PHYSICAL REVIEW B VOLUME 39, NUMBER 16 1 JUNE 1989

Superconducting state in an oxygen hole metal

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(Received 1 February 1989)

We study within BCS theory the properties of an effective Hamiltonian to describe conduction by holes through an oxygen anion network. The Hamiltonian contains an on-site repulsive interaction U_p and a modulated hopping interaction Δt that yields a larger hopping amplitude between sites when other holes are present on those sites. The superconducting state is found to be s wave with an energy-dependent gap. Superconductivity is restricted to low hole densities and the critical temperature increases with the hopping amplitude. The particular form of the interaction allows for superconductivity even in the presence of large Coulomb repulsion, up to $U_p/\Delta t \approx 30$. We discuss the behavior of the tunneling density of states, specific heat, gap ratio, and coherence length as a function of hole density and parameters in the Hamiltonian, and the relationship between our results and existing, as well as possible future, experimental results on high-T_c oxides. Our model provides a natural explanation for the spread in gap values observed in different experiments, for the observed broadening of the resistive transition in a field, and for the observed superconducting glass behavior.

I. INTRODUCTION

The superconductivity of the high-T_c oxides has been examined by a variety of experimental techniques in the past two years.[1] Although some important aspects have remained controversial, a set of characteristic features has been established. Superconductivity is found to occur at low levels of hole doping only[2] and with a short coherence length (few lattice spacings).[3] In many cases pressure is found to have an unusually large effect in increasing the transition temperature[4] (in conventional superconductors pressure more usually decreases T_c). A Bardeen-Cooper-Schrieffer-type (BCS) peak has been reportedly observed in the ^{17}O NMR relaxation rate just below T_c, with exponential decay at low temperatures.[5] Several other experimental observations, such as tunneling[6] and London penetration depth,[7] point towards the existence of a finite energy gap over the entire Fermi surface below T_c, and the existence of Josephson tunneling[8] between high-T_c oxides and conventional superconductors establishes that the superconducting state has conventional s-wave symmetry. These experimental results point to a superconducting state that has some peculiar features but is otherwise not too different from what is found in conventional superconductors. An excellent review of experimental constraints on theories of high-T_c superconductivity has recently been given by Little.[9]

In this paper we study the properties of an effective Hamiltonian recently derived to describe the superconductivity of the high-T_c oxides.[10] The Hamiltonian describes propagation of holes through an oxygen anion network, with an interaction term that modulates the hopping between nearest-neighbor sites if other holes are present on those sites. This Hamiltonian was derived from a more fundamental one describing the local interaction of holes with the outer electronic shell in O^{2-} anions.[11] Preliminary results for the effective Hamiltonian[10] showed that it displays s-wave superconductivity with the following characteristic features: The critical temperature increases rapidly as the hopping amplitude increases, and it goes to zero if the number of holes becomes too large. In addition, the energy gap was found to be of comparable magnitude to the Fermi energy, which implies a short coherence length. These properties are not found in usual BCS superconductors but are, as mentioned above, characteristic features of the high-T_c oxides.

In this paper we examine the properties of the superconducting state that is obtained from the effective Hamiltonian within BCS theory, clarify the origin of the features found in Ref. 10, and calculate various properties that could be amenable to experimental confirmation. Section II discusses the effective Hamiltonian and the solution of the BCS equation. We examine the dependence of T_c on various parameters and discuss the specific features that lead to superconductivity even in the presence of appreciable Coulomb repulsion. In Sec. III we discuss the behavior of the tunneling density of states, the gap ratio, specific heat, and coherence length, particularly their dependence on hole density.

There is another set of experimental findings that is peculiar to the oxide superconductor materials but could appear to be related not to intrinsic properties but to various "dirt effects." These include the broadening of the resistive transition in a field,[12] the superconducting glass behavior[13] and low critical currents,[14] and the spread in gap values inferred from tunneling[15,16] and infrared[17] experiments. As we discuss in the conclusion, all these effects can be qualitatively understood within the model discussed here. A quantitative understanding will come from a Ginzburg-Landau formulation and is deferred to a future publication.

II. HAMILTONIAN AND SOLUTION OF BCS EQUATION

The effective Hamiltonian is given by[10]

$$H=-t_p\sum_{\langle i,j\rangle,\sigma}(c_{i\sigma}^{\dagger}c_{j\sigma}+\text{H.c.})+U_p\sum_i n_{i\uparrow}n_{i\downarrow}$$
$$-\Delta t\sum_{\langle i,j\rangle,\sigma}(c_{i\sigma}^{\dagger}c_{j\sigma}+\text{H.c.})(n_{i,-\sigma}+n_{j,-\sigma})-\mu\sum_{i,\sigma}n_{i\sigma}\,, \quad (1)$$

where i,j are nearest-neighbor sites on a two-dimensional square lattice. It describes the direct hopping of holes from O^{2-} to nearest-neighbor O^{2-} anion in a two-dimensional CuO_2 plane. This Hamiltonian arises from elimination of a degree of freedom describing the deformation of the outer O^{2-} electronic shell by the presence of the hole on that anion.[11] The on-site repulsion U_p and the hopping t_p are renormalized from their bare values U and t by elimination of this degree of freedom, which also generates the interaction term Δt. This term represents an increased ability for a hole to hop if another hole is present at its own site or at the site where it is hopping to, and its physical origin is enhanced quantum-mechanical overlap of the background wave function in the presence of other holes.

We propose the Hamiltonian Eq. (1) as containing the essential physics of high-temperature superconductivity. This is, of course, quite different from it containing all the physics of high-T_c oxides. In particular, the magnetic degrees of freedom associated with Cu $d_{x^2-y^2}$ orbitals are left out. Those orbitals will hybridize with O $p\sigma$ orbitals, and their interplay will largely determine the magnetic properties. The Hamiltonian [Eq. (1)] instead describes O orbitals that are predominantly hybridized to the same orbitals on nearest-neighbor O sites; thus presumably of $p\pi$ character. Our point of view does not even imply that these are the only states close to the Fermi energy, merely that it is conduction of holes through this band that drives the superconductivity.

We estimate the bare direct hopping between oxygens in the range 0.5 to 1 eV,[18] and a renormalization $t_p/t=0.1$.[11] The O on-site repulsion U_p has been estimated around 5 eV.[18] The modulated hopping amplitude Δt is found to be proportional to t and in the range $\Delta t/t=0.3$ to 0.4.[10] We can only estimate these parameters approximately at this point and so we will examine the dependence of the properties found on varying the various parameters in that range.

