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Chemistry

Superconducting properties of copper oxide high-temperature superconductors

(YBaCuO/LaSrCuO/magnon pairing/generalized valence bond calculations/Heisenberg coupling term)

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ABSTRACT **The equations for the magnon pairing theory of high-temperature copper-oxide-based superconductors are solved and used to calculate several properties, leading to results for specific heat and critical magnetic fields consistent with experimental results. In addition, the theory suggests an explanation of why there are two sets of transition temperatures ($T_c \approx 90$ K and $T_c \approx 55$ K) for the $Y_1Ba_2Cu_3O_{6+x}$ class of superconductors. It also provides an explanation of why $La_{2-x}Sr_xCuO_4$ is a superconductor for only a small range of x (and suggests an experiment to independently test the theory). These results provide support for the magnon pairing theory of high-temperature superconductors. On the basis of the theory, some suggestions are made for improving these materials.**

We recently proposed the magnon pairing mechanism (1) to explain the high-temperature superconductivity in ceramic copper oxide superconductors (2–4). This model was derived from the results of generalized valence bond (GVB) calculations (5) and was used to predict some qualitative features of these systems. With the magnon pairing mechanism (1) we have now calculated several properties of the superconducting phase. The results on specific heat, critical magnetic fields, Hall effect, penetration depth, coherence length, and dependence upon doping generally agree with experiment and, in some cases, explain rather puzzling results. Several predictions are made that could be tested with further experiments.

REVIEW OF THE MODEL

The GVB calculations (5) indicate that the $La_{2-x}Sr_xCu_1O_4$, $Y_1Ba_2Cu_3O_{6+x}$, and $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ classes of superconductor oxides (2–4) have the following essential features:

(*i*) $Cu^{II}(d^9)$ sites lie in an essentially square Cu—O sheet having linear Cu—O—Cu bonds with the singly occupied Cu *d* orbital localized in the plane of four short Cu—O bonds ($R_{CuO} \approx 1.9$ Å).

(*ii*) The spins of adjacent *d* orbitals are coupled antiferromagnetically (by means of the intervening oxygen) with a Heisenberg coupling term, J_{dd}, ranging from −100 K to −250 K (depending on the system).

(*iii*) Oxidation of the system beyond cupric (Cu^{II}) leads not to Cu^{III} but rather to holes localized in the $p\pi$ (nonbonding) orbitals of oxygens ($O^{2-} \rightarrow O^-$). These $p\pi$ orbitals are localized in the plane containing the short Cu—O bonds to the adjacent copper.

(*iv*) The migration of an oxygen hole from one site to another leads to energy bands with a reasonably high density of states ($N_0 \approx 1.2$ states per eV per sheet of Cu) and to high electrical conductivity.

(*v*) The magnetic coupling of the singly occupied oxygen orbital (the hole) with the two adjacent copper atoms is ferromagnetic, with a Heisenberg coupling term of $J_{OCu} = +330$ to $+400$ K (depending on the system). This leads to ferromagnetic coupling of the spins of the two Cu atoms, despite the antiferromagnetic J_{dd}. Because of the more positive oxygen, the value of J_{dd}^+ for the Cu atoms adjacent to the hole is about 30% smaller than J_{dd}.

A qualitative view of the magnon pairing model of superconductivity is as follows. Adjacent Cu spins have a tendency to be opposite when separated by a normal O^{2-} but tend to repolarize parallel (ferromagnetic) when separated by an oxygen hole (O^-). As the conduction electron (O^- hole) moves from site to site, it tends to leave behind a wake where adjacent copper spins are ferromagnetically paired. As a second conduction electron is scattered, it is favorable to be scattered into the wake of the first electron, since there is already ferromagnetic polarization of the copper spins, leading to a favorable interaction. The net result is an attractive interaction between conduction electrons which leads to superconductivity. In the next section we outline the approach used to calculate the quantitative aspects of superconductivity.

