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Effective interactions in an oxygen-hole metal

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We study the properties of an effective Hamiltonian to describe the propagation of holes through the oxygen anion network in a high-T_c superconductor. Approximate parameters for our Hamiltonian are derived from atomic properties of O. The effective interaction between holes and the effective bandwidth for the holes are studied by diagonalization of finite clusters. The effective interaction is found to be attractive for realistic parameters; in the same regime, there is significant band narrowing. Consequences of our results for normal and superconducting properties of high-T_c oxides are discussed.

I. INTRODUCTION

To elucidate the mechanism responsible for high-T_c superconductivity in oxides is perhaps the most challenging question in condensed-matter physics today. High-temperature superconductivity has already been found in a wide variety of materials, and substantial experimental information has accumulated to date.[1] A variety of theoretical models have already been proposed;[1] however, many of those are specific to only certain subsets of materials. For example, magnetic mechanisms would not be expected to apply to oxides that do not contain Cu.[2] Given the lack of compelling evidence to show that superconductivity in the Cu oxides is in any way related to its magnetism, and the absence of superconductivity found in simulation studies of model systems,[3] it is natural to doubt the validity of magnetic mechanisms. A variety of charge-fluctuation mechanisms have also been proposed,[1] but many of them are specific to particular structures or components.

It is well known that theorists have had difficulty in the past predicting superconducting T_c's or even whether a material would be superconducting.[4] A variety of "plausible" mechanisms of excitonic type have been proposed in the past[5] and also for the new materials, and one can usually come up with reasonable-looking calculations that predict or explain superconductivity that are difficult to prove wrong. However, many assumptions and uncontrolled approximations usually enter these calculations.

We believe the right answer to the puzzle, in addition to providing a plausible pairing mechanism, should be able to correlate a wide variety of experimental facts. In this paper we investigate an answer that we believe satisfies those conditions:[6] high-temperature superconductivity occurs in materials where conduction occurs through holes in anions with filled shells.

In Ref. 6 we proposed a model Hamiltonian to describe the propagation of holes through a lattice of anions with filled shells. The basic idea is that the presence of a hole on a given anion will modify drastically the wave function of its "background," the electrons in the outer filled shell, unlike the case of *electrons* outside closed shells. It was proposed in Ref. 6 that this local interaction between the hole and the outer filled shell is the essential physics that leads to high-temperature superconductivity. In this paper we substantiate this proposal by analyzing in detail the properties of the model Hamiltonian for the case of oxygen by diagonalization of small clusters. We find that this model Hamiltonian is likely to lead to superconductivity for realistic parameters.

We start in Sec. II by discussing the properties of the model Hamiltonian for a single site, and in Sec. III we derive plausible parameters for the Hamiltonian for the case of oxygen mainly from atomic physics considerations. In Sec. IV we analyze the effective interaction between holes and the effective bandwidth of holes by diagonalizing clusters of 2, 4, and 8 sites with 0, 1, and 2 holes, and in Sec. V we study the doping dependence in the 8-site cluster. We conclude in Sec. VI by discussing the implications of our results to our understanding of high-T_c superconductivity.

II. ATOMIC HAMILTONIAN

We describe the interaction between a closed-shell anion and up to two added holes by the site Hamiltonian:[6,7]

$$H_{\text{site}} = V(n_\uparrow + n_\downarrow)\sigma_z + \omega(\cos\theta\sigma_z + \sin\theta\sigma_x) + U_0 n_\uparrow n_\downarrow \ , \tag{1}$$

where the pseudospin operators σ_z, σ_x describe two states of the background outer filled shell, and n_σ is the hole occupation number with spin $\sigma = \uparrow, \downarrow$. V is the interaction strength between the holes and the outer shell, and U_0 the bare interaction between two holes. The parameter θ determines the overlap of the background wave function with and without holes, and ω represents an excitation energy of the outer shell.

The ground-state energy of the Hamiltonian Eq. (1) with n holes is

$$E_0(n) = -(V^2 n^2 + \omega^2 + 2Vn\omega\cos\theta)^{1/2} + U_0\delta_{n,2} \tag{2}$$

and the effective interaction between two added holes is

$$U_{\text{eff}} = E_0(2) + E_0(0) - 2E_0(1) \ . \tag{3}$$

Another important quantity is the overlap between the ground-state wave function with different number of holes, n, $|0;n\rangle$ given by

$$S(0,1)=\langle 0;0|0;1\rangle\ , \tag{4a}$$

$$S(1,2)=\langle 0;1|0;2\rangle\ , \tag{4b}$$

$S(0,1)$ determines the single-hole effective bandwidth in a lattice of anions. The effective hopping for holes is

$$t_{\text{eff}}=tS(0,1)^2 \tag{5}$$

with t the bare hopping. A small $S(0,1)$ will give rise to an effective narrow band.

Figure 1 shows U_{eff} versus ω, and Fig. 2 the corresponding overlaps, for $V=1$, $U_0=0$, and various values of θ. Results for other V's are obtained by simple scaling; $U_0\neq 0$ simply adds to U_{eff} and does not modify the overlaps. We see that the effective interaction is most attractive for $\theta\to\pi$, and $\omega\sim V$; for $\theta\to\pi$, $S(0,1)$ is small for $\omega<V$ and large for $\omega>V$, and $S(1,2)$ behaves in the opposite way. These results are easy to understand from the strong-coupling limit: for $\omega<V$ and $\theta\to\pi$ the states of the background $|\uparrow\rangle,|\downarrow\rangle$ in the basis of eigenstates of σ_z are

$$|0;n=0\rangle=|\uparrow\rangle,\quad E=-\omega\ , \tag{6a}$$

$$|0;n=1\rangle=|\downarrow\rangle,\quad E=-V+\omega\ , \tag{6b}$$

$$|0;n=2\rangle=|\downarrow\rangle,\quad E=-2V+\omega\ , \tag{6c}$$

and $U_{\text{eff}}=-2\omega$, while for $V<\omega<2V$

$$|0;n=0\rangle=|\uparrow\rangle,\quad E=-\omega\ , \tag{7a}$$

$$|0;n=1\rangle=|\uparrow\rangle,\quad E=V-\omega\ , \tag{7b}$$

$$|0;n=2\rangle=|\downarrow\rangle,\quad E=-2V+\omega\ , \tag{7c}$$

with $U_{\text{eff}}=2\omega-4V$. That is, in the first case the first hole will change drastically the state of the background and the second hole only slightly, and the converse occurs in the second case. As θ is reduced, the effective attraction becomes smaller and the overlaps increase. For the case of interest in this paper, oxygen anions, the situation described by Eq. (6) is qualitatively applicable, as we discuss in Sec. III.