The parameters in the BCS reduced Hamiltonian

$$H_{\text{red}}=\sum_{k,\sigma}(\varepsilon_k-\mu)c_{k\sigma}^{\dagger}c_{k\sigma}+\sum_{k,k'}V_{kk'}c_{k\uparrow}^{\dagger}c_{-k\downarrow}^{\dagger}c_{-k'\downarrow}c_{k'\uparrow} \quad (2)$$

are given in our model by

$$\varepsilon_k=-2t_p(\cos k_x+\cos k_y)\,, \quad (3)$$

and

$$V_{kk'}=-\frac{K}{2}(\cos k_x+\cos k_y+\cos k_x'+\cos k_y')+U_p\,, \quad (4)$$

with $K=8\Delta t$. Superconductivity is determined by the BCS equation[19]

$$\Delta_k=-\frac{1}{N}\sum_{k'}V_{kk'}\Delta_{k'}[1-2f(E_{k'})]/2E_{k'}\,, \quad (5)$$

$$E_k=\sqrt{(\varepsilon_k-\mu)^2+\Delta_k^2}\,, \quad (6)$$

along with the constraint condition for the density of holes n:

$$n=1-\frac{1}{N}\sum_k\frac{\varepsilon_k-\mu}{E_k}[1-2f(E_k)]\,, \quad (7)$$

with $f(\varepsilon)$ the Fermi distribution function. The form of the interaction $V_{kk'}$ implies that the gap has a functional form

$$\Delta_k=\Delta\left(\frac{\cos k_x+\cos k_y}{2}+c\right), \quad (8)$$

and Eq. (5) yields the coupled equations

$$1=K(I_1+cI_0)\,, \quad (9a)$$

$$c=K(I_2+cI_1)-U_p(I_1+cI_0)\,, \quad (9b)$$

with the density determined by

$$n=1+8t_pI_1+2\mu I_0\,, \quad (10)$$

with

$$I_l=\frac{1}{N}\sum_k\left(\frac{\cos k_x+\cos k_y}{2}\right)^l\frac{1-2f(E_k)}{2E_k}\,. \quad (11)$$

At the critical temperature $\Delta\to 0$ and we obtain from Eq. (9) the single equation

$$1=K^2(I_0I_2-I_1^2)-U_pI_0+2KI_1 \quad (12)$$

to determine T_c.

We have solved Eq. (12) numerically for different values of the chemical potential μ and other parameters in the Hamiltonian. The hole density for each case at T_c was found from Eq. (10), or equivalently $n=(2/N)\sum_k f\times(\varepsilon_k-\mu)$; in Fig. 1 we show the dependence of n on chemical potential for three values of the temperature for future reference.

Figures 2–4 show the dependence of T_c on hole density for various cases. Parameters were chosen so that the third curve is common to the three figures, with $U_p=5$ eV,

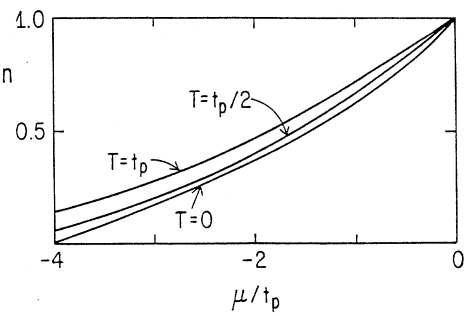

FIG. 1. Hole density vs chemical potential for three values of temperature.

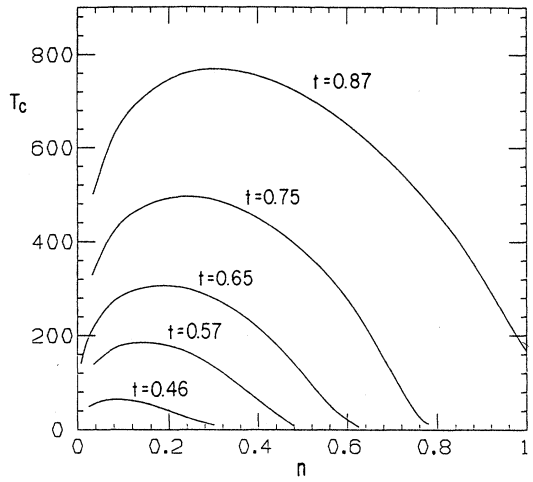

FIG. 2. Dependence of critical temperature on hole density for various values of the hopping t (in eV). $K=3.44t$, $U_p=5$ eV.

$t=0.65$ eV, $\Delta t=0.43t$. Recall in addition the relations

$$t_p=0.1t\,, \tag{13a}$$

$$K=8\Delta t\,. \tag{13b}$$

Figures 2–4 show the effect of varying t, U_p, and K/t, respectively. Note that we obtain a set of quasiuniversal curves as a function of hole density, particularly for the cases where superconductivity is restricted to very low density. In particular, there is a definite relation between the point where T_c peaks and the point where it goes to zero. T_c is enhanced by increasing t or K/t, and suppressed by increasing U_p. In particular, T_c vs n is approximately constant if U_p and K are varied so that the ratio U_p/K^2 remains constant. This is easy to understand from Eq. (12) if the first two terms on the right-hand side dominate, which is found to be the case at low densities.

To further understand these dependences, we have used a simple model to solve Eq. (12) analytically. We take the density of states g to be constant throughout the band. Then the occupation is given simply by $n\approx 1+\mu/4t_p$ (for sufficiently low temperatures). With the same approximations, I_1 and I_2 are readily determined in terms of I_0:

$$I_1=(1-n)\left[I_0-\frac{1}{8t_p}\right], \tag{14a}$$

$$I_2=(1-n)^2 I_0-\frac{1-3n+(3n^2/2)}{8t_p}\,. \tag{14b}$$

Finally, I_0 is given by

$$I_0=\frac{1}{8t_p}\ln[4.53\beta_c t_p\sqrt{n(2-n)}]\,. \tag{15}$$

The approximate T_c equation then becomes

$$T_c\approx 4.53t_p\sqrt{n(2-n)}\exp\left[-\frac{[1+k(1-n)]^2}{k(k+2)(1-n)+(kn)^2/2-u}\right], \tag{16}$$

where $k\equiv gK$ and $u=gU_p$ ($g=1/8t_p$). Equation (16) displays clearly the qualitative trends that arise from the interaction Eq. (4). T_c rises initially as a function of hole density, n, since the Fermi energy is proportional to the hole density. However, Eq. (16) also indicates that there will be a maximum, and T_c will eventually decrease as a function of hole concentration. In particular, the condition for $T_c\to 0$ is given by

$$k(k+2)(1-n_{\max})+\frac{(kn_{\max})^2}{2}=u\,. \tag{17}$$

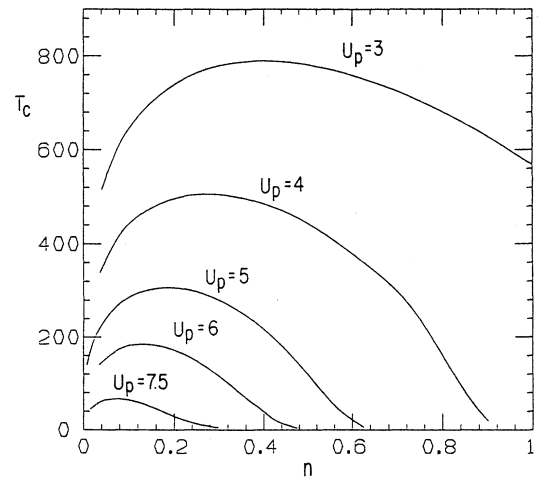

FIG. 3. Dependence of critical temperature on hole density for various values of the on-site repulsion U_p (in eV). $t=0.65$ eV, $K=3.44t$.