THE SUPERCONDUCTING STATE

Interaction Potential. For a two-dimensional CuO sheet with Cu–Cu distances of *a* and *b* in the *x* and *y* directions, the lowest-order interaction between two $Op\pi$ holes is given by

$$V_{\bar{\mathbf{k}}\downarrow-\bar{\mathbf{k}}\uparrow,\mathbf{k}\uparrow-\mathbf{k}\downarrow} = -P(\mathbf{Q})W, \qquad [1]$$

where $W = J_{pd}^2/\Delta E$,

$$P(\mathbf{Q}) = 1 + \frac{1}{2}\cos \mathbf{Q}\cdot\mathbf{a} + \frac{1}{2}\cos \mathbf{Q}\cdot\mathbf{b} + 2\cos\left(\frac{1}{2}\mathbf{Q}\cdot\mathbf{a}\right)\cos\left(\frac{1}{2}\mathbf{Q}\cdot\mathbf{b}\right),$$

and $\mathbf{Q} = \mathbf{k} - \bar{\mathbf{k}}$. In deriving Eq. **1**, we use the random phase approximation for the Cu spins and write the average excitation energy for a Cu spin-flip as $\Delta E = 8\tau\beta|J_{dd}|$. Here τ is related to the average spin correlation between adjacent sites (1), and $\beta = (J_{dd}^+ + J_{dd})/2J_{dd} \approx 0.85$ accounts for the decrease in $|J_{dd}|$ when the neighboring oxygen is O^- rather than O^{2-}.

Coupling the $(\mathbf{k}, -\mathbf{k})$ pair into a triplet state leads to an attractive net interaction potential of

$$V_{\mathbf{kk}} = -[P(\mathbf{Q}) - P(\mathbf{Q}')]W, \qquad [2]$$

where $\mathbf{Q}' = \mathbf{k} + \bar{\mathbf{k}}$.

Factorization of the Interaction Potential. To solve the gap equation $\Delta_{\mathbf{k}} = -\sum_{\bar{\mathbf{k}}} V_{\mathbf{k}\bar{\mathbf{k}}}\Delta_{\bar{\mathbf{k}}}(1 - 2f_{\bar{\mathbf{k}}})/2E_{\bar{\mathbf{k}}}$, where $E_{\mathbf{k}} = (\xi_{\mathbf{k}}^2 +$

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Abbreviations: GVB, generalized valence bond; BCS, Bardeen–Cooper–Schrieffer.

$|\Delta_{\mathbf{k}}|^2)^{1/2}$ and $f_{\mathbf{k}} = 1/(e^{\beta E_{\mathbf{k}}} + 1)$, we decompose the Q-dependent factor in Eq. 2 to obtain

$$V_{\mathbf{k}\bar{\mathbf{k}}} = -W \sum_{i=1}^{4} \lambda_i \Psi_i(\mathbf{k})\Psi_i(\bar{\mathbf{k}}). \quad [3]$$

This leads to the new gap equation

$$g_i = \sum_{j=1}^{4} B_{ij} g_j, \quad [4a]$$

where

$$B_{ij} = W\lambda_i \sum_{\mathbf{k}} \Psi_i(\mathbf{k})\Psi_j(\mathbf{k}) \frac{(1 - 2f_{\mathbf{k}})}{2E_{\mathbf{k}}} \quad [4b]$$

and

$$\Delta_{\mathbf{k}} = \sum_{i=1}^{4} g_i \Psi_i(\mathbf{k}). \quad [4c]$$

For each temperature we solve Eq. 4 iteratively until self-consistency is achieved.

We find two sets of solutions to Eq. 4. Assuming the gap to be real, we find a self-consistent solution of the form $\Delta_{\mathbf{k}}^R = g(\Psi_1 \pm \Psi_2)$, leading to a gap that goes through zero (Ψ_3 and Ψ_4 are small compared with Ψ_1 and Ψ_2). On the other hand, allowing a complex gap leads to a self-consistent solution of the form $\Delta_{\mathbf{k}}^C = g(\Psi_1 \pm i\Psi_2)$, where $|\Delta_{\mathbf{k}}{}^C|$ depends on $\mathbf{k}$ but never goes to zero. In each system, the complex gap solution leads to an energy stabilization about 20% greater than for the real gap, and we report properties based only on $\Delta_{\mathbf{k}}^C$. It is possible that near T_c and near surfaces or grain boundaries the solutions would be more complicated.