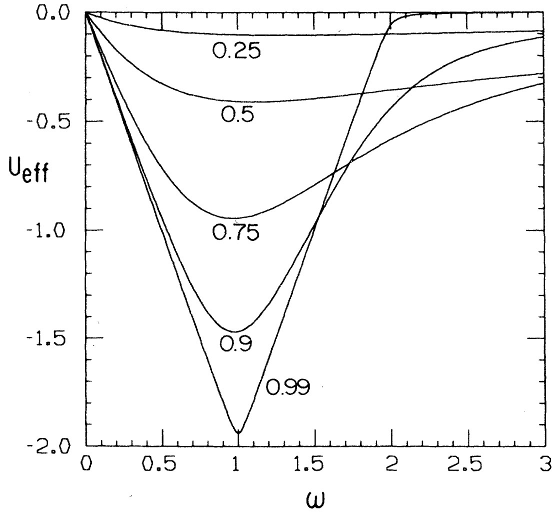

FIG. 1. Effective interaction of two holes on a single site with Hamiltonian Eq. (1) vs ω. $V=1$, $U_0=0$. The numbers next to the curves are the values of θ/π.

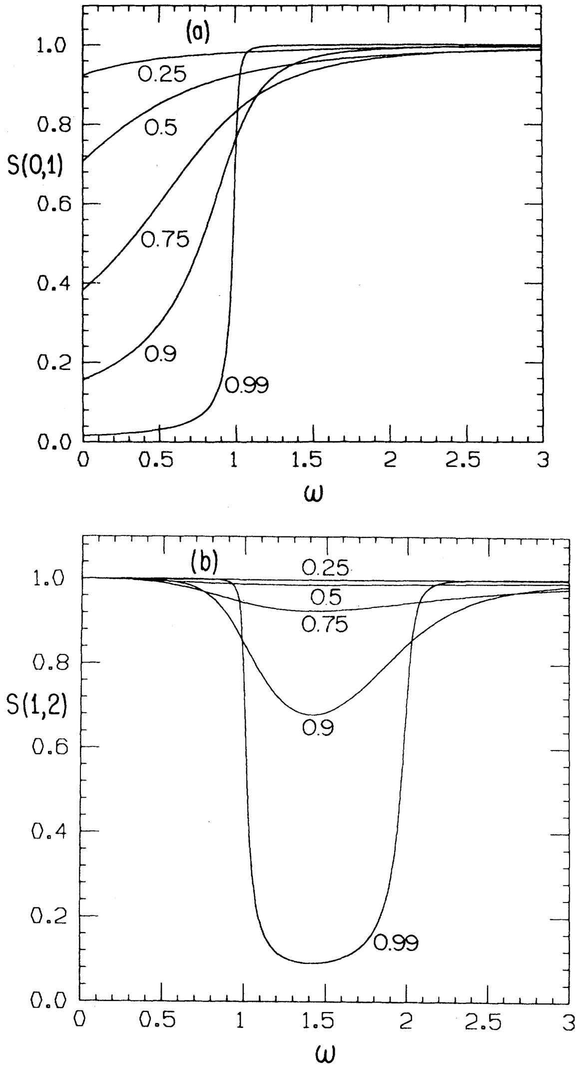

FIG. 2. Overlap of single-site wave functions with zero and one hole (a) and with one and two holes (b) [Eq. (4)] vs ω. $V=1$. Numbers next to curves are θ/π.

III. ATOMIC PARAMETERS FOR OXYGEN

We discuss here an estimate of the parameters in Eq. (1) for the case of oxygen. U_0 describes the bare interaction between two holes in O^{2-} without modifying the state of the outer shell. This can be estimated from the Slater integral[8] $F^0(2p,2p)\sim 20.5$ eV for O^0 (the spherically averaged Coulomb interaction between two electrons in the p shell). Alternatively, we can estimate it from the ionization energies of O^{3+} and O^{2+}:[9]

$$I(\mathrm{O}^{3+})=77.4\ \mathrm{eV}\ , \tag{8a}$$

$$I(\mathrm{O}^{2+})=54.9\ \mathrm{eV}\ , \tag{8b}$$

giving an estimate

$$U_0=I(\mathrm{O}^{3+})-I(\mathrm{O}^{2+})=22.5\ \mathrm{eV}\ . \tag{8c}$$

The reason for using O^{3+} and O^{2+} is to avoid including the effect of these electrons on other electrons in the p shell in the estimate of the bare U_0. These two estimates are very close, and we will consider $U_0=22.5$ eV to be an upper bound in what follows.

The first two terms in Eq. (1) describe the change in the orbitals and energies of the filled p shell when holes are added to O^{2-}, which may be called "static relaxation"[10] or simply polarization of the outer shell. This relaxation or polarization substantially *reduces* the U for two holes added to O^{2-}. The electron affinities of O^0 and O^- are[11]

$$E(\mathrm{O}^-)-E(\mathrm{O})=-1.45\ \mathrm{eV}\ , \tag{9a}$$

$$E(\mathrm{O}^{2-})-E(\mathrm{O}^-)=8.75\ \mathrm{eV}\ , \tag{9b}$$

where O, O^- and O^{2-} correspond to $n=2$, 1, and 0 holes, respectively. This yields an effective U of

$$U_{\mathrm{eff}}=E(\mathrm{O}^{2-})+E(\mathrm{O})-2E(\mathrm{O}^-)=10.2\ \mathrm{eV}\ .$$

This reduction from the bare $U\sim 20$ eV to the effective U is accounted for in the Hamiltonian Eq. (1) by the interaction of the holes with the background (the pseudospin) with appropriate values of V and ω. We do not attempt to compute V and ω from first principles but choose them to satisfy Eq. (9). Table I lists values of ω and V obtained in this fashion as a function of θ, as well as the overlaps of the ground-state wave functions Eq. (4).

