Superconductivity in an oxygen hole metal

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We study the properties of a model Hamiltonian to describe conduction by holes in a lattice of O^{2-} anions. An attractive interaction between nearest-neighbor holes with antiparallel spins exists in certain parameter regimes. The physical mechanism giving rise to this attraction is discussed. The model predicts extended *s*-wave superconductivity with high critical temperatures with dependence on hole density consistent with observations on oxides.

It was recently pointed out[1] that the process of electrical conduction by holes in an anion network is likely to be fundamentally different from conduction by electrons in a simple metal: A conducting electron only modifies slightly the states of the other electrons in its atom, while a hole causes a large disruption on the electrons of the outer shell where it goes into. Small cluster calculations[2] on a model Hamiltonian for holes in an anion network showed that this disruption can give rise to an effective narrow band and an effective attractive interaction between holes. The physical origin of the band narrowing was discussed in Ref. 2. In this paper we clarify the physical origin of the attractive interaction and examine its consequences for superconductivity. We believe these considerations to be of relevance to the physics of superconductivity in oxides.[3]

The model Hamiltonian is given by:[1]

$$H=-t\sum_{\substack{\langle ij\rangle\\ \sigma}}(c_{i\sigma}^{+}c_{j\sigma}+\text{h.c.})+V\sum_i(n_{i\uparrow}+n_{i\downarrow})\sigma_z^i +\omega\sum_i(\cos\theta\sigma_z^i+\sin\theta\sigma_x^i)+U_0\sum_i n_{i\uparrow}n_{i\downarrow}\ , \tag{1}$$

where $c_{i\sigma}^{+}$ creates a hole of spin σ on the O^{2-} anion at site i. The anion is represented by a two-level system: The eigenstates of σ_z^i, $|+\rangle$ and $|-\rangle$, describe two states of the filled outer shell. t is the direct hopping amplitude for holes on neighboring anions.

Diagonalization of the Hamiltonian for a single site with n holes yields the eigenstates

$$|n\rangle=[a(n)|+\rangle+|-\rangle]/[1+a^2(n)]^{1/2}\ , \tag{2a}$$

$$|\bar{n}\rangle=[-|+\rangle+a(n)|-\rangle]/[1+a^2(n)]^{1/2}\ , \tag{2b}$$

$$a(n)=\frac{-\omega\sin\theta}{Vn+\omega\cos\theta+(V^2n^2+\omega^2+2V\omega n\cos\theta)^{1/2}}\ , \tag{2c}$$

with energies for the ground state $|n\rangle$ and excited state $|\bar{n}\rangle$:

$$E(n)=-(V^2n^2+\omega^2+2V\omega n\cos\theta)^{1/2}\ , \tag{3a}$$

$$\bar{E}(n)=-E(n)\ , \tag{3b}$$

respectively. If the energies of the excited states relative to those of the ground states, $\bar{E}(n)-E(n)$, are much larger than the hopping t, an effective Hamiltonian that is approximately equivalent to (1) is obtained by projecting onto the lowest state for given occupation at each site:

$$H_{\text{eff}}^{(1)}=-t_p\sum_{\substack{\langle ij\rangle\\ \sigma}}(c_{i\sigma}^{+}c_{j\sigma}+\text{h.c.})+U_p\sum_i n_{i\uparrow}n_{i\downarrow} -\Delta t\sum_{\substack{\langle ij\rangle\\ \sigma}}(c_{i\sigma}^{+}c_{j\sigma}+\text{h.c.})(n_{i,-\sigma}+n_{j,-\sigma}) \tag{4}$$