Transition Temperature. As T approaches T_c, the gap and hence the g_i must go to zero. This leads to $B_{ij} = \delta_{ij}$ and hence to

$$T_c = 1.13\ \alpha|J_{dd}| \exp\left[-\frac{8\tau\beta|J_{dd}|}{\lambda N_0(J_{pd})^2}\right], \quad [5]$$

where $\lambda = \lambda_1 = \lambda_2 >> \lambda_3 = \lambda_4$, N_0 is the density of electron states, and αJ_{dd} is the effective range of the $K_\perp$ integration (perpendicular to the Fermi surface). The upper bound on α is 4, and we estimate $\alpha \approx 2$.

RESULTS

Using Eq. 4, we solved numerically to obtain the $\Delta(\mathbf{k})$ at various temperatures for three classes of systems,

$La_{2-x}Sr_xCu_1O_4$ (denoted 2-1-4),

$Y_1Ba_2Cu_3O_{6+x}$ (denoted 1-2-3),

and

$(TlO)_2Ba_2Ca_{n-1}Cu_nO_{2n+2}$ (with n layers of Cu—O sheets, denoted Tl-n layer),

and used these results to calculate specific heats, critical fields, and other properties at various temperatures.

The 2-1-4 system involves six-coordinate Cu sites (with apex oxygens above and below the Cu—O sheets), while the 1-2-3 and Tl-n systems (with $n \geq 2$) involve five-coordinate sites with apex oxygen on only one side of the Cu—O sheet. In all cases we used the experimental crystal structure and carried out the GVB calculations as in ref. 5, with Cu_2O_p clusters (p = 11, 9, and 9 for 2-1-4, 1-2-3, and Tl-2, respectively) using an array of additional ions (216, 200, and 299, respectively) to represent the electrostatic field of the crystal. These calculations were carried out for two charge states to yield J_{dd} for the neutral and J_{OCu} and J_{dd}^+ for the positive ion, as in Table 1. The electron transfer matrix elements were calculated as in ref. 5 to obtain similar band structures for all three systems, leading to the density of states N_0. We used $\alpha = 2$ (see above) for all systems. The λ comes from Eq. 3 but depends sensitively on the concentration of holes in the Cu—O sheets (x_s), as discussed in the next section.

The average spin correlation of adjacent Cu spins, τ, is difficult to calculate because of the dynamic nature of the coupling between the oxygen and copper spins. Given all other parameters, the value of τ needed for Eq. 5 to yield T_c = 93 K for $Y_1Ba_2Cu_3O_7$ is 0.0167. Using τ = 0.0167 for $La_{1.85}Sr_{0.15}CuO_4$ would lead to T_c = 32.6 K, in reasonable agreement with the observed T_c = 37 K. This close agreement provides support for the overall magnon pairing mechanism; however, in the balance of this paper we will use the value τ = 0.0159 for $La_{2-x}Sr_xCuO_4$ (but will assume τ to be independent of x), adjusted to yield T_c = 37 K at x = 0.15 (x_s = 0.10, see below).

In general, for Bi-, Tl-, and Pb-containing materials (6), $(AO)_mM_2Ca_{n-1}Cu_nO_{2n+2}$, the n = 1 case leads to six-coordinate Cu—O sheets (as in 2-1-4) and the four known such systems lead to T_c = 0, 12, 50, and 90 K, whereas the $n \geq 2$ systems have two five-coordinate Cu—O sheets (as in 1-2-3, with additional four-coordinate Cu—O sheets for $n > 2$) and the five known n = 2 systems lead to T_c = 90, 90, 90, 90, and 110 K, while the four known n = 3 systems lead to T_c = 110, 110, 122, and 122 K, and the n = 4 system leads to T_c = 122 K. We calculated only the n = 2 case but presume the results to be relevant for $n \geq 2$.

Using the calculated parameters (J_{dd}, J_{OCu}, N_0, β) for the

Table 1. Quantities used in calculating superconducting properties

Parameter	$La_{1.85}Sr_{0.15}Cu_1O_4$	$Y_1Ba_2Cu_3O_7$	$Tl_2Ba_2Ca_1Cu_2O_8$
J_{dd}, K	−204.7	−94.0	−175.4
J_{OCu}, K	383.2	330.1	396.0
β*	0.841	0.860	0.872
x_s	0.10	0.25	(0.25)†
λ	0.558	1.17	1.17
N_0‡	1.23	1.19	1.42
α	(2.0)§	(2.0)§	(2.0)§
T_c (τ = 0.0159), K	(≈37.0)	≈97	≈167
T_c (τ = 0.0167), K	≈33	(≈93)	≈160¶

*$\beta = (J_{dd} + J_{dd}^+)/2J_{dd}$.
†Assumed, based on $Y_1Ba_2Cu_3O_7$.
‡Units are eV^{-1} per sheet Cu atom.
§Assumed.
¶Using λ = 0.91 (for x_s = 0.18) and all other quantities the same leads to T_c = 123 K.