Now we know that O^{2-} does not exist in free space, while O^- does. That is, the "wave function" of O^{2-} in free space extends to infinity, while the wave function of the outer electrons in O^- is not very different from that in O.[12] In the solid, O^{2-} is stabilized by Madelung energy, but we still expect its wave function to be substantially more extended and distorted from spherical symmetry than that of O^- and O. Bussmann *et al.*[13] have emphasized that O^{2-} in perovshites exhibits a strongly anisotropic charge distribution. That is, the overlap $S(0,1)$ should be small and the overlap $S(1,2)$ should be close to unity, situating us in the case qualitatively described by Eq. (6), i.e., $\theta\to\pi$, $\omega<V$.

TABLE I. Parameters of the effective atomic Hamiltonian Eq. (1) that satisfy the conditions (9), and hence $U_{\mathrm{eff}}=10.2$ eV. The overlaps S are defined in Eq. (4).

θ/π	ω (eV)	V (eV)	$S(0,1)$	$S(1,2)$
1	6.15	21.04	0	1
0.9	6.41	21.12	0.221	0.9993
0.8	7.30	21.38	0.434	0.997
0.7	9.37	21.96	0.634	0.993
0.6	14.76	23.42	0.812	0.987
0.5	55.71	32.43	0.966	0.986

An estimate for the overlap $S(1,2)$ can be obtained from atomic wave functions;[12] the radial part of the atomic $2p$ function for O and O^- is shown in Fig. 3; the overlap yields

$$S(1,2)\sim 0.91\ , \tag{10}$$

which is close to 1 but somewhat smaller than the values found in Table I for any θ. We believe this discrepancy is due to the oversimplification in modeling the background by a two-level system, but does not invalidate the assertion that our effective Hamiltonian contains the essential physics. The overlap $S(0,1)$ should be a better way to determine θ as it depends sensitively on it. Unfortunately, we do not have at the moment a way to estimate $S(0,1)$, as it will involve the wave functions in the solid and depends on the other ions in the system as well as the overall structure. Nevertheless, the above considerations, plus the fact that the effective bandwidth for holes appears to be quite small (as discussed later), lead us to believe that $S(0,1)$ is small. Note that within our model, small $S(0,1)$ implies θ close to π, which is most favorable to a large attractive U_{eff}, and a small t_{eff}, the ideal situation for high-T_c superconductivity. We believe that $\theta/\pi\sim 0.8$ to 0.9 is a reasonable choice for our case of interest. Note also that the values of V and ω obtained (Table I) are of order of magnitude of Slater integrals and atomic excitation energies, respectively.

The parameters derived in this section can be expected to be only approximate at best. Thus, in the next two sections we will study the effective interaction for a range of parameters to understand the qualitative trends.

IV. EFFECTIVE INTERACTION IN CLUSTERS

We describe the propagation of holes through the lattice of anions by the Hamiltonian

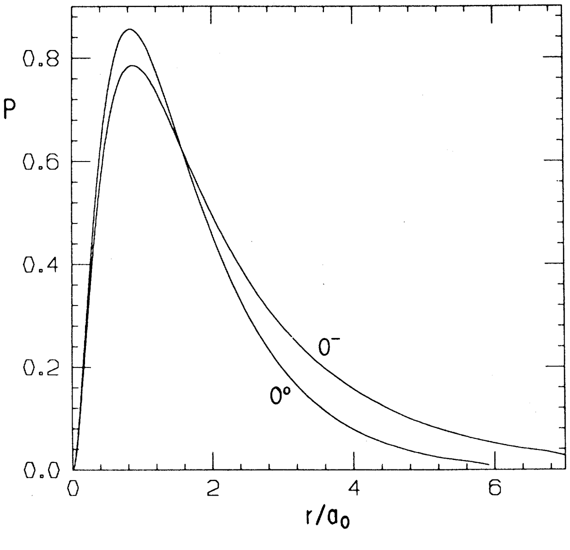

FIG. 3. Atomic wave functions for O and O^-. $P(r)/r$ gives the radial part of the $2p$ atomic wave function.

$$H=\sum_{\langle i,j\rangle} t(c_{i\sigma}^{\dagger}c_{j\sigma}+\text{H.c.})+V\sum_i (n_{i\uparrow}+n_{i\downarrow})\sigma_z^i$$
$$+\omega\sum_i(\cos\theta\sigma_z^i+\sin\theta\sigma_x^i)+U_0\sum_i n_{i\uparrow}n_{i\downarrow}\ . \qquad (11)$$

We discussed an estimate of the atomic parameters in the previous section. For the case of O, the effective atomic U is $U_p=10.2$ eV. However, in the oxide superconductors U_p is estimated from various calculations and experiments to be about $\frac{1}{2}$ this value.[14] The reduction occurs from polarization processes not included in our Hamiltonian. Nevertheless, we believe U_{eff} for any anion will be positive or else lead to an unstable situation: in particular, if U_p was negative for oxygen in the oxides any added holes would immediately pair to form O^0 that would tend to leave the sample creating vacancies.