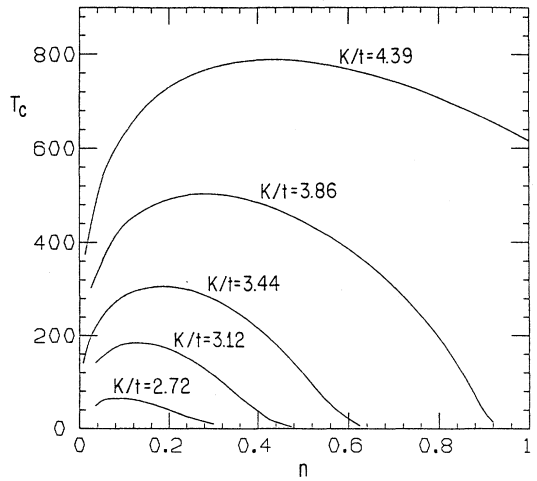

FIG. 4. Dependence of critical temperature on hole density for various values of the hopping interaction K. $t=0.65$ eV, $U_p=5$ eV.

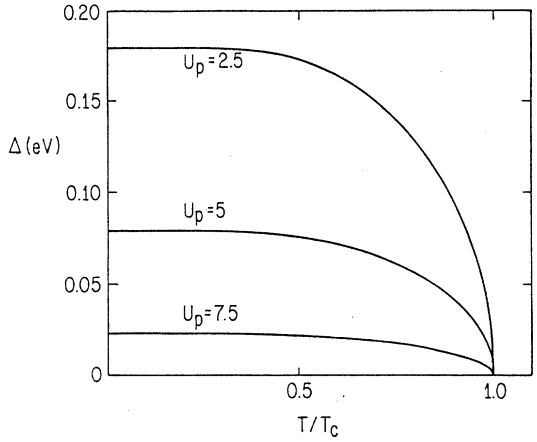

FIG. 5. Dependence of gap on temperature. Δ is the prefactor in Eq. (8). $K=3.44t$, $t=0.65$ eV, $n=0.125$. U_p is given in eV, and the critical temperatures are $T_c=845$, 298, and 58.2 K for $U_p=2.5$, 5, and 7.5 eV, respectively. The values of c for these cases at $T/T_c=0.95$ and $T/T_c=0.1$ are 0.061, 0.051; -0.200, -0.207; -0.432, -0.434 for $U_p=2.5$, 5, and 7.5 eV, respectively.

For $K/t_p=34.4$, $U_p=5$ eV, and $t_p=0.065$ eV, for example, Fig. 2 indicates that $n_{\max}\approx 0.6$ while Eq. (17) gives 0.96. The discrepancy is due to the fact that the actual density of states is not constant.

Equation (16) does not exhibit a perfect scaling relation for T_c/t_p as a function of n. However, for large K, for example, it predicts that T_c vs n remains constant for $U_p/K^2=$const, as Figs. 3 and 4 verify. For smaller K values, Eq. (16) gives a scaling relation for low densities:

$$\frac{(1+k)^2}{k(k+2)-u}=\text{const}. \tag{18}$$

Equation (18) is remarkably accurate over the entire parameter range exhibited in Figs. 3 and 4. For example, for $K/t_p=27.2$, 31.2, and 38.6 (see Fig. 4), Eq. (18) predicts that the same T_c vs n can be approximately obtained using $K/t_p=34.4$ and $U_p=7.49$, 5.94, and 4.05 eV, respectively. The actual values used are 7.5, 6.0, and 4.0 eV, respectively. Thus, while Eq. (16) disagrees with Figs. 3 and 4 in absolute magnitude, it gives the scaling relation very accurately.

The reason that superconductivity is confined to low densities is that the attractive part of the interaction Eq. (4) is largest for $\mathbf{k}=\mathbf{k}'=0$. Thus, the attractive part of the interaction at the Fermi surface decreases steadily as we add more holes, while the repulsive part of the interaction remains constant. This is seen in the analytical solution Eq. (16) above in the n dependence of the terms involving the attractive part of the interaction K in the exponent. Because the cutoff in the integrals is given on one side by the Fermi energy, T_c first increases with hole concentration [prefactor in Eq. (16)] and then decreases as the reduction in the attractive interaction becomes dominant.

Below T_c, we solve Eqs. (9) and (10) for Δ, c, and μ. It is found that Δ follows the usual behavior as a function of temperature, while c is essentially temperature independent. Figure 5 shows Δ [the prefactor in Eq. (8)] vs T for three values of U_p for the parameters of Fig. 3 with $n=0.125$. The values of c at T_c found for these cases are $c=0.06$, -0.20, and -0.43 for $U_p=2.5$, 5.0, and 7.5, respectively. That is, with increasing U_p the gap is suppressed and c becomes increasingly negative. The values of c are found to be only weakly dependent on hole density and essentially independent of temperature. In Fig. 6(a) we show c vs U_p for $n=0.125$ and the parameters of Fig. 3, and Fig. 6(b) shows the dependence of c on density for $U_p=2.5$, 5, and 7.5 eV.

At this point we may wonder how it is possible to obtain superconductivity in the presence of such large on-site repulsion. The reason turns out to be twofold: the energy dependence of the attractive part of the interaction, and the large multiplicative factor arising in the attractive part of the interaction that can be understood from phase-space arguments. We discuss these two points separately in what follows.

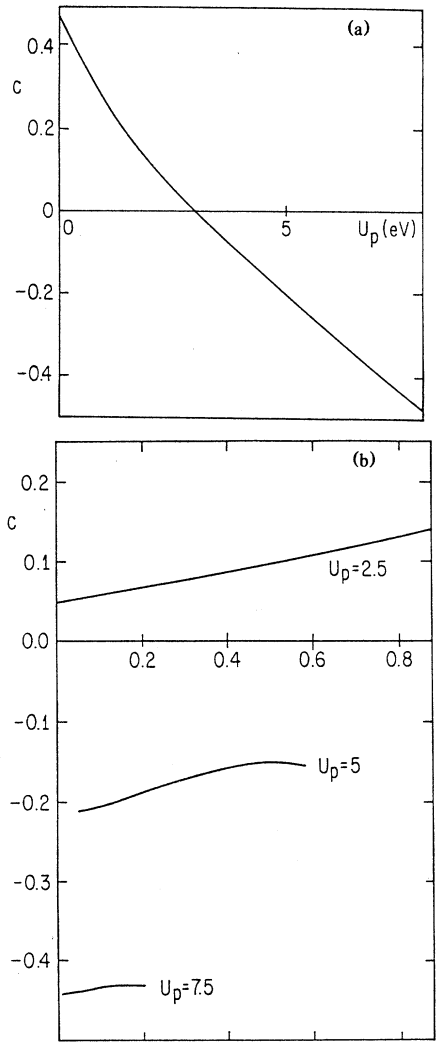

FIG. 6. (a) Dependence of c on U_p. $K=3.44t$, $t=0.65$ eV, $n=0.125$. (b) Dependence of c on density. $K=3.44t$, $t=0.65$ eV, $U_p=2.5$, 5, and 7.5 eV.