Tl-2 layer system and assuming other parameters estimated as for $Y_1Ba_2Cu_3O_7$ ($x_s = 0.25$, $\tau = 0.0167$) leads to $T_c = 160$ K for Tl-2. This is in reasonable agreement with experiment, providing additional support for the magnon pairing model. We believe that the fluctuations in T_c for these Tl-n systems are due to variations in x_s and suggest that $x_s = 0.25$ (the same value as for 1-2-3) would yield $T_c \approx 160$ K for Tl-n (with $n \geq 2$). The highest observed T_c of 122 K suggests $x_s = 0.18$ for the Tl-n systems ($n \geq 2$).

Dependence on Doping. The number of holes in the Cu—O sheets x_s is critical to the superconductivity. The valence band maximum is at the M point, $(\pi/a, \pi/b)$, and thus as $x_s \rightarrow 0$, the Fermi surface collapses around the M point. From Eq. 1 this leads to $V_{trip} \rightarrow 0$ and hence to $\Delta \rightarrow 0$ as $x_s \rightarrow 0$.

1-2-3 system. For $Y_1Ba_2Cu_3O_{6+x}$, Hall measurements (7) have been reported for various x and used to estimate x_H, the concentration (per cell) of carriers contributing to the conductivity. We assume that hole in the chains (which are disordered and incomplete) cannot contribute significantly to x_H, so that the Hall coefficient measures the concentration of holes per sheet (x_s), $x_H = 2x_s$. For $x = 1$, the experiments lead to $x_s \approx 0.25$ and $T_c = 92$ K, while for smaller x, the experiments lead to smaller x_s and decreased T_c. In Fig. 1 we show the predicted T_c versus x_s (using the same values for J, N_0, τ, α, and β but allowing λ to change with x_s) and compare with the experimental data. The close correspondence provides support for the magnon pairing model. It is important to note that such a rapid change of T_c with x_s would not be expected for a simple Bardeen–Cooper–Schrieffer (BCS) system (singlet pairs rather than triplet pairs).

The observation that the $Y_1Ba_2Cu_3O_{6+x}$ system tends to have either a high T_c around 93 K or a lower T_c around 60 K we associate with the special stabilization of $x_s = 0.25$ for x near 1 (because holes in the oxygen chain cannot get closer than alternate sites) and $x_s = 0.125$ for x near 0.5 (again related to the capacity for chains to carry holes). Assuming all calculated parameters except x_s (and hence λ) are unchanged, the theory predicts $T_c \approx 45$ K for $x_s = 0.125$, while $T_c = 93$ K for $x_s = 0.25$.

2-1-4 systems. In Fig. 2 (solid line) we show how the predicted T_c varies with x_s for the 2-1-4 system. These results are in agreement with experiment for $x < 0.1$ but not for higher values. However, as predicted earlier (5), the GVB calculations lead to a relative ionization potential (IP) from the sheet O versus the apex O that varies linearly with doping, $IP_a - IP_s = 0.38 - (0.38/0.13)x$, so that for $x > 0.13$, the most stable location of the hole is predicted to be at the apex oxygen, not at the sheet oxygen. (This occurs because $La^{3+} \rightarrow Sr^{2+}$ leads to a less attractive potential near the apex oxygen.) This suggests that for $x > 0.1$, an increasing fraction of

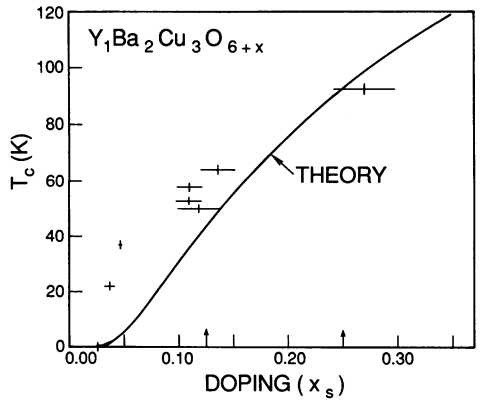

FIG. 1. Predicted dependence (solid line) of T_c on x_s for 1-2-3. Experimental results from Hall effect measurements (7) are shown as crosses with magnitude representing experimental errors.