In this section we will demonstrate that the Hamiltonian Eq. (11) can lead to an effective attractive interaction, and hence to superconductivity, for a wide range of parameters even when the on-site interaction is large and repulsive. We find the ground-state energy of the Hamiltonian Eq. (11) $E_N(n)$ on clusters of size N containing n holes and compute the effective interaction between two holes:[15]

$$U_{\text{eff}}=E_N(n+2)+E_N(n)-2E_N(n+1)\ . \qquad (12)$$

We considered clusters of size $N=2$, 4, and 8, as shown in Fig. 4. In order for the results of the different clusters to resemble each other as much as possible, we have chosen periodic boundary conditions in all cases and in the two-site cluster the hopping was taken to be twice as large as in the 4- and 8-site clusters. With that choice, the single-hole bandwidth in the noninteracting case is $8t$ for all the clusters studied.

If $U_{\text{eff}}<0$, as the cluster size diverges it will lead to superconductivity unless another instability like charge-density wave (CDW) occurs. For an almost empty band, however, and short-ranged interactions, no tendency to CDW occurs. Because of the high polarizability of the oxygen anions the long-range interaction between O holes will be highly screened and thus can be neglected.

Let us start with the parameters derived in the previous section. Figure 5 shows U_{eff} for two holes versus hopping t for $N=2$, 4, and 8 with $V=21.4$, $\omega=7.3$, $U_0=22.5$, and $\theta=0.8\pi$. For $t=0$ the effective interaction is zero as the two added holes go on different sites (the effective interaction for a single site is repulsive). As t is turned on U_{eff} first increases but for sufficiently large t it becomes increasingly negative as t increases. The minimum t that yields an attractive interaction increases somewhat with cluster size and is $t\sim 1$ for $N=8$. The direct hopping between O holes in the oxide superconductors is estimated at about 0.65 eV,[14] and there should be additional contributions from hopping through the cations. We should remember, however, that our parameters are only approximate; in particular, U_0 should probably be taken smaller, as mentioned before. With $U_0=17$ eV we get an effective on-site repulsion of $U_p=4.7$ eV, close to various estimates,[14] and a minimum t where U_{eff} becomes negative of $t=0.55$ for the 8-site cluster. Also taking θ closer to π it is easy to reduce further the values of t that yield attractive interactions. Note that the fact that the interaction becomes more attractive as t increases suggests that the superconducting T_c will increase with pressure.

We find in this and the following cases that as the size of the cluster increases the magnitude of the effective interaction decreases. This is reasonable as the effective hopping of holes from cluster to cluster will also decrease with cluster size. Similar behavior is observed in the attractive Hubbard model.[16]

Figure 6 shows the dependence of U_{eff} on U_0. Note that the effective interaction remains attractive up to very large values of U_0, $U_0=22.3$ eV for the 8-site cluster. This corresponds to an effective on-site repulsion $U_p=10.0$. For these parameters, U_p becomes negative for $U_0<12.3$. Thus there is a wide range of physically acceptable values of U_0 that yield $U_p>0$ and $U_{\text{eff}}<0$ in the clusters. As the cluster becomes bigger the maximum U_0 that yields attractive interactions decreases somewhat.

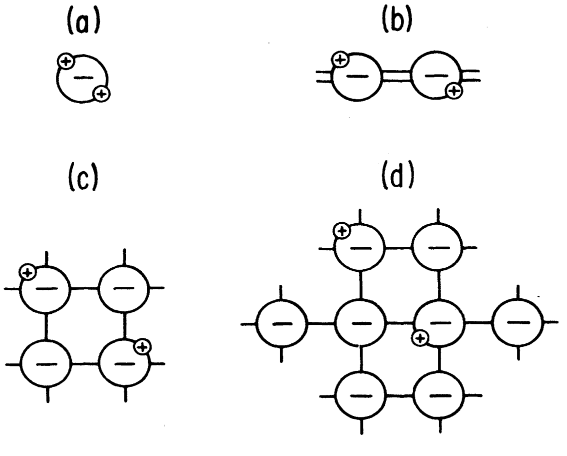

FIG. 4. Clusters used in exact diagonalization calculations. Periodic boundary conditions were used in all cases, and for $N=2$ the hopping was taken twice as large as for $N=4$ and 8.

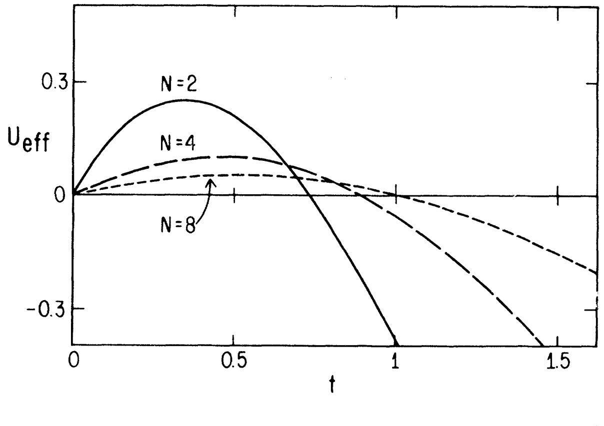

FIG. 5. Dependence of U_{eff} on hopping t. $V=21.4$, $\omega=7.3$, $U_0=22.5$, and $\theta=0.8\pi$. The effective interaction for a single site is $U_{\text{eff}}=10.2$ eV in this case.

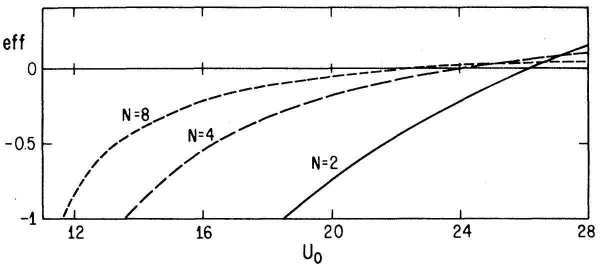

FIG. 6. Dependence of $U_{\rm eff}$ on on-site repulsion U_0. $V=21.4$, $\omega=7.3$, $t=1$, and $\theta=0.8\pi$.

