Virtual Electric Quadrupole Fluctuations: A Mechanism for High T_c

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We present the first detailed study of a mechanism for high-T_c superconductivity where oxygen-hole pairing is mediated via the exchange of virtual fluctuations of copper electric quadrupole moments. The excitation scale $\Delta \simeq 0.1$–0.5 eV is large enough for high T_c, but the interaction is still significantly retarded. This mechanism explains the absence of superconductivity in doped La_2NiO_4, the pressure dependence of T_c, and the different character of the 60-K and 90-K phases of $YBa_2Cu_3O_{7-\delta}$ (through filling-dependent gap nodes). Experimental tests of the model are proposed.

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The discovery of copper-oxide–based materials with unprecedented high superconducting transition temperatures[1–3] and anomalously small isotope effects[4] has led to proposals for a number of purely electronic pairing mechanisms of magnetic[5–7] or charge-fluctuation character.[8–11]

Under the latter heading, Weber[10,11] has suggested that the pairing of oxygen p holes in the high-T_c materials may be mediated by intrasite charge transfer between linear combinations of $3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$ levels on the nominally divalent copper ions. In his original formulation, the effective attraction between the holes vanishes in tetragonal symmetry, and thus apparently does not explain Tl-Ba-Ca-Cu-O,[3] for example.

In this paper we provide a detailed investigation of a mechanism which allows for intrasite-charge-transfer–induced attraction *in all symmetries*. The key feature of the mechanism is the interaction between the electric quadrupole moments of the oxygen- and copper-hole charge distributions.

We can account for (i) the possibly different character of the superconducting states in $(La_{1-x},Sr_x)_2CuO_{4-y}$, 60-K $YBa_2Cu_3O_{7-\delta}$,[12–14] and 90-K $YBa_2Cu_3O_{7-\delta}$;[14–16] (ii) differing observed pressure sensitivities among copper oxides;[17] (iii) the observed correlation between T_c and d-level splitting;[18] (iv) a predeliction for pairing with gap nodes hinted at by some experiments;[14–16] and (v) a possible link to exotic $A15$ and heavy-electron superconductors. We propose specific experimental tests for the mechanism.

The model for the CuO_2 planes is shown schematically in Fig. 1. It is clear that upon doping excess holes go into oxygen orbitals,[5,21] though there is still no clear experimental discrimination between nonbonding π orbitals[22] and bonding σ orbitals.[7] For *calculational simplicity only* we have taken the holes to reside in the nonbonding π_z orbitals of the planar oxygens.[19]

We represent the charge degrees of freedom of the Cu ions by a pseudo-spin-$\frac{1}{2}$ variable τ, which is valid for large $3d$ Coulomb repulsion and large excitation energies to d_{xy}, d_{xz}, and d_{yz} levels. $\tau_z = [3L_z^2 - L(L+1)]/12 = +\frac{1}{2}\ (-\frac{1}{2})$ corresponds to occupancy of the $d_{x^2-y^2}$ ($d_{3z^2-r^2}$) level, while $\tau_x \sim L_x^2 - L_y^2$ (L the orbital angular momentum) flips the pseudospin. These two levels are degenerate at cubic Cu sites. Electric field gradients induced by, e.g., Jahn-Teller distortion of the octahedra in $(La_{1-x},Sr_x)CuO_{4-y}$ polarize τ_z and induce a crystal-field splitting Δ. Typical Δ values are believed to be in the 0.1–0.5-eV range.[10,18,23] The Hamiltonian for the copper ion at site i is

$$H_Q = -\Delta\tau_{zi} + \bar{t}\tau_{xi}\,. \tag{1}$$

The mixing coefficient $\bar{t}$ is nonzero in orthorhombic symmetry, and arises primarily from virtual hopping through oxygen σ orbitals.