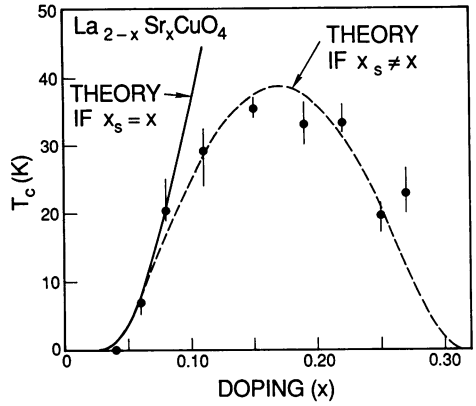

FIG. 2. The solid line shows the predicted dependence of T_c on x_s for 2-1-4, while the broken line shows the predicted T_c versus x using the relation between x and x_s from the text. Experimental T_c values are given versus x (x_s has not been measured).

the holes are on the apex oxygens rather than the sheet oxygens. At atmospheric pressure, oxygen vacancies are observed for $x > 0.15$. We suggest that this is because a high concentration of holes on the apex oxygens favors oxygen vacancy formation.

In Fig. 2 (broken line) we show the T_c predicted from magnon pairing theory, assuming that $x_s = x$ for $x \leq 0.06$, $x_s = 0$ for $x \geq 0.34$, with x_s/x varying linearly between these limits (assuming no vacancy formation). This approximates the variation of x_s with x expected if $IP_a = IP_s$ at $x = 0.17$ (calculated crossing point at $x = 0.13$). As indicated in Fig. 2, the predictions are in good agreement with experiment (8), explaining the experimental results that $T_c \approx 0$ K for $x < 0.06$ and for $x > 0.3$. These predictions could be tested independently by measuring the number of holes (x_s) contributing to the Hall current as a function of x. This is a difficult experiment because apex holes also contribute to the normal conductivity for the 2-1-4 system.

Specific Heat. We calculated the electronic specific heat for the 2-1-4 system and found a change at T_c of $(\Delta C_s/T_c) = 8.4$ mJ/mol·K^2 and an electronic specific heat for the normal state of $\gamma_e = 5.79$. Combining these results leads to $\Delta C_s/\gamma_e T_c = 1.45$, which is close to the value for BCS theory, $\Delta C_s/\gamma_e T_c = 1.43$.

A direct measurement of $\Delta C/T_c$ was made by Batlogg *et al.* (9), using quasi-adiabatic methods. They found a specific heat gap of $\Delta C/C = 1\%$ at T_c and $(\Delta C/T_c)_{exp} = 7.6 \pm 1.8$ mJ/mol·K^2, in excellent agreement with theory. However, we should point out that the experimental situation is not settled. Similar experiments by Maple *et al.* (10) revealed no transition in ΔC, while similar experiments by Nieva *et al.* (11) led to $\Delta C/C = 8\%$. This latter experiment leads to a best estimate of $\gamma_e = 18 \pm 2$ mJ/mol·K^2.

Critical Magnetic Fields. Above the critical magnetic field, H_c, the free energy of the normal state is lower than that of the superconducting state (because of the Meissner effect). Assuming a magnetic field in the c direction (perpendicular to the Cu—O sheet), we calculated H_c as a function of T. For the 1-2-3 system these calculations lead to $H_c(0) = 0.74$ T and $(dH_{c2\perp/d})_{T_c} = -0.80$ T/K (where T denotes tesla).