In Fig. 7 we examine the dependence of $U_{\rm eff}$ on θ for the case $V=21.4$, $\omega=7.3$, $U_0=17$, and $t=1$. $U_{\rm eff}$ is attractive in the region of large θ, as expected. For the single site, these values of the parameters yield values of $U_{\rm eff}$ that are not unreasonable: $U_{\rm eff}=2.6$, 3.0, 3.8, 4.7, 5.8, and 6.9 eV for $\theta=0.95$, 0.9, 0.85, 0.8, 0.75, and 0.7, respectively. The effective interaction changes sign approximately at the same value of $\theta\sim0.7\pi$ in all cases.

As mentioned earlier, we can estimate the single-hole effective hopping $t_{\rm eff}$ from the overlap of the single site wave functions with zero and one hole, Eq. (5). Alternatively, we can look at the energy lowering of a single hole in a cluster compared to its energy in a single site to obtain an estimate for its bandwidth. This energy lowering is $-4t$ in the noninteracting case. Thus we define an "effective hopping" derived from the N-site cluster by

$$t_{\rm eff}^{(N)}=\{E_N(1)-E_N(0)-[E_1(1)-E_1(0)]\}/4\ . \qquad (13)$$

In Fig. 8 we plot these effective hoppings as a function of θ for the same parameters as Fig. 7. The fact that the estimates obtained through the various methods give very similar results gives us confidence in our procedure to estimate $t_{\rm eff}$, and in particular in the simple expression Eq. (5). Note that $t_{\rm eff}$ goes to zero as $\theta\to\pi$, as we had found in Fig. 2(a) for $\omega<V$. Figures 7 and 8 clearly show that the region where the interaction is most attractive is also the region that gives rise to the most band narrowing. For this case, $t_{\rm eff}$ is less than $0.35t$ in the region where $U_{\rm eff}<0$; the band band-narrowing is about 5 for $\theta=0.8\pi$ and 12 for $\theta=0.9\pi$.

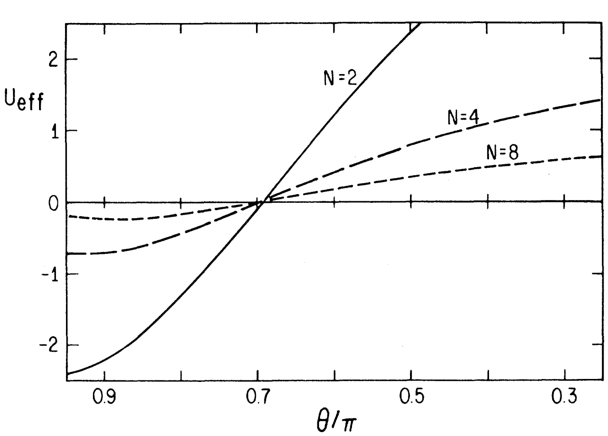

FIG. 7. Dependence of $U_{\rm eff}$ on overlap parameter θ. $V=21.4$, $\omega=7.3$, $U_0=17$, and $t=1$.

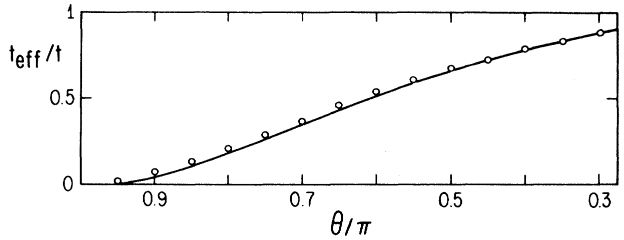

FIG. 8. Effective hopping for a single hole vs θ from Eq. (5) (solid line). $V=21.4$, $\omega=7.3$, $U_0=17$, and $t=1$. The circles show $t_{\rm eff}$ calculated from the $N=2$ cluster as described in the text [Eq. (13)]. The results from 4- and 8-site clusters are indistinguishable from the ones for $N=2$.

We consider next the dependence of the effective interaction on V. Figure 9 shows $U_{\rm eff}$ versus V for $\omega=7.3$, $U_0=17$, $\theta=0.8\pi$, and $t=1$. It decreases monotonically with V, as one would expect. The value of V where $U_{\rm eff}$ changes sign is almost the same for all clusters, $V\sim12$ for this case. For the single site, $U_{\rm eff}$ decreases slowly with V in this interval, from 6.8 at $V=10$ to 4.3 at $V=32$.

Finally, Fig. 10 shows $U_{\rm eff}$ versus ω for $V=21.4$, $\theta=0.8$, $U_0=17$, and $t=1$. It shows a minimum at low frequency that becomes sharper as the cluster size increases. This is presumably associated with the reduction of the instantaneous repulsive U_0 to a weaker "pseudopotential," and this reduction is most effective for low frequencies. $U_{\rm eff}$ also starts to decrease at large ω; this is associated with the on-site $U_{\rm eff}$ becoming negative.

We have also calculated the energy of a third particle added to the 8-site cluster to see if there is a tendency to condensation rather than pairing. The quantity[16]

$$\Delta'=E_N(3)-E_N(2)-[E_N(1)-E_N(0)] \qquad (14)$$

was calculated and found to be always positive, indicating that there is no tendency to an instability in the regimes where $U_{\rm eff}<0$. This is in contrast to the model discussed

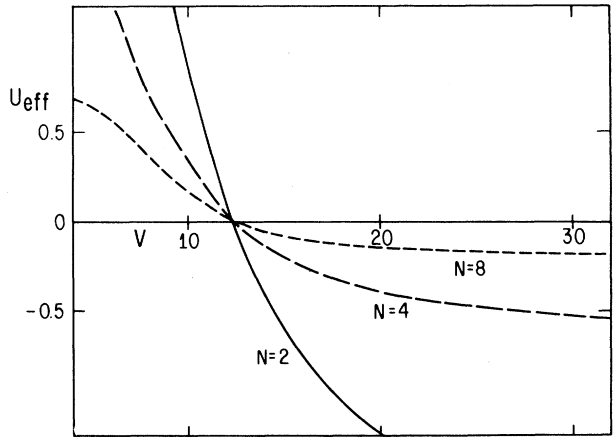

FIG. 9. Dependence of $U_{\rm eff}$ on V. $\omega=7.3$, $U_0=22.5$, $t=1$, and $\theta=0.8\pi$.