The main results of our paper follow from the interaction between the oxygen-hole charge operators on a square [cf. Fig. 1(b)] and the central copper pseudospin flip operator τ_x; this interaction exists in all the cuprate

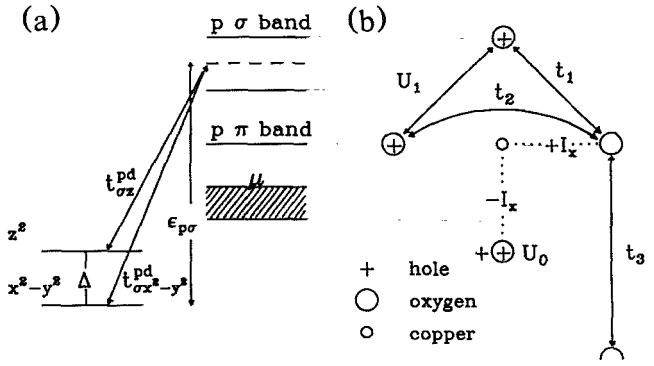

FIG. 1. (a) Model hole energy-level diagram. The copper sites possess a single localized, strongly correlated hole in a nominally stable $d_{x^2-y^2}$ level with an excited $d_{3z^2-r^2}$ level. Each copper state d_γ may hybridize via the hopping matrix element $t^{pd}_{\sigma\gamma}$ with oxygen σ states centered at energy $\epsilon_{p\sigma}$. Doping adds to the π_z band filled to the chemical potential μ (see Refs. 19 and 20). (b) Model interactions and oxygen hopping. A single copper-oxygen plaquette is shown. Pairs of oxygen holes experience on-site and nearest-neighbor Coulomb repulsions U_0 and U_1. The holes move via the hopping matrix elements t_1, t_2, and t_3. The interaction I_x causes a flip of the quadrupole moment when an oxygen hole is present.

superconductors. We focus on tetragonal symmetry, where the simplest allowed two-center[24] form of the interaction between Cu quadrupole moments and those of the neighboring oxygen charges is

$$H_{Qp} = I_x Q_{pi}^{(-)} \tau_{xi} + I_z Q_{pi}^{(+)} \tau_{zi}, \tag{2}$$

where the operators

$$Q_p^{(\pm)} = n_{pi+x} + n_{pi-x} \pm (n_{pi+y} + n_{pi-y}),$$

n_{pj} being the oxygen π_z hole on site j, and I_x and I_z are coupling constants. Note that $Q_{pi}^{(-)}$ has the x^2-y^2 symmetry of τ_x.

The I_x term in Eq. (2) is the source of the pairing mechanism. From second-order perturbation theory, Eq. (2) yields an interaction between oxygen holes on the square surrounding the copper site i of the form

$$H_{\text{pair}} = -(I_x^2/2\Delta)(Q_{pi}^{(-)})^2. \tag{3}$$

Equation (3) arises from virtual $d_{3z^2-r^2}$ occupancy, which may be viewed as a fluctuation of the Cu quadrupole moment. Equation (3) yields attraction between a pair of holes on the same site, repulsion between a pair of nearest-neighbor holes, and attraction between next-nearest-neighbor holes on opposite sides of the copper ion. We explore the consequences of Eq. (3) more fully below.[25]

We believe I_x may be sizable, with several contributions which are only easily estimable within the atomic limit. The most obvious of these is $I_{x,c}$ (the aspherical Coulomb interaction[26]) which is given by

$$I_{x,c} = \left| e^2 \int d\mathbf{r} \int d\mathbf{r}' \phi_{x^2-y^2}(\mathbf{r}') \phi_{3z^2-r^2}(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} |\psi_p(\mathbf{r}')|^2 \right|, \tag{4}$$

where $\phi_{d\gamma}$ and ψ_p represent copper and oxygen wave functions. We have estimated $I_{x,c}$ (using ionic Hartree-Fock orbitals) to be of order 0.1–0.2 eV.