with

$$U_p=E(0)+E(2)-2E(1)\ , \tag{5a}$$

$$\Delta t=\bar{t}_p-t_p\ , \tag{5b}$$

$$t_p=\langle 0|1\rangle^2 t\ , \tag{5c}$$

$$\bar{t}_p=\langle 0|1\rangle\langle 1|2\rangle t\ . \tag{5d}$$

Estimates for the parameters of the site Hamiltonian can be obtained from atomic properties.[2] The ionization energies[4] of O^{+3} and O^{+2} yield an estimate for the bare Coulomb repulsion between holes of $U_0=22.5$ eV. From the electron affinities[5] of O^0 and O^- we obtain an estimate for the effective interaction between two holes added to O^{2-} of $U_p=10.2$ eV. The difference between U_0 and U_p is due to the polarization of the outer shell by the holes, and should be accounted for by appropriate values of the parameters V and ω. The parameter θ determines the overlap between the anion outer shell wave function with and without holes. As discussed in Ref. 2, we believe $\theta\to\pi$ is appropriate as it implies a large band narrowing. For example, choosing $\theta=0.85\pi$ yields $\omega=6.8$ eV, $V=21.2$ eV (ω and V vary by less than 20% for θ/π between 0.7 and 1), which are of the order of atomic excitation energies and Slater integrals, respectively; for this case, $t_p/t=0.1$.

Important physics is contained in the fact that the overlap $\langle 0|1\rangle$ is much smaller than the overlap $\langle 1|2\rangle$ as $\theta\to\pi$ (see Fig. 2 of Ref. 2, for $\omega<V$), which implies $t_p\ll\bar{t}_p$ in Eq. (5). This means that there is a larger amplitude for a hole to hop on a nearest-neighbor site if another hole is already there. Elimination of doubly occupied sites from the Hamiltonian Eq. (4) in perturbation

theory in t_p yields an effective attractive interaction between nearest-neighbor holes with antiparallel spins, similarly to what is obtained in the strong coupling Hubbard model:[6]

$$V_{\text{eff}}^{\langle ij\rangle}=\frac{\bar{t}_p^{\,2}}{U_p}(\sigma_i\sigma_j-n_in_j)\ . \tag{6}$$

In contrast to the Hubbard model, however, the hopping $\bar{t}_p$ in Eq. (6) is *different* from the single particle hopping t_p. Thus, the difference between potential energy gained and kinetic energy lost by nearest-neighbor holes is

$$\frac{\bar{t}_p^{\,2}}{U_p}-t_p=\langle 0|1\rangle^2 t\left[\langle 1|2\rangle^2\frac{t}{U_p}-1\right]\ . \tag{7}$$

Since $\langle 1|2\rangle\sim 1$ for $\theta\to\pi$ and since (6) is valid for $\bar{t}_p\ll U_p$, that is $\langle 0|1\rangle t/U_p\ll 1$, Eq. (7) can easily be *positive* leading to a *true* attractive interaction between nearest-neighbor antiparallel spins, in contrast to what happens in the Hubbard model.[7]

To second order in t one obtains several contributions to the effective Hamiltonian. The dominant contribution in the parameter regime of interest is a term of the form

$$H_{\text{eff}}^{(2)}=\alpha\sum_{\langle ij\rangle}(\sigma_i\cdot\sigma_j-n_in_j)\ , \tag{8}$$

$$\alpha=\left[\frac{\langle 1|\bar{0}\rangle^2\langle 1|2\rangle^2}{2\bar{E}(0)+U_p}-\frac{\langle 0|1\rangle^2\langle 1|\bar{0}\rangle^2}{4\bar{E}(0)}-\frac{\langle 0|1\rangle^2\langle\bar{1}|0\rangle^2}{4\bar{E}(1)}-\frac{\langle 1|\bar{0}\rangle^2\langle 0|\bar{1}\rangle^2}{4[\bar{E}(0)+\bar{E}(1)]}\right]t^2\ , \tag{9}$$

i.e., of the same form as Eq. (6). It describes the contribution to the nearest-neighbor attraction from virtual excitations of the outer shell. By "undoing" the transformation that led to Eq. (6), we can rewrite Eq. (8) simply as an extra contribution to the hopping between anions with nearest-neighbor holes in the Hamiltonian Eq. (4), $\Delta t\to\Delta t^{(2)}$, with