To compare with experiment, it is necessary to estimate the magnetic penetration length λ_L and the coherence length ξ. Using the London formula $\lambda_L = (m^*c^2/4\pi n_s e^2)^{1/2}$, the calculated effective mass ($m^*/m_e = 1.9$ for 2-1-4) and assuming n_s to be the number of O holes in the sheets, we obtain $\lambda_L = 1400$ Å from 1-2-3 ($x_s = 0.25$) and $\lambda_L = 2200$ Å for 2-1-4 ($x_s = 0.10$). To obtain the coherence length ξ, we used the calculated $H_c(0)$, the above value for λ_L, and the Ginzburg–Landau relation for $H_c(0) = \phi_0/(2\pi\sqrt{2}\,\xi\lambda)$. The result is $\xi = 23$ Å for

1-2-3 and $\xi = 38$ Å for 2-1-4. The conversion to the experimentally measured critical field H_{c2} is $H_{c2} = \sqrt{2}\, H_c\lambda/\xi$.

The only measurement (on single crystals) with the field perpendicular to the CuO plane is by Worthington *et al.* (12) for 1-2-3. For a sample with $T_c = 87$ K, they found

$$\left(\frac{dH_{c2\perp}}{dT}\right) = -0.71 \text{ T/K} \quad \text{for} \quad T < 78 \text{ K}$$

and

$$\left(\frac{dH_{c2\perp}}{dT}\right) = -0.46 \text{ T/K} \quad \text{for} \quad 78 < T < 87.$$

These values are in reasonable agreement with our predicted value of −0.80, providing support for the current model. The high-temperature knee in H_c versus T at $T \approx 78$ K is not understood. It might be an experimental artifact (the measured $T_c = 87$ K is below the usual value of $T_c = 93$ K). It might result from a sensitivity to surface regions where the properties may be different. For example, the calculated slope depends on x_s, which might be different near the surface. [For the real gap solution, we calculate $(dH_{c2\perp}/dT) = -0.65$ T/K.]

Magnitude of J_{dd}. There are no directly determined values of J_{dd} for the CuO systems. However, accurate experiments have been reported on K_2NiF_4, which has the same layered structure as $La_2Cu_1O_4$. The Neél temperature (13†) for K_2NiF_4 is $T_N = 97$ K, and neutron scattering leads to an (in-plane) Heisenberg coupling term of $J_{dd} = -52$ K (13) and −56 K (14†) [the out-of-plane value is less than 0.2 K (14)].

To determine the accuracy of our calculations for J_{dd}, we carried out the same GVB calculations on Ni_2F_{11} clusters, leading to $J_{dd} = -51$ K. This is in good agreement with experimental results, suggesting that the exchange integrals calculated with GVB are accurate (to about 10%).

Estimates have previously been made for J_{dd} of the CuO systems. Lyons *et al.* (15†, 16†), using Raman light scattering, found an inelastic peak at 0.37 eV for $La_2Cu_1O_4$ and 0.32 eV for $Y_1Ba_2Cu_3O_6$ (both semiconductors, not superconductors). They found that this peak rapidly disappears as the systems are doped ($x > 0$) and interpreted this inelastic transition as a double Cu spin-flip. Linear magnon theory leads to $\Delta E = 5.4\, J_{dd}$ for this process, suggesting $J_{dd} \approx -790$ K for 2-1-4 and $J_{dd} \approx -680$ K for 1-2-3. There is no direct evidence showing that the observed process involves the Cu spins, and we believe that the large discrepancy with the calculated J_{dd} values argues against this interpretation. We suggest that the undoped system may have a small number of oxygen vacancies, leading to extra electrons in the system, which would lead to local Cu^I (d^{10}) sites. From GVB calculations on the clusters used for 2-1-4 but with one O vacancy, we calculate the electron transfer process Cu^{II}—Cu^I to Cu^I—Cu^{II} to have an excitation energy of 0.4 eV and suggest that the transition observed in Raman light scattering is associated with such electron transfer excitations. Small amounts of doping would remove the extra electron from these Cu^I sites, leading to disappearance of the peak with small x, as observed. For the 2-1-4 system this might be testable directly by experiments at high O_2 pressure, which might decrease the number of oxygen vacancy sites and by our suggestion lead to the disappearance of the 0.4 eV peak near $x = 0$.