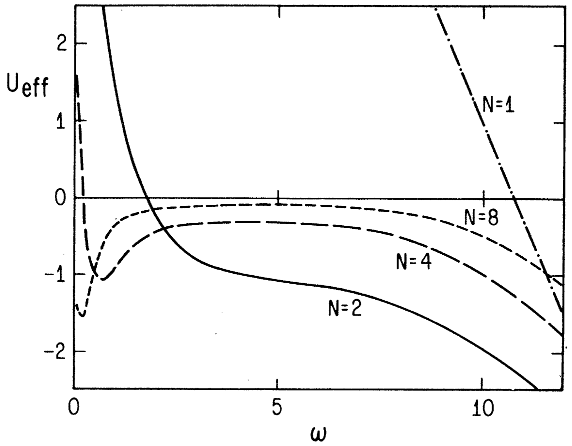

FIG. 10. Dependence of U_{eff} on ω. $V=21.4$, $U_0=22.5$, $t=1$, and $\theta=0.8\pi$.

in Ref. 11, where the attractive interaction could easily lead to an instability.

V. DOPING DEPENDENCE

To obtain information on the dependence of the effective interaction on band filling, we now consider U_{eff} on 8-site clusters for 2, 3, and 4 particles and compare it with the one for 0, 1, and 2 particles. Unfortunately, there is a sensitive dependence on the shape of the cluster and the boundary conditions. For the 8-site cluster with periodic boundary conditions we find $U_{\mathrm{eff}}<0$ for 2, 3, 4 particles even as $V\rightarrow 0$. This is related to the fact that there is a large degeneracy at the Fermi energy for this case in the noninteracting case: the single-particle energy level structure is one state at $E_1=-4t$ and six states at $E_2=0$, the Fermi energy for 3 to 14 particles. A similar situation was observed recently in studies of the repulsive Hubbard model near half-filling:[16] in one dimension for sizes N multiple of 4, $U_{\mathrm{eff}}<0$ was found around half-filling because of the degenerate states at the Fermi ener-

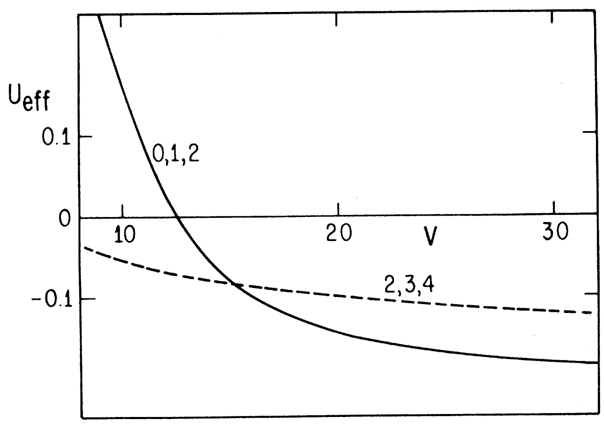

FIG. 11. U_{eff} vs V for 8-site cluster of Fig. 3. $\omega=7.3$, $U_0=17$, $t=1$, and $\theta=0.8\pi$ for 0,1,2 and 2,3,4 particles.

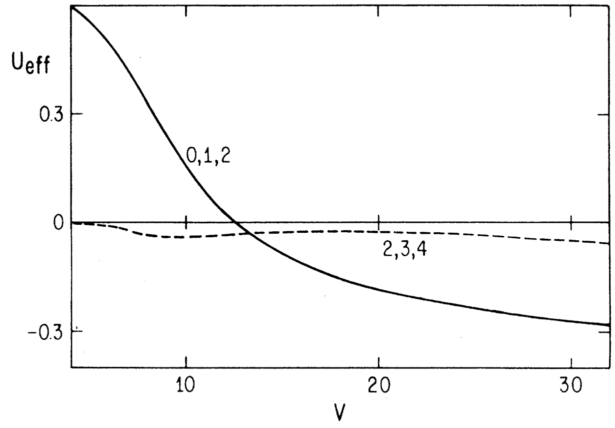

FIG. 12. U_{eff} vs V for 4×2 cluster. $\omega=7.3$, $U_0=17$, $t=1$, and $\theta=0.8\pi$.

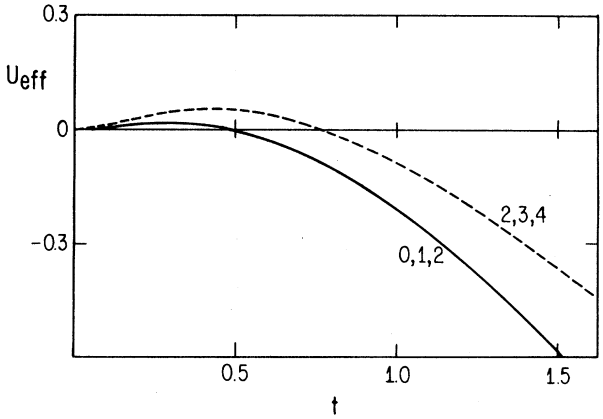

FIG. 13. U_{eff} vs t for 4×2 cluster. $V=21.4$, $\omega=7.3$, $U_0=17$, and $\theta=0.8$.

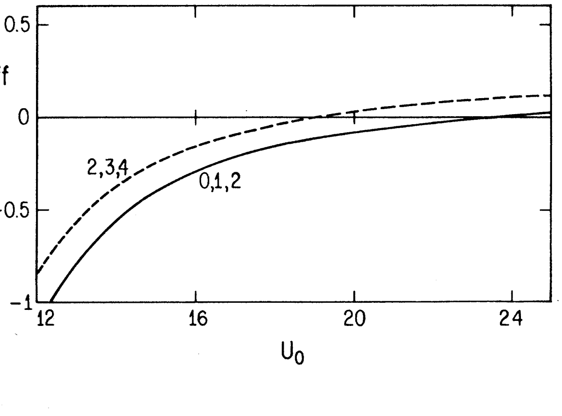

FIG. 14. U_{eff} vs on-site repulsion U_0 for 4×2 cluster. $V=21.4$, $\omega=7.3$, $t=1$, and $\theta=0.8\pi$.