$$\Delta t^{(2)}=[(\bar{t}_p)^2+\alpha U_p]^{1/2}-t_p\ . \tag{10}$$

We have diagonalized the Hamiltonian Eq. (4) with the second-order contribution Eq. (8) [in the form Eq. (10) except for small U_p where (10) breaks down] on small clusters and compared with results from diagonalization of the full Hamiltonian Eq. (1). The effective Hamiltonian accurately reproduces the bandwidth for single-hole conduction[2] as well as the effective attractive interaction between holes (within 10%) in the parameter range of interest. Results for a two-site system (that can be obtained analytically) are shown in Fig. 1, for the case $\theta=0.85\pi$, $\omega=6.8$, $V=21.2$. We have chosen values of $U_0=22.5$, 17.3, and 14.8 which yield values of $U_p=10.2$, 5, and 2.5, respectively. In the oxide superconductors U_p is believed to be around 5 eV.[8] Note the excellent agreement between the exact and second-order perturbative results. Both the first- and second-order contributions to Δt help in reducing the repulsive interaction from what it would be in a Hubbard model and making it attractive for large t, the relative importance of the first-order versus the second-order term increasing as U_p decreases. In larger clusters the effective interaction becomes attractive for smaller values of t.[2]

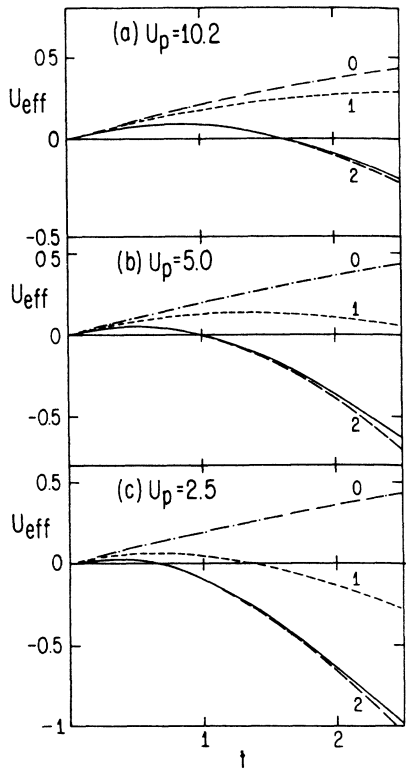

FIG. 1. Effective interaction for two holes in a two-site cluster. $V=21.2$, $\omega=6.8$, $\theta=0.85\pi$, and (a) $U_0=22.5$, (b) $U_0=17.3$, (c) $U_0=14.8$. The solid line is exact diagonalization of Eq. (1), long-dashed line labeled 2 (short-dashed line labeled 1) are the second-order (first-order) results of the effective Hamiltonian. The dash-dotted line labeled 0 are results for a Hubbard model with no change in hopping when two holes are nearest neighbors.

We solve the Bardeen-Cooper-Schrieffer (BCS) gap equation

$$\Delta_k=\frac{1}{N}\sum_{k'}V_{kk'}\Delta_{k'}[1-2f(\epsilon_{k'}-\mu)]/2(\epsilon_{k'}-\mu) \tag{11}$$

with the interaction potential from the effective Hamiltonian (4)

$$V_{kk'}=-4\Delta t^{(2)}[\cos(k_xa)+\cos(k_ya)+\cos(k_x'a)+\cos(k_y'a)]+U_p \tag{12}$$

on a two-dimensional square lattice. The form of $V_{kk'}$ implies a gap function with functional form:

$$\Delta_k=\Delta\left[\frac{\cos k_x+\cos k_y}{2}+c\right]\ , \tag{13}$$

i.e., extended s wave. For the cases shown in Fig. 1, $t_p\cong 0.1t$ and $\Delta t^{(2)}\cong 0.43t$ ($\Delta t^{(2)}$ varies by about 15% for U_p between 2.5 and 10). Results for T_c versus hopping t are shown in Fig. 2 for band filling $n=0.125$ ($\frac{1}{8}$ hole per oxygen). T_c increases rapidly with t and is suppressed by U_p, as expected. For $U_p=5$ eV, $t=0.65$ eV (as estimated