Maximum T_c. In Eq. 5, the maximum T_c would occur if the term in the exponent were zero, leading to $T_c^{max} = 1.13\, \alpha J_{dd}$. However, the derivation of this equation includes only the lowest-order interactions and is not valid for the limit of very large coupling. To estimate the form for T_c at stronger coupling, one can use (17) $T_c = [\langle\omega\rangle/1.20]\exp[-1.04(1+\eta)/\eta]$, valid for $\eta \approx 1$, where in our case $\eta = \lambda N_0(J_{pd})^2/8\tau\beta|J_{dd}|$. The upper limits are $\langle\omega\rangle < 4J_{dd}$ (for $\alpha = 4$) and the exponential term $< e^{-1}$. This leads to $T_c < 1.23\, J_{dd}$ (Eq. 5 would give the same result if $\alpha \to 1.09$ as $\eta \to \infty$). For $\eta >> 1$, the correct formula (17) is $T_c = 0.18(\langle\omega^2\rangle\eta)^{1/2}$, where $\langle\omega^2\rangle = 2/\eta \int \alpha^2F(\omega)\, \omega\, d\omega$; estimating the integral in $\langle\omega^2\rangle$ using various forms for $F(\omega)$ leads to $T_c < J_{dd}$. Using $T_c^{max} \approx 1.23\, J_{dd}$ with our calculated values of $J_{dd} \leq 205$ K leads to $T_c^{max} < 250$ K. (We consider this to be an upper bound; a more conservative estimate of $T_c^{max} < J_{dd} \approx 200$ K given in ref. 1 is probably closer to the real limit.) This provides hope that the recent enormous advances in increasing T_c may continue (currently the highest confirmed T_c is ≈125 K). On the other hand, it suggests that the current class of systems based on CuO sheets will not achieve room temperature T_c.

Non-Cu—O High-Temperature Systems. The ceramic $Ba_{1-x}K_xBiO_3$ shows superconductivity with $T_c = 30$ K for $x = 0.4$ (18, 19). The magnon pairing mechanism has nothing to say about this system since there are no localized magnetic atoms. Systems such as $BaBiO_3$ with a formal Bi^{IV} oxidation state tend to disproportionate to a mixed valence state $Ba_2Bi^{III}Bi^VO_6$, with clearly defined (20) Bi^{III} sites [larger cavity because of the $(6s)^2$ pair of valence electrons] and Bi^V sites (small cavity). Upon doping with K, such an ordered arrangement is not possible (the Bi atoms are equivalent). However, it is plausible that conduction involves hopping of the electrons between Bi^{III} and Bi^{IV} sites and/or between Bi^{IV} to Bi^V, either of which should couple strongly to lattice vibrations. Thus we believe that this system involves lattice coupling much as in BCS theory.

NEW HIGH T_c MATERIALS

Cu—O Type. Among compounds with CuO layers, some are superconducting and some are not (21). We suggested (1, 5) that the major issue here is arranging the cations so that the oxygen holes are in sheets rather than in apex or other locations. Thus, systems that are not superconducting might be converted into superconductors by rearranging the cations (varying the ionic radius and charge). Indeed, we believe that the critical issue in all current materials is arranging the environment of cations so as to maximize x_s. For example, the magnon pairing theory suggests that if the $La_{2-x}Sr_xCuO_4$ system could be modified to have $x_s = 0.25$ (leading to $\lambda = 1.17$, but leaving all other parameters the same), then T_c would increase to 139 K!

A second approach would be to eliminate all oxygens not in the sheets in such a way that the holes must remain in the sheets. For example, if the apex O^{2-} were all replaced by F^-, the holes would be expected to lead to O^- in the sheets (rather than F radicals in the apex position), allowing $x_s = x$. (However, if some F ions end up in the sheet, the superconducting properties might be much worse.) Such a system might be designed by finding a structure in which cations near the apex positions would prefer F to O.