Possibly more important than $I_{x,c}$ is a contribution $I_{x,v}$ arising from virtual occupation of the oxygen σ orbitals (analogous to spin superexchange between the copper and oxygen holes), which has been previously noted by Shelankov, Zotos, and Weber.[27] For $\Delta, U_1 \ll \epsilon_{p\sigma}$, $\epsilon_{p\sigma}$ being the energy difference between bonding σ levels and the copper $d_{x^2-y^2}$ level and U_1 the intersite p-p Coulomb interaction, this quadrupolar p-d superexchange is given by

$$I_{x,v} \approx -t_{\sigma x^2-y^2}^{pd} t_{\sigma 3z^2-r^2}^{pd} \left(\frac{1}{\epsilon_{p\sigma}} - \frac{1}{\epsilon_{p\sigma}+U_0} \right), \tag{5}$$

with $t_{\sigma\gamma}^{pd}$ the copper-oxygen hopping and U_0 the on-site oxygen-hole Coulomb repulsion defined in Fig. 1.

Physically, $I_{x,v}$ arises from dynamically broken tetragonal symmetry through the interaction U_0 in the presence of the π hole. $I_{x,v}$ is largest when $U_0 \to \infty$ where it is about $1/\sqrt{3}$ times the oxygen (σ)-copper (x^2-y^2) magnetic superexchange (assuming $t_{\sigma\gamma}^{pd} \simeq 1$–$1.5$ eV and $\epsilon_{p\sigma} \simeq 2$–$4$ eV[28]). We thus expect that this term can be as large as 0.5–0.6 eV.

Equation (3) is largely independent of which oxygen orbitals holes go into upon doping.[29] This distinguishes the present mechanism from magnetic mechanisms[6,7] which require holes in the σ orbitals. For holes in the hybridizing σ orbitals, (i) $I_{x,v}$ is finite even when $U_0 = 0$; and (ii) there are coupled pseudospin-spin interactions whose influence upon the pairing is as yet unexplored.

We note two important qualitative features of this mechanism.

(1) Lack of superconductivity in doped La_2NiO_4.—As Weber has stressed,[10] when Hund's rules apply, pairing mechanisms based upon intrasite d-d excitations fail for doped La_2NiO_4. The analogous fluctuations for the $3d^8$, $S=1$ divalent Ni ions are transitions to rather highly excited doubly occupied $S+0$ levels, which are allowed only through the weak spin-orbit coupling.

(2) Reduction of the Coulomb repulsion by retardation.—If as expected Δ is 0.1–0.5 eV, this is considerably smaller than reasonable estimates for the full oxygen bandwidth W.[20,28] Thus retardation effects will renormalize the bare Coulomb interactions U_0, U_1 to the much smaller values U_0^*, U_1^* {$U_0^* = U_0/[1+(U_0/W)\times\ln(W/2\Delta)]$, with U_1^* similarly defined}. Still, Δ is large enough to explain the high-T_c values.[23]

We have performed a weak-coupling stability analysis at T_c of the linearized superconducting gap equation for all singlet pair wave functions. We have included the interaction of Eq. (3) as well as the Coulombic pseudopotentials U_0^* and U_1^*. The T_c estimate for the most stable pair wave-function representation labeled by Γ is $k_B T_c \simeq 1.13(\Delta^2+\bar{t}^2)^{1/2}\exp(-1/\lambda_\Gamma)$. While this calculation is rigorous only for weak coupling, we expect the results to remain largely intact in more realistic studies.

We find that B_1 or (x^2-y^2)-like next-nearest-neighbor d-wave pairing is favored. The origin is clear: On-site and/or nearest-neighbor repulsion strongly suppresses A_1 (s-wave) and B_2 (xy-like d-wave) pairing. The B_1 state is the simplest singlet with a pair wave-function node (to avoid the hard core) for which there is attractive coupling.

Results for λ_{B_1} for a particular parameter set are shown in Fig. 2(a). The qualitative features are identical for all choices of oxygen hopping matrix elements t_1, t_2, and t_3. At low filling n, λ_{B_1} vanishes, so only for appreciable n is B_1-like pairing plausible.