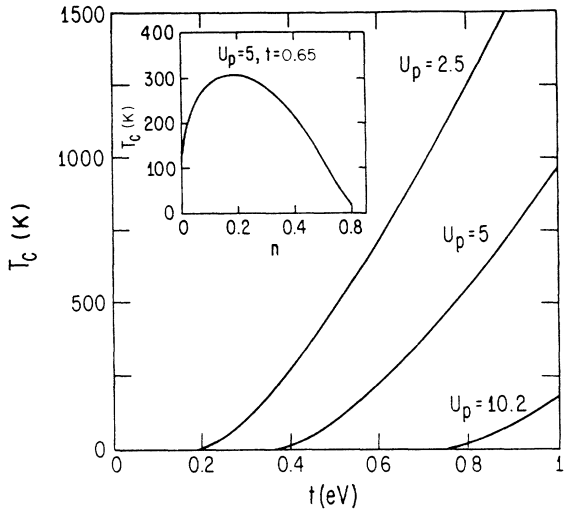

FIG. 2. T_c versus hopping t from the BCS solution of the Hamiltonian Eq. (4). $t_p=0.1t$, $\Delta t=0.43t$, $n=0.125$. The inset shows T_c vs n for $t=0.65$ eV, $U_p=5$ eV.

for these materials[8]) we obtain $T_c \approx 300°$ K. This result should not be expected to be accurate, as T_c may be reduced by fluctuations on BCS and enhanced by interplane coupling; nevertheless, the fact that T_c comes out of the right order of magnitude is remarkable. The inset in Fig. 2 shows the density dependence of T_c for $U_p=5$ eV, $t=0.65$ eV. Because the attractive part of the interaction Eq. (12) becomes smaller with increasing $\mathbf{k},\mathbf{k}'$, as the filling becomes large T_c drops, in qualitative agreement with experiment.[9] (We expect, however, the BCS estimate to become less accurate as n increases.) The ratio of the zero-temperature gap $\Delta_0=\langle \Delta_k \rangle_{\epsilon_F}$ to the Fermi energy ϵ_F is large, implying a short coherence length. For $U_p=5$ eV, $n=0.125$, we obtain $\Delta_0/\epsilon_F=0.40$, 0.94, and 1.56 for $t=0.5$, 0.65, and 0.8 eV, respectively; for those same cases, $2\Delta_0/kT_c=3.6$, 3.74, and 4.10. T_c will increase with pressure, as pressure will increase the magnitude of t.

In summary, we have shown that an attractive interaction between nearest-neighbor holes with antiparallel spin arises in a model for hole conduction through oxygen anions. The physical origin is enhanced hopping for holes on nearest-neighbor anions, or equivalently enhanced hybridization of orbitals of nearest-neighbor anions with holes, brought about through the deformation of the outer shell orbitals by the holes that go into those same shells. The form of the effective interaction implies a definite energy dependence for the gap, of s-wave symmetry. The attractive part of the interaction Eq. (12) is strongest at the bottom of the band, drops to zero at the half-filled band, and becomes repulsive beyond. Because of this and the presence of the k-independent repulsive interaction U_p, superconductivity will be confined to the low-density regime. A detailed analysis of the implications of the form of the gap Eq. (13) will be given elsewhere. This mechanism will naturally be coupled to a lattice distortion whereby two neighboring oxygens move toward each other to make the O^-—O^- bond shorter, leading to a partial isotope effect.

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