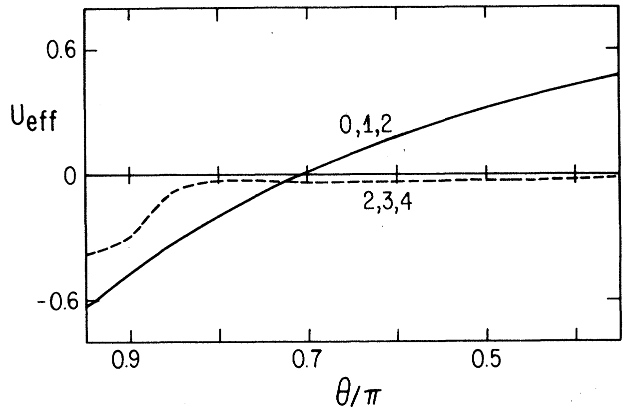

FIG. 15. U_{eff} vs θ for 4×2 cluster. $V=21.4$, $\omega=7.3$, $U_0=17$, and $t=1$.

gy. Similar effects occur in two dimensions. This is an unphysical artifact of finite systems, and the effect should disappear as the cluster size increases. In addition to the 8-site cluster of Fig. 4, we have therefore considered a 4×2 cluster with periodic boundary conditions where the single-particle energy level structure has less degeneracy: the lowest state at $E_1=-4t$ is nondegenerate and the next state at $E_2=-2t$ is doubly degenerate only.

Figure 11 shows U_{eff} versus V for the 8-site cluster of Fig. 1 for 0,1,2 and 2,3,4 particles. Over most of the range studied the higher doped case shows less attractive interaction; we believe the crossing for small V is related to the unphysical effect discussed above. Similarly, Fig. 12 shows the same case for the 4×2 cluster, exhibiting qualitatively similar behavior but less attraction in the higher doped case.

Figure 13 shows the dependence on hopping t for the 4×2 lattice. Once again, for higher doping the interaction becomes less attractive. Figure 14 shows the dependence on U_0, exhibiting the same qualitative effect. In Fig. 15 we show the dependence on θ. Here again there is a small attractive interaction in the higher doped case in a region where the lower-doped case is repulsive, which we believe is due to the unphysical effect discussed above; for $\theta\rightarrow\pi$, however, where the interaction becomes strong, once again the lower doped case shows a larger effective attraction.

To summarize, despite some difficulty in interpretation due to boundary effects, we believe the results discussed in this section strongly suggest that the effective attractive interaction in our model will *decrease* as the band-filling increases. This is easy to understand qualitatively: for small band filling the holes have room to move around and avoid the repulsive on-site interaction while still taking advantage of the retarded attractive interaction; as the band filling increases, the effect of the repulsive interaction becomes stronger and will at some level of filling lead to a net effective repulsive interaction at the Fermi surface in the parameter regime where the effective interaction for a single site is repulsive.

VI. DISCUSSION

We have studied the effective interaction of holes in small clusters with an effective Hamiltonian to describe the interaction of holes with the filled outer shell of O^{2-} anions. We found this effective interaction to be attractive in a wide range of parameters that include our estimates for the case of O^{2-} anions from atomic properties. The following findings we believe deserve special attention.

(1) The effective interaction is found to be attractive in the same regime where there is significant band narrowing, θ close to π. Many experimental observations point towards a small polaron model to explain the normal-state properties, as discussed by Scalapino *et al.*[17] for the case of electron-phonon interactions. Their analysis of the normal-state properties applies equally well to the "electronic polaron" that our model describes in the region $\theta\rightarrow\pi$. Consistent with experimental information, our model predicts a large enhancement of the thermodynamic density of states manifest in an enhancement of susceptibility and specific-heat coefficient by the same ratio in that regime. In addition, as discussed in Ref. 17, optical properties, thermopower, and resistivity measurements are also consistent with conduction by small polarons. Our analysis of the single-site problem (Sec. II) showed that the fact that the overlap of the wave function of O^{2-} with that of O^- is expected to be much smaller than the corresponding one for O^- and O^0 puts us necessarily in the region of parameter space $\theta\rightarrow\pi$ in our effective Hamiltonian that gives rise to a narrow band. This is also the region that gives rise to the strongest effective attraction. We believe the combination of these facts is very strong evidence in support of our picture.

(2) The energy scale of the effective interaction (ω) is much larger than the effective hopping t_{eff}. This implies that within the standard BCS treatment of superconductivity the cutoff in the BCS integral equation for T_c will be given on one side by the Fermi energy rather than the energy scale of the interaction. This leads to a dependence of T_c on density of holes $T_c\propto n^{1/2}$, which is consistent with what is observed experimentally for small doping. Our comparison of the effective interaction in the 8-site cluster for 0,1,2 particles and 2,3,4 particles indicated that the effective attraction would be reduced as the doping increases. This suggests that as a function of n T_c would first increase due to increasing Fermi energy, reach a maximum, and then drop due to the decrease in the attractive interaction. This is consistent with what is observed experimentally.[18]

(3) The effective interaction becomes more attractive with increasing t, which suggests that the effect of pressure should be to raise T_c. This is observed in all the oxide superconductors. This behavior also provides an explanation for the lower T_c's observed in the non-Cu oxides compared to the Cu oxides: the O-O distance in $Ba_{1-x}K_xBiO_3$ for example is 3.04 Å,[19] while it is only $\sim$2.75 Å in $YBa_2Cu_3O_{7-\delta}$; thus, one would expect the effective hopping between oxygens to be smaller in the former case. Note also that if the hopping t is too small

the effective interaction is not attractive, which is one possible reason for the absence of superconductivity in other oxides.