Cu—X Type. To replace the O with other anions X, we believe that it is important to retain the CuX_2 sheets with linear Cu—X—Cu bonds. To obtain the highest possible T_c, the equation for T_c^{max} suggests maximizing $|J_{dd}|$. Based on the Neél temperatures for the MnO, MnS, and MnSe systems, we expect $|J_{dd}|$ to be about 40% larger for S or Se in place of O. Thus the limiting temperature might be $T_c^{max} \approx 350$ K for Cu—S sheets rather than $T_c^{max} \approx 250$ K for Cu—O sheets (bear in mind that these are upper limits). There are, however, many other factors to consider. Most important, the Cu—S sheets must be two-dimensional (with weak coupling between adjacent layers) and must yield S $p\pi$ holes upon doping. A three-dimensional system with strong coupling between Cu spins in different layers would lead to long-

†The J in this paper is defined as twice our value.

range order in the Cu spins (τ large), making it unfavorable for the conduction electrons (S $p\pi$ holes) to flip the Cu spins. Thus one would need layered systems analogous to the 2-1-4, 1-2-3, or Tl-n systems. We know of no such examples involving S or Se. In addition, the structure must be stable for large concentrations of holes (x_s). The ferromagnetic coupling J_{SCu} is likely to be smaller than J_{OCu} (because of the longer bond length), so that it may be more difficult to achieve the limiting temperature for S systems.

Other Metals. To find replacements for Cu, there are several factors to consider. First, any such replacement will probably lead to a longer M—O bond and hence a smaller J_{OM}. Other things being equal, a large J_{dd} is favored by both small bond distance and more electropositive metals, suggesting Sc–Cr. However, for metals with n unpaired d electrons (e.g., Cu^{2+} has $n = 1$, Ni^{2+} has $n = 2$, Mn^{2+} has $n = 5$), the J_{dd} decreases as n increases. Thus, these criteria favor d^1 and d^9 systems, making Sc^{2+}, Ti^{3+}, V^{4+}, or Cr^{5+} reasonable possibilities. However, for a d^1 system in a pseudooctahedral environment, the three t_{2g}-like orbitals are of similar energy, making such systems less favorable (since d_{xy} must be stabilized). In addition to Cu^{2+}, potential d^9 systems would include Ag^{2+} and Au^{2+}; however, considerations of size, electronegativity, and spin-orbit coupling all seem to favor Cu. Thus these considerations suggest that Cu^{2+} is the optimal choice for the metal.

SUMMARY

The agreement with experiment for various properties predicted by using the magnon pairing model of superconductivity provides strong support for the validity of this model for the Cu—O systems. All quantities are related to the fundamental parameters of the system (J_{dd}, J_{OCu}, band structure). Some approximations have been made in the solutions to these equations. Nevertheless, the fundamental parameters are well defined, and hence improved calculational approximations will eventually lead to precise predictions of all properties. In this theory, the superconducting properties are related to fundamental structural, chemical, and physical properties, allowing one to use qualitative reasoning in contemplating how to improve the properties.

Note Added in Proof. After submission of this paper, a news report (22) appeared stating that Z. Kąkol, J. Spałek, and J. Honig (Purdue University) have evidence suggesting that $La_{2-x}Sr_xNiO_4$ might be superconducting, with a T_c between 4 and 70 K. We have not calculated the properties for this system, but assuming that holes lead to $O^{2-} \rightarrow O^-$ (as in Cu) rather than to $Ni^{2+} \rightarrow Ni^{3+}$ and assuming $J_{ddNi} = \frac{1}{2}J_{ddCu} = -100$ K (see above) with all other parameters (including x_s and τ) as for $La_{1.85}Sr_{0.15}Cu_1O_4$, we predict $T_c = 66$ K for $La_{1.85}Sr_{0.15}NiO_4$. Thus it is plausible that the Ni system leads to superconductivity *if* the holes go on the NiO_2 sheets. Because of the lower J_{dd}, the maximum T_c for a NiO_2 system should be about half of that for a CuO_2 system (i.e., ≈100 K instead of ≈200 K).

In addition, a second report (23) shows that $Nd_{1.85}Ce_{0.15}Cu_1O_4$ is a superconductor ($T_c = 24$ K) but that conduction is dominated by electrons rather than holes. GVB calculations on this system lead to $J_{dd} = -137$ K for the undoped system. For the doped system (extra electron), the GVB calculations lead to a resonating state involving Cu^{I} (d^{10}) and Cu^{II} (d^9), with a nearest-neighbor resonance stabilization of 0.32 eV. This leads to a description of conduction involving a heavy magnon (one down-spin, several up-spin) whose motion is impeded by the antiferromagnetic coupling. This leads to magnon-mediated attractive coupling between the heavy magnons, much as for oxygen holes. However, we have not yet succeeded in estimating the T_c.

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