Because the energy dispersion relation Eq. (3) has the same k dependence as the interaction we can eliminate everywhere the k dependence in favor of energy dependence. The gap is given from Eq. (8) by

$$\Delta(\varepsilon)=\Delta\left[-\frac{\varepsilon}{4t_p}+c\right], \tag{19}$$

and the interaction from Eq. (4)

$$V(\varepsilon,\varepsilon')=K\left[\frac{\varepsilon+\varepsilon'}{4t_p}\right]+U_p\,. \tag{20}$$

The T_c equation is

$$\Delta\left[-\frac{\varepsilon}{4t_p}+c\right]=\Delta\int d\varepsilon' g(\varepsilon')\left[-K\frac{(\varepsilon+\varepsilon')}{4t_p}-U_p\right]\left[-\frac{\varepsilon'}{4t_p}+c\right]\frac{1-2f(\varepsilon'-\mu)}{2(\varepsilon'-\mu)}\,, \tag{21}$$

with $g(\varepsilon)$ the density of states. Figure 7 shows the energy dependence of the gap for three values of U_p. As U_p increases c decreases and the gap changes sign for lower energy, and hence lower values of the density. In Fig. 8 we show the net effective interaction versus energy for these cases, where we have set one value of the energy to the lower cutoff:

$$V_{\text{eff}}\equiv V(-4t_p,\varepsilon)=-K\left[1-\frac{\epsilon}{4t_p}\right]+U_p\,. \tag{22}$$

Note that for $U_p=5$ and $U_p=7.5$, V_{eff} is always repulsive, and yet there is a region where the T_c equation (21) can be satisfied, as seen in Fig. 3. The reason is, of course, identical to the one that gives the Coulomb renormalization in the usual electron-phonon case:[20] because the attractive part of the interaction is energy dependent while the repulsive part is not, the gap can adjust its sign to take advantage of the large repulsion at high energies, or equivalently to reduce the effective Coulomb repulsion in the low-energy region where the attractive part is largest. Note that even with the relatively small energy dependence of the effective interaction in our case this effect is significant, because of the fact that the interactions are much larger than the hopping. Thus, we find that at low densities the energy dependence allows for finite T_c for cases where U_p is up to about a factor of 2 larger than the maximum value of the attractive interaction at the bottom of the band in the parameter range of interest.

The second reason for being able to overcome the on-site repulsion is the "phase-space factor" associated with the modulated hopping interaction. At the bottom of the band, we have from Eqs. (20) and (13b)

$$V(-4t_p,-4t_p)=16\Delta t+U_p\,, \tag{23}$$

that is, we get a factor of 16 in the modulated hopping term. This factor can be written as

$$16=4\times\text{spin}\times d\,. \tag{24}$$

The factor of 4 arises from the fact that Δt acts in hopping *from* and *to* a given site, and both when the hole of opposite spin is at the site the other hole is hopping *to* or *from*. The factor of spin ($=2$) is obvious, and the dimensionality factor d ($=2$ in this case) comes from the fact that Δt acts in hopping from a site in all possible directions. Thus, the combination of this phase-space factor and the energy dependence of the interaction is what allows us to obtain superconductivity up to approximately $U_p/\Delta t\sim 30$ in the range of parameters studied. For example, $U_p=7.5$ eV and $\Delta t=0.28$ eV yields a maximum T_c of 67 K (Fig. 3). Note that, everything else being equal, the situation would be even more favorable in three dimensions as the attractive part of the interaction is further enhanced by a factor $\frac{3}{2}$.

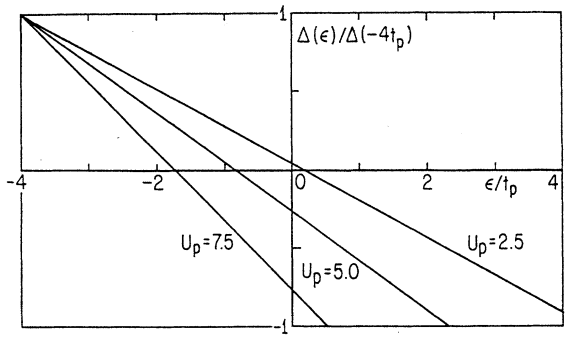

FIG. 7. Energy dependence of the gap, Eq. (14). $K=3.44t$, $t=0.65$ eV, $n=0.125$. U_p given in eV.

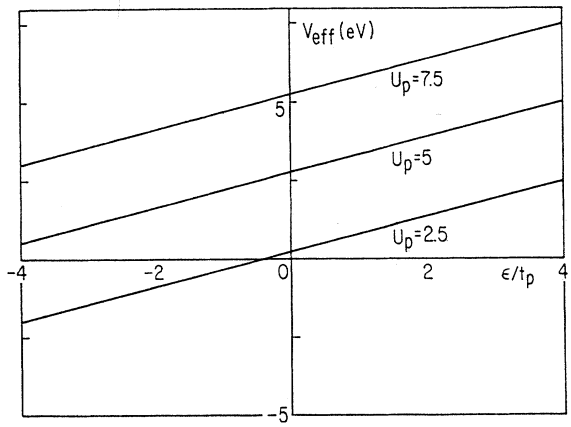

FIG. 8. Energy dependence of the effective interaction equation (17) with one energy argument set at the bottom of the band. $K=3.44t$, $t=0.65$ eV, $n=0.125$. U_p given in eV.

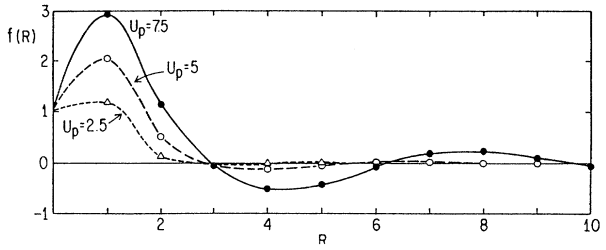

FIG. 9. Pair wave function normalized to 1 at the origin [Eq. (25)] vs R (in the x direction). $K=3.44t$, $t=0.65$ eV, $n=0.125$. U_p given in eV, a=nearest-neighbor distance.