(4) Finally, we would like to stress, as discussed in Ref. 6, that we expect this generalized mechanism to be responsible also for the "transient" high-temperature superconductivity observed in CuCl (Ref. 20) and CdS (Ref. 21) occurring through hole conduction in Cl^- and S^{2-} anions respectively, and to play a role in other "conventional" superconductors. For example, our model would naturally explain why superconductivity occurs under pressure in the semimetals and semiconductors in the right portion of the Periodic Table.[22]

To conclude, we believe that the picture of high-temperature superconductivity discussed in this paper and in Ref. 6 is quite compelling. We have shown that our model yields effective attractive interactions for realistic parameters, and that it seems to be able to correlate a variety of experimental facts. A more realistic calculation of the parameters in our effective Hamiltonian is clearly feasible, and also a more detailed description of the local interaction of the hole with the outer shell background appears to be within reach. Combined with a calculation of the superconducting T_c by nonperturbative Monte Carlo calculations or reliable analytic means, these calculations should definitively establish the validity of the mechanism discussed here.

The mechanism discussed here is incompatible with electrons being the charge carriers in the CuO_2 planes, as recently proposed for $Nd_{2-x}Ce_xCuO_{4-y}$.[23] We speculate that in these materials electron doping of Cu^{2+} causes transfer of electrons in neighboring O^{2-} to other nearby Cu^{2+} because of nearest-neighbor Coulomb repulsion, the net result being creation of hole carriers on O^{2-} anions. This becomes possible in these materials due to the absence of apical O^{2-} ions, which lowers the energy for transferring electrons from O^{2-} to the Cu^{2+} ions.

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[1] Proceedings of the International Conference on Higher Temperature Superconductors and Materials and Mechanisms of Superconductivity, Interlaken, Switzerland, 1988, edited by J. Müller and J. L. Olsen [Physica C **153-155**, (1988)].

[2] L. F. Mattheiss, E. M. Gyorgy, and D. W. Johnson, Phys. Rev. B **37**, 3745 (1988); R. J. Cava *et al.*, Nature (London) **332**, 814 (1988); B. Batlogg *et al.*, Phys. Rev. Lett. **61**, 1670 (1988).

[3] J. E. Hirsch, in *Theories of High Temperature Superconductivity,* edited by J. W. Halley (Addison-Wesley, Redwood City, CA, 1988), p. 241.

[4] B. T. Matthias, in *Superconducting: Proceedings of the International Conference on the Science of Superconductivity, Stanford, 1969,* edited by F. Chilton (North-Holland, Amsterdam, 1971), p. 69.

[5] V. L. Ginzburg, Usp. Fiz. Nauk **101**, 185 (1970) [Sov. Phys. Usp. **13**, 335 (1970)], and references therein.

[6] J. E. Hirsch, Phys. Lett. A **134**, 451 (1989); also in *Mechanisms of High Temperature Superconductivity,* edited by H. Kamimura and A. Oshiyama (Springer, Berlin, 1989), p. 34.

[7] This type of Hamiltonian has been used in the past in models for excitonic superconductivity: W. A. Little, Phys. Rev. **134**, A1416 (1964); and Int. J. Quant. Chem. **15**, 545 (1981); R. Bari, Phys. Rev. Lett. **30**, 790 (1973); J. E. Hirsch and D. J. Scalapino, Phys. Rev. B **32**, 117 (1985); **32**, 5639 (1985). However, the parameter regime discussed here is very different than the one considered in these excitonic models: for example, the excitation energy ω will be taken here to be much larger than the hopping amplitude from site to site.

[8] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960).

[9] C. E. Moore, *Atomic Energy Levels,* Natl. Bur. Stand. (U.S.) NBS Circ. No. 467 (U.S. GPO, Washington, D.C., 1949), Vol. I.

[10] D. A. Shirley, Phys. Rev. A **7**, 1520 (1973).

[11] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Wiley, New York, 1988).

[12] D. R. Hartree, *The Calculation of Atomic Structures* (Wiley, London, 1957), p. 171.

[13] A. Bussmann *et al.*, Ferroelectrics **25**, 343 (1980).

[14] A. K. McMahan, R. M. Martin, and S. Satpathy, Phys. Rev. B **38**, 6650 (1988); E. B. Stechel and D. R. Jennison, *ibid.* **38**, 4632 (1988); M. Schluter, M. S. Hybertsen, and N. E. Christensen, Physica C **153-155**, 1217 (1988) and (unpublished); G. A. Sawatzky (unpublished).

[15] J. E. Hirsch and D. J. Scalapino, Phys. Rev. B **32**, 5639 (1985); in this paper on "double valence fluctuating molecules" a mechanism for attractive interactions somewhat related to the one explored here was discussed.

[16] J. E. Hirsch, E. Loh, D. J. Scalapino, and S. Tang, Phys. Rev. Lett. **60**, 1668 (1988); Phys. Rev. B **39**, 243 (1989); and (unpublished).

[17] D. J. Scalapino, R. T. Scalettar, and N. E. Bickers, in *Proceedings of the International Conference on Novel Mechanisms of Superconductivity,* edited by S. E. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 475.

[18] J. B. Torrance *et al.*, Phys. Rev. Lett. **61**, 1127 (1988).

[19] R. J. Cava *et al.*, Nature **332**, 814 (1988).

[20] T. H. Geballe and C. W. Chu, Commun. Solid State Phys. **9**, 115 (1979).

[21] G. W. Homan *et al.*, Physica B+C **107**, 9 (1982).

[22] H. Stern, Phys. Rev. B **8**, 5109 (1973); N. B. Brandt and N. I. Ginzburg, Contemp. Phys. **10**, 355 (1969).

[23] Y. Tokura *et al.*, Nature **337**, 345 (1989).