The B_1-symmetry gap function generates line nodes on the full 3D Fermi surface. As is well known, these nodes will have characteristic signatures in low-energy probes,

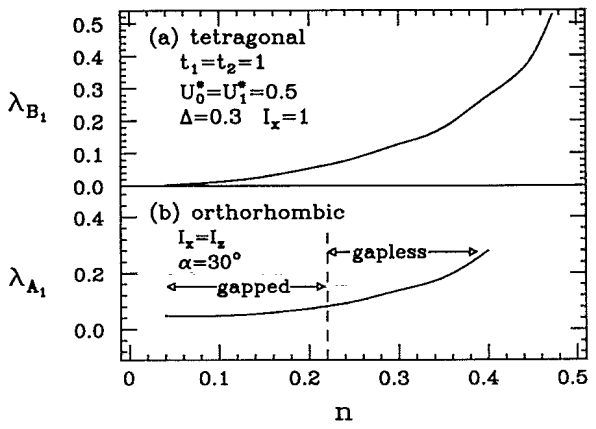

FIG. 2. Effective coupling constant as a function of filling n for (a) tetragonal and (b) orthorhombic symmetry. For (a), only the quadrupolar-fluctuation–mediated interactions and retardation-renormalized Coulomb pseudopotentials U_0^* and U_1^* are included. The stable symmetry at T_c is B_1 (x^2-y^2-like). For low filling, λ_{B_1} vanishes as n^2. Note the assumed equality of Coulombic pseudopotentials U_0^* and U_1^* (not U_0 and U_1). In (b), all parameters are as for (a) except as noted in the figure; mixing between $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ copper levels and x^2+y^2 and x^2-y^2 pair wave functions is properly included.

which we discuss further below. Nonetheless, a nodeless gap function of A_1 or s-wave-like symmetry is not ruled out: It can be stabilized for low n by reducing the nearest-neighbor repulsion through additional pairing mechanisms.

Weber's original mechanism provides such an effect in orthorhombic symmetry.[10] With $\bar{t}$ nonzero, a rotation of the pseudospin quantization axis to render Eq. (1) diagonal gives $H_Q=-(\Delta^2+\bar{t}^2)^{1/2}\tau_z'$, with mixing angle $\alpha=\tan^{-1}(\bar{t}/\Delta)$. Then the I_z term of Eq. (2) provides a coupling to the rotated operator τ_x' of the form $I_z\sin(\alpha)\tau_x'Q_{pi}^{(+)}$. When I_x and I_z have the same sign, the additional coupling reduces the nearest-neighbor repulsion relative to next-nearest-neighbor attraction by the factor $\cos(\alpha+\phi)/\cos(\alpha-\phi)$, $\phi=\tan^{-1}(I_z/I_x)$.

In orthorhombic symmetry (x^2+y^2)- and (x^2-y^2)-like gap functions have A_1 symmetry and mix. Still, pairing with nodes occurs for large enough n. The gap function has the approximate form $a(n)+b(n)\cos(2\theta)$ (θ the angle about the k_z axis). For the parameters of Fig. 2(b), when $n>0.21$, $|b(n)|>|a(n)|$, and nodes appear at

$$\theta=\pm\cos^{-1}[-a(n)/b(n)]/2,$$

$$\pi\pm\cos^{-1}[-a(n)/b(n)]/2.$$

A plot of the A_1-symmetry coupling constant appears in Fig. 2(b).

These results suggest the following interpretation of existing T_c vs n data for orthorhombic $YBa_2Cu_3O_{7-\delta}$: (1) The 60-K phase of $YBa_2Cu_3O_{7-\delta}$ obtained for low-oxygen content[12] may correspond to the small-n end of Fig. 2(b), with a nodeless gap function. This is consistent with recent optical data.[13] (2) The 90-K phase may correspond to the large-n regime of Fig. 2(a) with gap nodes. Data consistent with gap nodes include Knight-shift[14,16] and spin-lattice relaxation data for in-plane Cu nuclei,[14] and some[15] (but not all[30]) of the London penetration-depth experiments on $YBa_2Cu_3O_{7-\delta}$ in the 90-K phase. (3) Similarly, $(La_{1-x}, Sr_x)_2CuO_{4-y}$ probably has no gap nodes due to reduced nearest-neighbor repulsion, as the optimal T_c value is reached at low filling ($x=0.15$ corresponds to an oxygen band filling of 0.075). This is supported by NMR data which suggests nodeless pairing.[31]