Finally, it is interesting to examine what the pair wave function looks like in real space. We plot in Fig. 9

$$f(R)=\langle c_{R\downarrow}c_{0\uparrow}\rangle/\langle c_{0\downarrow}c_{0\uparrow}\rangle\,, \tag{25}$$

with

$$\langle c_{R\downarrow}c_{0\uparrow}\rangle=\frac{1}{N}\sum_k \Delta_k \frac{1-2f(E_k)}{2E_k}e^{i\mathbf{k}\cdot\mathbf{R}}\,, \tag{26}$$

at $T=0.5T_c$ for three values of U_p: 2.5, 5, and 7.5 eV, with transition temperatures $T_c=845$, 298, and 58 K, respectively. $f(R)$ is peaked at the nearest-neighbor site, as one would expect. As U_p increases, the amplitude at $R=0$ is depressed relative to the one at the nearest-neighbor site but remains appreciable. That is, the pair wave function is unable to avoid the on-site Coulomb repulsion because of its symmetry and thus T_c is depressed. $f(R)$ decays more slowly as U_p increases because T_c decreases and the coherence length becomes larger. The behavior of the coherence length is discussed in the next section.

III. DENSITY OF STATES, GAP RATIO, SPECIFIC HEAT, AND COHERENCE LENGTH

The formulation of the BCS equation (5) differs from the usual approach in two respects: There is no cutoff about the Fermi level, so that the finite bandwidth will play a role, particularly for low hole densities, and the potential is energy dependent (Fig. 8), leading to a strongly energy-dependent gap (Fig. 7). In this section we examine some of the consequences of these features on several superconducting properties.

T_c as a function of hole concentration is replotted in Fig. 10 with t varying from 0.55 to 0.75 eV. As discussed in the previous section, an increase in t has a similar effect as an increase in K/t or a decrease in U_p, so we confine our presentation to the first variation alone. One of the most crucial superconducting properties is the gap ratio $2\Delta_0/k_BT_c$; the standard BCS result is 3.53, and it is well known that small anisotropy tends to reduce the average gap, whereas strong-coupling (retardation) effects increase the gap ratio. We define the gap edge as the energy at which the tunneling density of states is nonzero. To compute this property, recall that the normal-state density

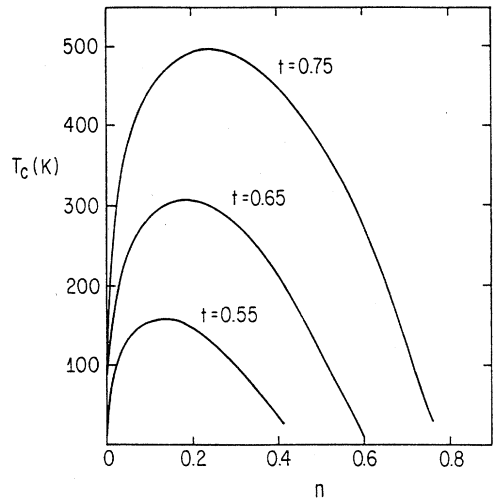

FIG. 10. T_c vs hole density for three values of hopping t (in eV). $K=3.44t$, $U_p=5$ eV.

of states for this model is given by

$$N_N(\varepsilon)=\frac{1}{2\pi^2 t_p}K_0\left[1-\left(\frac{\varepsilon}{4t_p}\right)^2\right], \tag{27}$$

where K_0 is the complete elliptic integral of the first kind. In the real system the logarithmic singularity at $\varepsilon=0$ will, of course, be rounded due to coupling to the third dimension, but it plays no role here anyway, as we are interested in low hole densities. The superconducting density of states is given by[21]

$$N_s(\omega)=\frac{1}{N}\sum_k[u_k^2\delta(\omega-E_k)+v_k^2\delta(\omega+E_k)]\,, \tag{28}$$

where $u_k^2\equiv\frac{1}{2}[1+(\varepsilon_k-\mu)/E_k]$ and $v_k^2\equiv\frac{1}{2}[1-(\varepsilon_k-\mu)/E_k]$. The special form of the gap function given in Eq. (19) allows the integration of Eq. (28) to be carried out analytically. The results are illustrated in Fig. 11(a) [dI/dV is proportional to $N_s(\omega)$ at $T=0$] for a typical set of parameters (see figure caption). Essentially, the BCS square-root singularity is superposed on the normal-state density of states. Structure occurs artificially because of the sharp cutoff in the normal-state density of states. However, the monotonic energy dependence of the gap (Fig. 7) also gives rise to an inherent asymmetry in the I-V characteristic [see Figs. 11(a)–11(c)]. This asymmetry is not due to the asymmetry in the normal-state density of states; it remains even if a constant normal-state density of states is used. For higher energies, the rapid rise in the normal-state density of states causes an additional asymmetry. The gap edge is then given by the minimum of $E(\varepsilon)=[\varepsilon^2+\Delta^2(\varepsilon)]^{1/2}$, which is

$$\Delta_0=\frac{\Delta}{4t_p}\frac{4t_pc-\mu}{[1+(\Delta/4t_p)^2]^{1/2}}\,. \tag{29}$$

We use Eq. (29) to define the finite temperature gap, $\Delta_0(T)$. $\Delta_0(T)$ is very BCS-like in appearance, exhibiting a divergent slope at T_c. Plots are shown in Figs.

