig. 1, where there are O($2p$) holes of opposite spins at b and c. There is an instantaneous magnetic moment at a, which is somewhat smaller than the full moment since the spins are delocalized. It is opposite to the spin of one of the other of the O($2p$) holes. Exchange of the holes at b and c may be accomplished by an (ab) interchange, followed by an (ac) interchange. An estimate of the associated energy is $-v_0$ where

$$v_0=\langle(n_{d\uparrow}-n_{d\downarrow})^2\rangle\left(\frac{t^2}{U_p+\epsilon}+\frac{t^2}{U_d-\epsilon}\right)^2(2J)^{-1}. \tag{4}$$

Here, the quantity in brackets is the matrix element for the (ab) or (bc) exchange. Delocalization of the Cu moment has been taken into account by the omission of V from the denominators and by inclusion of the factor $\langle(n_{d\uparrow}-n_{d\downarrow})^2\rangle$, where $n_{d\sigma}$ is the number operator for a Cu hole of spin σ at the site.[15] This factor is about 0.73 for $U_d=4t_d$. The denominator $2J$ in Eq. (4) is the energy to break the four bonds between a and its Cu neighbors. For large U_d, $J=4t_d^2/U_d$ but, for weaker coupling, this value is reduced because the probability that a is surrounded by opposite spins is less than 1[15] and because the holes at b and c partially block the exchange. The interaction v_0 is the primary source of pairing, and the BCS transition temperature[21] is given by the condition for a nontrivial solution of

$$\Delta_{\mathbf{k}}=-\frac{1}{(2\pi)^2}\int d\mathbf{k}'\, v_{\mathbf{k}-\mathbf{k}'}\frac{\tanh(\frac{1}{2}\beta_c\epsilon_{\mathbf{k}'})}{2\epsilon_{\mathbf{k}'}}\Delta_{\mathbf{k}'}, \tag{5}$$

where $\beta_c=(k_B T_c)^{-1}$, and $\epsilon_{\mathbf{k}}=-\bar{t}e_{\mathbf{k}}$. This is a two-dimensional mean-field-theory result and T_c would be somewhat reduced by phase fluctuations. The potential $v_{\mathbf{q}}$ is given by

$$v_{\mathbf{q}}=U_p-0.57v_0(\cos q_x a+\cos q_y a), \tag{6}$$

where the factor 0.57 allows for six neighbors coupled by exchange and for the transformation from $a_{\mathbf{i}\sigma}$ to $b_{\mathbf{k}}$, averaged over the Fermi surface for $\delta=0.15$. (A second-neighbor coupling generated by this transformation has been omitted.) The cosine potential (6) is separable and Eq. (5) may be solved analytically. The solu-

tion which is even in $\mathbf{k}$ and excludes the repulsion U_p is the d state

$$\Delta_{\mathbf{k}}=\Delta_0(\cos k_x a-\cos k_y a) \tag{7}$$

which gives

$$k_B T_c \sim E_0 e^{-7\pi\bar{t}/v_0}, \tag{8}$$

where the prefactor is a cutoff of the order of the O($2p$) Fermi energy (600 K). All is of this assumes $\delta=0.15$. The value of T_c is sensitive to the assumed parameters but it is easy to obtain transition temperatures between 30 and 40 K since v_0 is of the order of 1 eV. It is characteristic of the oxide superconductors that $E_0/k_B T_c$ is relatively small,[22] in this case about 20.

As δ increases, the change in the Fermi surface will cause both E_0 and the magnitude of the exponent in Eq. (8) to increase, and eventually T_c will fall. This may not be the reason for the absence of superconductivity in doped La_2CuO_4 for $x>0.2$, which might have more to do with the role of oxygen defects.[23] Indeed, the CuO_2 planes in $YBa_2Cu_3O_{9-\delta}$ are quite similar to those in La_2CuO_4, and the high T_c may simply be a consequence of increased carrier density, as expected from the present model. For some values of the parameters, the interchange of a and b lowers the energy, and a real bound pair (spin polaron) will form. This does not appear to happen in doped La_2CuO_4 but it should be kept in mind in the interpretation of experiments on other materials.

It is important to notice that in obtaining superconductivity from purely repulsive interactions, the binding of a pair was a consequence of their coupling to other degrees of freedom, just as for the exchange of spin fluctuations or other collective modes. This is essential. In the strong-coupling limit, it is possible to rearrange a repulsive *pairing force* to give an effective attractive interaction[24] of order t^2U, without involving other electrons, but it can be shown that this cannot give rise to superconductivity.

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Note added.—A recent muon-spin-relaxation measurement[25] shows that ω_p is 1.5 to 2 times as high in $Ba_2YCu_3O_{9-\delta}$ (with $\delta=2.1$) as in doped La_2CuO_4, and also gives evidence for s-wave pairing. The change in ω_p suggests that the Fermi surface for O($2p$) holes may be at the zone corners, where in fact d-state pairing is less favorable than s-state pairing. In the present model, it is possible to construct a uniform s-state wave function which does not allow two O($2p$) holes to occupy the same site,[26] since there are two oxygen sites per unit cell. It may also be that U_p, which only enters into the gap equation (5) and does not affect the preceding argument, is small. The experiment could also be explained by the existence of real pairs rather than Cooper pairs. Although Cooper pairing was assumed in Eqs. (5)–(7), since it seems to be consistent with other experiments, real pairs should occur[26] in the present model for small enough δ.

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