We emphasize that a key feature of this theory is the dependence of T_c upon Δ. Taken literally, weak-coupling theory gives $T_c\simeq\Delta\exp[-B(n)\Delta]$ where $B(n)$ is determined by the above symmetry analysis. Ignoring the possible doping dependence of Δ,[32] this suggests that the theory has an optimal n-dependent splitting $\Delta_{\max}(n)$. Assuming experimental Δ values exceed $\Delta_{\max}(n)$, this idea leads to two experimental connections:

(a) Mechanism for large dT_c/dP in $(La_{1-x}, Sr_x)_2CuO_{4-y}$ and small dT_c/dP in $YBa_2Cu_3O_{7-\delta}$ (Ref. 17).—With the above assumptions, reduction of Δ will first enhance T_c. In $(La_{1-x},Sr_x)_2CuO_{4-y}$, pressure may drive the octahedra towards cubic symmetry thus reducing Δ and driving up T_c. In contrast, $YBa_2Cu_3O_{7-\delta}$ possesses one apex oxygen for each planar copper so local cubic symmetry is always broken, and thus Δ is expected to be less sensitive to pressure.

(b) Inverse correlation of T_c with Δ.—Recent polarized x-ray absorption experiments at the copper sites suggest T_c diminishes with increasing Δ.[18]

There are clear experimental tests of this mechanism. Direct measurements of Δ should be made, and Δ should be varied over as large a range as possible by doping,[32] pressure, and materials synthesis to determine how strongly correlated T_c is with Δ. The A_1 (B_1) in-plane component of the Raman tensor for orthorhombic (tetragonal) symmetry can probe the relevant quadrupolar transition and should provide the best measure of Δ. Combined uniaxial pressure and Raman experiments would be particularly useful here. In particular, c-axis pressure for $(La_{1-x},Sr_x)_2CuO_{4-y}$ should raise T_c, while uniform in-plane pressure should diminish it, in opposition to the simplest expectations for magnetic mechanisms.

We now discuss the role of the Cu spins in this model. In the doped regime the destruction of long-ranged magnetic order is likely due to frustrating interactions induced by the oxygen holes.[11,22] This requires a large value for the oxygen-copper exchange coupling $|J_{pd}|\approx 0.5$ (0.1) eV for σ (π) orbitals.[7,28]

While J_{pd} is large, a small pair-breaking rate is possible, small due to the apparent residual Cu-Cu antiferromagnetic correlations.[33] Flipping the Cu moments re-

quires a large characteristic excitation energy $\Delta_M \simeq 0.3$ eV.[34] Assuming an ordered quasi-2D antiferromagnet gives the Born-approximation estimate for the pair-breaking parameter $\alpha_{pb} = 1/\tau_{pb} k_B T_c \simeq J_{pd}^2/W\Delta_M$ at T_c, with $1/\tau_{pb}$ the pair-breaking rate. α_{pb} should be small to avoid significant T_c suppression.[35] Taking $W = 2$ eV, $\alpha_{pb} \approx 0.5$ (0.02) for σ (π) orbitals. However, in the more realistic limit of short-range order, the gap to local spin flips leads us to expect α_{pb} will be multiplied by a factor of order $\Delta_M \exp(-\eta\Delta_M/k_B T_c)/k_B T_c$, $\eta \lesssim 1$. Hence, particularly for the π orbitals, we expect $\alpha_{pb} \ll 1$.

Finally, the quadrupole pairing mechanism of this paper may apply to other exotic superconducting materials. The normal-state properties of the heavy-electron superconductor UBe_{13} may be largely explained by Kondo quenching of a non-Kramers quadrupolar doublet,[36] and the concommitant quasielastic quadrupolar fluctuations could mediate the superconductivity. Several $A15$ materials undergo apparent band Jahn-Teller transitions above T_c,[37] suggesting that virtual inelastic quadrupole fluctuations in the distorted structure may add to the attractive potential.

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