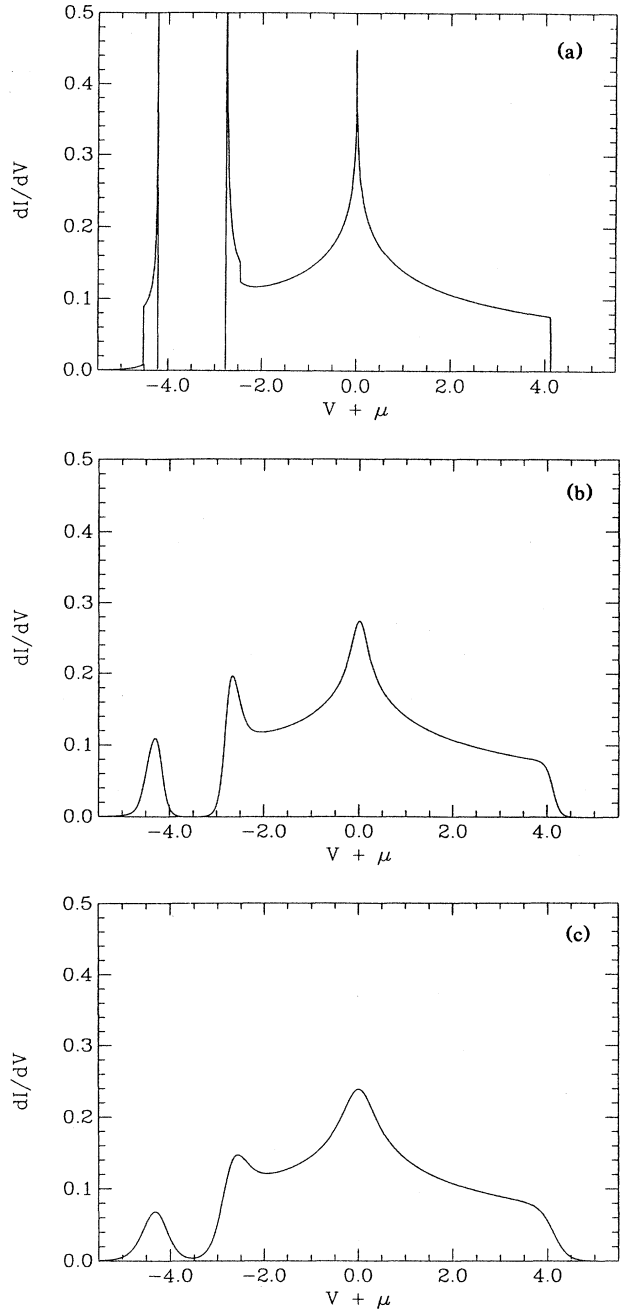

FIG. 11. dI/dV vs $V+\mu$ (units of t_p) for (a) $T=0$, (b) $T/T_c=0.2$, and (c) $T/T_c=0.4$. The units of dI/dV are arbitrary. In (a), however, the ordinate is the superconducting density of states, $N_s(V)$, in units of $1/t_p$. $k=3.44t$, $U_p=5$ eV, $n=0.1$.

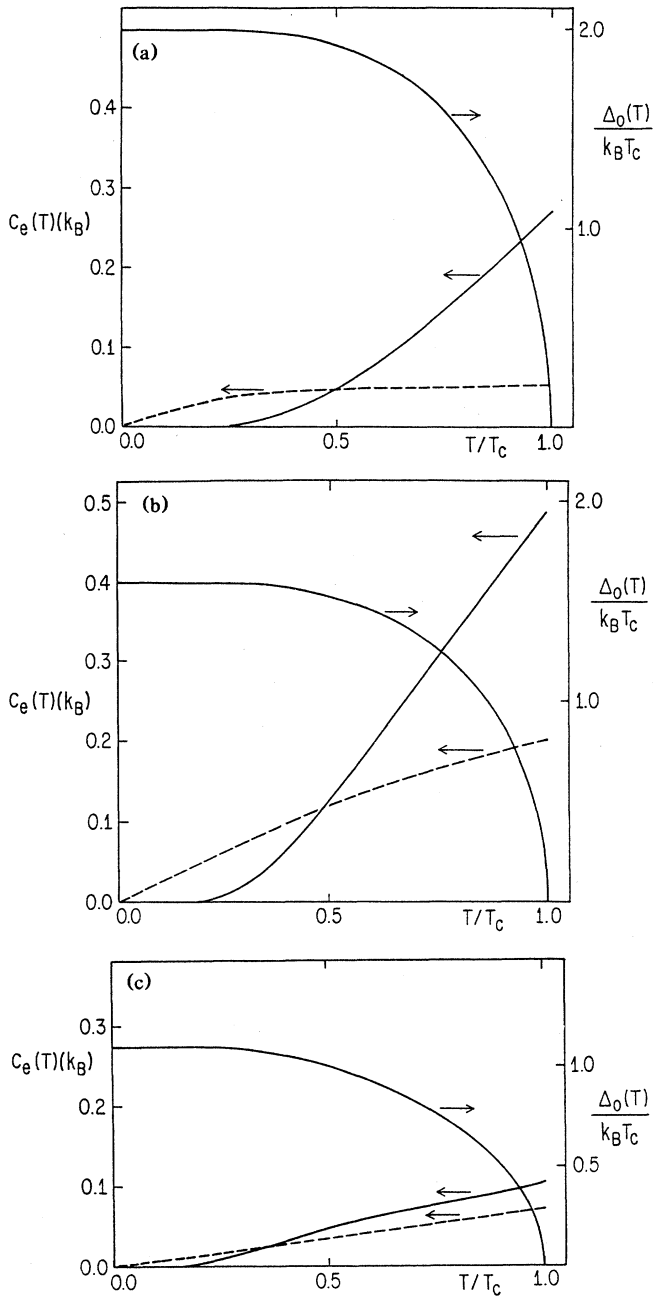

FIG. 12. Plot of normalized gap edge, $\Delta_0(T)/k_BT_c$, and superconducting (solid line) and normal-state (dashed line) specific heat as a function of reduced temperature T/T_c, for hole densities, (a) $n=0.05$, (b) $n=0.20$, and (c) $n=0.55$. $K=3.44t$, $U_p=5$ eV, and $t=0.65$ eV.

12(a)–12(c) for the parameters of Fig. 3 with $U_p=5$ eV at three hole densities. Figure 13 illustrates the zero-temperature values of $2\Delta_0/k_BT_c$ versus hole density for three different hopping parameters. Values slightly above the BCS value are achieved at low densities, but $2\Delta_0/k_BT_c$ is lower than the BCS value 3.5 over a large concentration range. Infrared measurements on oxides[17] have tended to give values of $2\Delta_0/k_BT_c$ lower than the BCS value, which is very unusual in conventional superconductors. In our model, the origin is easily understood from the energy dependence of the gap (Fig. 7). As n increases the chemical potential increases and the gap edge Eq. (29), which is approximately $\Delta(\varepsilon=\mu)$, decreases. On the other hand, the value of T_c is determined by $\Delta(\varepsilon)$ over the entire ener-

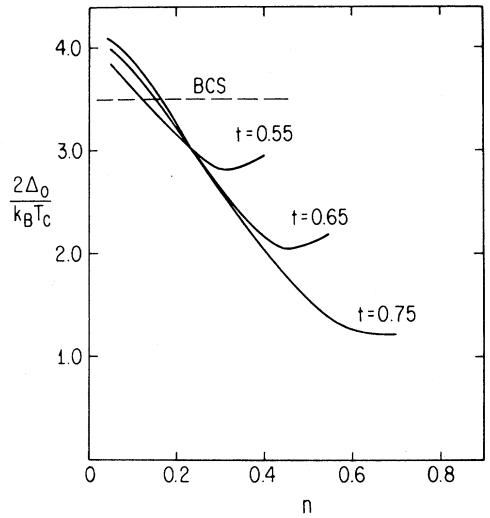

FIG. 13. Zero-temperature gap ratio, $2\Delta_0/k_BT_c$, vs hole density n for various values of hopping T (in eV). $K=3.44t$, $U_p=5$ eV.

gy range and the contribution from ε near the bottom of the band makes T_c decrease less rapidly, resulting in the marked decrease of $2\Delta_0/k_BT_c$ shown in Fig. 13.

Tunneling characteristics have been calculated using the standard model for a normal-superconducting junction:[22]

$$I_{sn}=C_n\int_{-\infty}^{\infty}N_s(\varepsilon)[f(\varepsilon)-f(\varepsilon+V)]d\varepsilon, \tag{30}$$

where C_n contains the tunneling matrix element between states of equal energy in the two materials and the density of states at the Fermi level of the normal metal. In Fig. 11 we plot dI/dV vs V at $T=0$, $T/T_c=0.2$, and $T/T_c=0.4$ for typical parameters (see figure caption). Note the asymmetry in the dI/dV curves due to the energy dependence of the gap. The values of the gap found in point-contact tunneling experiments[16] have tended to be larger than those found in infrared measurements, and we will discuss a likely origin of this in the next section.

Another property which has traditionally yielded information about the superconducting state is the electronic specific heat, C_e. In the superconducting state, it is given by[19]

$$C_{es}=2k_B\frac{\beta^2}{N}\sum_k f(E_k)[1-f(E_k)]\left[E_k^2+\beta E_k\frac{dE_k}{d\beta}\right]. \tag{31}$$

The normal-state value is given by the same expression with $\Delta_k\equiv 0$. Plots of $C_{es}(T)$ and $C_{en}(T)$ vs T are shown in Fig. 12 for typical parameters. There is a definite jump at T_c, and an exponential decay in the superconducting specific heat at low temperatures. The normal-state specific heat is linear at low temperatures, although note that for very low hole densities it becomes constant well below T_c because of the fact that the Fermi level is well within k_BT_c of the lower edge of the band. The normalized specific-heat jump,

$$\frac{\Delta C(T_c)}{C_{eN}(T_c)}\equiv\frac{C_{es}(T_c)-C_{en}(T_c)}{C_{en}(T_c)},$$

is plotted in Fig. 14 as a function of hole density, for the same parameters as Fig. 13. The universal BCS value is 1.43. Much larger values are attainable at very low densities. This is mainly a normal-state effect, however, since (see Fig. 12, $n=0.05$) the normal-state specific heat at T_c is much lower than it would be if it remained linear, as assumed usually. The drop as a function of hole density is fairly sharp, resulting in values of $\Delta C(T_c)/C_{en}(T_c)$ much lower than 1.43 at higher densities. The drop is due to the decrease in the gap ratio discussed above, since $\Delta C(T_c)/C_e(T_c)\propto 1/T_c(\partial\Delta^2/\partial T)_{T_c}$. Although there is a spread in the specific-heat jump values reported in the literature for the high-T_c oxides, they tend to be somewhat lower than the BCS value.

Finally, we compute a coherence length in the superconducting state. We use $\xi_0(T)\equiv(2\sqrt{2}/\pi)\langle R^2\rangle^{1/2}$, where

$$\langle R^2\rangle=\frac{\sum_R f^*(R)R^2f(R)}{\sum_R f^*(R)f(R)} \tag{32}$$

is the mean-square radius of a hole pair. $f(R)$ is the pair amplitude given in Eq. (25). The numerical factor is used so that ξ_0 reduces to the usual BCS coherence length, $\xi_0(0)=\hbar v_F/\pi\Delta(0)$. The summations in Eq. (32) are over all sites. It is expected that[23] $\xi_0(0)\approx\xi_{GL}(0)$, where $\xi_{GL}(0)$ is the Ginzburg-Landau coherence length. However, near T_c they differ considerably, as ξ_{GL} diverges, whereas $\xi_0(T)$ does not. In Fig. 15, we plot $\xi_0(0)$ as a function of density, for the parameters of Fig. 13. There is a dramatic increase for densities beyond the maximum T_c. This essentially reflects the fact that T_c/E_F is decreasing towards zero. As remarked earlier, this increase

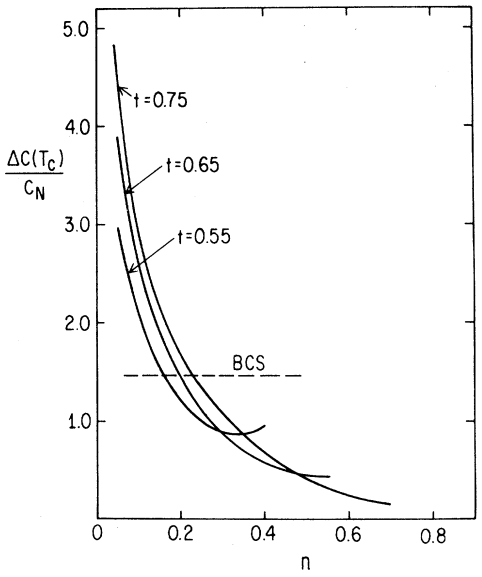

FIG. 14. Specific-heat jump $\Delta C(T_c)/C_{en}(T_c)$ vs n for three values of t (in eV). $K=3.44t$, $U_p=5$ eV.

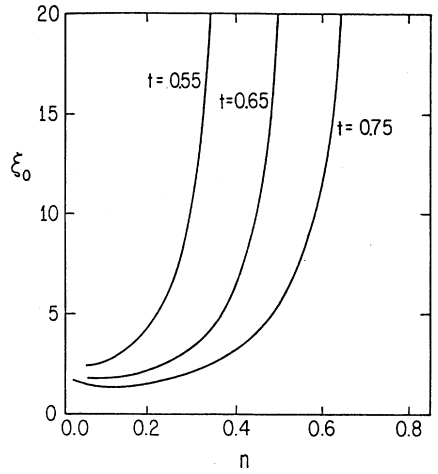

FIG. 15. Coherence length at $T=0$, $\xi(0)$ (measured in lattice spacings) vs n for three values of t (in eV). $K=3.44t$, $U_p=5$ eV.

is manifested in $f(R)$ as an increased amplitude at further than nearest neighbor sites.

IV. CONCLUSIONS

We have studied the properties of an effective Hamiltonian to describe propagation of holes through an oxygen anion network within BCS theory. The characteristic feature of our Hamiltonian is that the interaction has the same momentum dependence as the kinetic energy. This is because the interaction term describes a modulation of the hopping process by the presence of other particles. This implies that the gap obtained in BCS theory can be considered a function of energy rather than momentum. Note that although we have considered only nearest-neighbor hopping here this feature would survive in a more general case with longer-range hoppings.

The superconductivity in our effective Hamiltonian has extended s-wave character with the following characteristic features.

(1) The energy gap has a strong energy dependence.

(2) T_c increases first as a function of number of holes, reaches a maximum and then decreases to zero; for most of the parameter range it is restricted to low densities.

(3) T_c increases with hopping t and hence with pressure.

(4) Because of the combined effect of an energy-dependent interaction and phase-space factors associated with the modulated hopping interaction, superconductivity can exist with a repulsive interaction substantially larger than the modulated hopping interaction, up to a factor of 30 in the parameter range considered.

(5) The pair wave function has largest amplitude at nearest-neighbor sites, so that the superconductivity can be roughly described as condensation of nearest-neighbor singlet pairs.

(6) The tunneling density of states exhibits the same square-root singularity as the usual BCS case. However, an inherent asymmetry arises due to the energy dependence of the gap.

(7) The gap ratio $2\Delta_0/k_BT_c$ varies strongly with density, being higher than the BCS value 3.5 at very low densities and lower at higher densities.

(8) The specific-heat jump $\Delta C/C$ is larger than the BCS value 1.43 at very low densities and decreases substantially below it as the density increases.

(9) The coherence length is very short at low hole density (few lattice spacings) and increases drastically for densities beyond the maximum T_c.

(10) Other features, like the temperature dependence of the gap and specific heat at low temperatures, are indistinguishable from the usual BCS behavior.

These features are necessary consequences of BCS theory applied to our effective Hamiltonian Eq. (1). We may ask which of these could be substantially changed by strong-coupling effects. It is clear that (1) to (6) are likely to survive at least qualitatively unchanged as they are direct consequences of the form of the interaction. We believe the density dependence found in (7) to (9) is also likely to survive strong-coupling effects although there could be important quantitative changes; for example, $2\Delta_0/k_BT_c$ could be enhanced by fluctuations depressing T_c more rapidly than Δ_0. Corrections to BCS theory are clearly worth future investigation.

We may next ask whether experimental observations on oxides to date provide support for the correctness of our model. As mentioned in the Introduction, we believe several clearly do: the density and pressure dependence of T_c, and the evidence for s-wave superconductivity, and a gap over the entire Fermi surface. In addition, some observations of tunneling density of states[24] suggest an asymmetry consistent with the one found in our model. The specific-heat jump at T_c is difficult to estimate accurately, but has been found to be close but somewhat lower than the BCS value,[25] which is not inconsistent with our findings.

Our treatment has assumed an infinite, perfectly homogeneous medium. However, real materials always have impurities, defects, and boundaries. It is clear that the energy dependence of the gap in our model [Eq. (19), Fig. 7] will bring about important effects in the presence of these perturbations. Consider the generalization of Eq. (19) in the presence of spatially dependent potentials:

$$\Delta(\varepsilon,r)=\Delta(r)\left[-\frac{\varepsilon-\varepsilon_0(r)}{4t_p}+c(r)\right]. \tag{33}$$

The dominant effect will be the variations in the local Madelung energy $\varepsilon_0(r)$. The gap value at the Fermi energy will then move up and down on the line in Fig. 7 in the presence of spatially varying potentials [to a first approximation one can neglect the variations in $\Delta(r)$ and $c(r)$]. Note that large changes will occur on a scale of t_p which we estimate at $\sim$65 meV.

The consequence of this is that small changes in the local potential will bring about large changes in $\Delta(\varepsilon_F,r)$ leading to weak links and nonsuperconducting regions, which would explain the superconducting glass behavior observed[13] as well as the low critical currents.[14] This will also lead to a wide distribution of "local coherence lengths" $\xi(r)\sim\hbar v_F/\Delta(\varepsilon_F,r)$ which would explain the

broadening of the resistive transition observed in a magnetic field:[12] the critical field $H_{c_2}=\phi_0/2\pi\xi^2$ would now span a *range* of values at given temperature. Finally, this would also explain the range in values of the gap measured. Infrared experiments[17] as well as break-junction tunneling experiments[16] measure a bulk gap and the ratio $2\Delta/kT_c$ should be around and possibly even substantially smaller than BCS, as seen in Fig. 13. On the other hand, as we approach the surface the local Madelung potential will decrease on the average moving us to the left in Fig. 7 and increasing the value of the local gap [Eq. (29) with μ shifted by the local Madelung potential]. This would account for the larger gap observed usually in point-contact tunneling experiments[15] and for the large variations found in these experiments due to local variations in the surface Madelung potential. Note that without the energy dependence of the gap, one would expect the gap at the surface to be smaller rather than larger than the bulk gap.[13] Although the amplitude of the gap $\Delta(r)$ in Eq. (33) may be smaller at the surface than on the bulk this effect will be superceded by the larger effect due to the energy dependence.

These considerations imply, if our model is correct, that these observed "dirt effects" are *intrinsic* to the superconductivity mechanism discussed here. Figure 7 suggests that the way to reduce them (besides better samples) is to increase the hopping energy t_p or to decrease the on-site repulsion U_p (thus increasing c). The first could be accomplished in structures with closer packing of oxygen, the second (and possibly also the first) with other anions instead of oxygen, like sulphur. In addition, working with low hole density should make these effects smaller (Fig. 7). Still, this feature of the mechanism discussed here may well turn out to be the most important one in its implications for practical applications of these materials.

We may next ask which future experiments could prove or disprove our model. First, our model was derived assuming *hole* conduction through an anion network.[10,11] If a recent Japanese report[16] on *electron* superconductivity in oxides is confirmed in that conduction *in the planes* occurred through electrons rather than holes it would cast serious doubts on the validity of our model. We speculate that future measurements on single crystals will show positive Hall coefficient with field perpendicular to the plane and negative one with field parallel to the plane, consistent with the reported overall negative coefficient in the polycrystalline sample studied[26] and with our model of hole conduction in the planes.

Various experiments involving what are surely difficult measurements as functions of hole density could clearly lend support for our model. For example, the set of quasi-universal curves for T_c found indicates that applying pressure should both increase the maximum T_c and the density where T_c goes to zero. In that respect it would be useful to be able to differentiate between pressure applied parallel and perpendicular to the planes as our prediction would specifically apply to the former. The density dependence of the specific-heat jump, gap ratio, and coherence length could be directly compared with the predictions of our model.

We have only treated here a two-dimensional model, and to understand the role of the third dimension is important, particularly since, strictly speaking, there is no true superconducting long-range order at finite temperatures in two dimensions. Thus it is important to understand how conduction occurs in the third direction. If conduction occurred dominantly through oxygen holes, the Hamiltonian Eq. (1) would be extended to include a hopping t_p' and interaction $\Delta t'$ in the third direction, with $\Delta t'/t_p'=\Delta t/t_p$. In that case all our conclusions remain qualitatively unchanged and the range of parameters where superconductivity occurs is enlarged [see discussions after Eq. (24)]. This indicates that approaching three dimensionality will give better conditions for high T_c. Unfortunately, as discussed elsewhere,[11] a three-dimensional arrangement is not compatible with the close packing of oxygen found in the Cu-O planes.

Measurements of the Hall effect with magnetic field parallel to the planes suggest, however, that conduction in the third direction is electron rather than holelike.[27] In that case we should add to our Hamiltonian Eq. (1) a hopping in the third direction without a corresponding modulated hopping interaction. Within BCS theory this term will depress T_c as it reduces the density of states. However, for sufficiently small third-dimensional coupling, it is physically obvious that such a term will enhance T_c. This question is subtle and will be further investigated in the future.

The generalization of the theory to account for spatially dependent fields and order parameter will allow for quantitative comparison with a wide variety of experimental observations. There is also a set of other quantities, not discussed here, that can be calculated and compared with experiment, like ultrasonic attenuation, NMR relaxation rate, and electrodynamic properties. These issues will also be considered in the future.

ACKNOWLEDGMENTS

This work was supported by NSF Grant No. DMR 85-17756 and the National Science and Engineering Research Council of Canada.

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