Polaronic superconductivity in the absence of electron-hole symmetry

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A major drawback of theories of superconductivity based on small polarons has been that the effective mass of the carriers becomes extremely large in the parameter regime where the effective interaction is attractive. An implicit assumption in these theories has been the existence of electron-hole symmetry. We consider here the Holstein model for small polarons and show that inclusion of electron-hole symmetry-breaking perturbations leads to a pairing mechanism that circumvents the above-mentioned difficulty. Such perturbations arise from a dependence of coupling constant and vibrational frequency on the density of carriers, as well as from anharmonicity in the vibrational potential. The possibility of using such a polaronic model arising from purely electron-phonon interactions to describe superconductivity in high-T_c oxides is considered. It is concluded that experimental evidence disfavors it, while it favors an electron-hole asymmetric small-polaron model arising from excitations with energies of electronic scale together with a small admixture of electron-phonon effects.

I. INTRODUCTION

Polaron models to describe various properties of high-temperature oxide superconductors have been proposed by several authors.[1-9] Most efforts have centered around polarons arising from electron-phonon interactions,[1-6] although spin-polaron[7,8] as well as electronic polaron models[9] have also been discussed.

Perhaps the most comprehensive work to date has been that of Alexandrov and Ranninger,[1,2] who have studied both normal and superconducting properties. In the model considered by Alexandrov[1] (a Holstein model for small polarons[10]) as well as in most other studies, tightly bound pairs exist above T_c (bipolarons) that Bose condense into the superconducting state as the temperature is lowered.[11,12] A major drawback of these models is that the pair effective mass becomes extremely large in the parameter regime where the polaron-polaron interaction is attractive, resulting in very low transition temperatures.

One approach proposed to circumvent this problem, pursued by Emin, [4] has been to consider a parameter regime that gives rise to large polarons rather than small ones, which are expected to have higher mobility. However, it appears that achieving this regime would require extreme fine-tuning of parameters, since the transition from a weakly coupled system to the small-polaron regime as a function of electron-phonon coupling appears to be extremely sharp.[13] Another proposed approach has been to use more complicated variational states than those associated with the usual Lang-Firsov transformation, involving two-phonon coherent states.[14,3] In our opinion it has not been convincingly established that these states are closer to the exact eigenstates of the Hamiltonian than the conventional ones.

In this paper we explore a third possibility, which involves adding to the conventional Holstein Hamiltonian various electron-hole symmetry-breaking perturbations. One such modification has already been discussed briefly elsewhere.[15] Our motivation is that there is no fundamental reason why a Hamiltonian describing a real system should be electron-hole symmetric, and hence we argue that the conventional Holstein Hamiltonian is nongeneric. These symmetry-breaking perturbations give rise to a kinetic pairing mechanism, which, depending on the sign of the perturbation, leads to pairing of carriers either at the bottom or top of the band. Physical arguments are presented to the effect that the sign of these perturbations is always such that pairing occurs at the top of the band, i.e., for holes. The resulting polaron pairs have a mobility that can be considerably larger than that of the individual polarons, in contrast to the situation in the conventional pairing mechanism where the pair mobility is always smaller than the single-particle mobility. In addition, the single-polaron mobility here can be substantially larger in the parameter regime of attractive pairing interactions than in the conventional one.

One such electron-hole symmetry-breaking perturbation is found to be anharmonic corrections to the harmonic-oscillator potential. There has recently been considerable interest in the possibility that anharmonic effects associated with oxygen vibrations may play a fundamental role in the superconductivity of high-T_c oxides.[16-20] Our treatment here suggests another reason for the possible importance of anharmonic effects besides the ones given by previous authors: We find that anharmonicity of less than 1% can induce superconductivity in the presence of substantial Coulomb repulsion.

It should also be pointed out that the possibility of asymmetry between electron and hole polarons in quasi-one-dimensional materials has recently been raised as an explanation for observed optical-absorption spectra.[21] Various tight-binding Hamiltonians have been proposed to model it.[21,22]

This paper is organized as follows. In Sec. II we briefly review the conventional pairing mechanism for bipolarons. Section III explains how electron-hole symmetry-

breaking perturbations give rise to a new source of pairing energy while at the same time enhancing the pair mobility. In Sec. IV we discuss the various generalizations of the Holstein Hamiltonian that give rise to this effect and argue that they are generic, i.e., that they will generally exist in real systems. We also give quantitative estimates for the magnitude of these perturbations that is required to give rise to superconductivity. In Sec. V we discuss the isotope effect arising in these Hamiltonians. Section VI discusses other physical aspects of these models, and Sec. VII considers the applicability of these models to high-T_c oxide superconductors. Concluding remarks are given in Sec. VIII.

II. PAIRING OF SMALL POLARONS: THE CONVENTIONAL MECHANISM

We consider a Holstein Hamiltonian describing the coupling of carriers (electrons or holes) to a local vibrational degree of freedom q_i. This degree of freedom can be thought of as either an internal vibrational coordinate of a molecule or a lattice displacement of the atom associated with an optic mode. The Hamiltonian for a site i is given by

$$H_i=\frac{p_i^2}{2M}+\frac{1}{2}Kq_i^2+\alpha q_i n_i+Un_{i\uparrow}n_{i\downarrow} , \tag{1}$$

with $n_i=n_{i\uparrow}+n_{i\downarrow}$ the number of carriers at a nondegenerate orbital at the site (0, 1, or 2) and p_i the momentum canonically conjugate to q_i. U is the electron-electron repulsion at the site. Note that this Hamiltonian is particle-hole symmetric: The transformation $n_{i\sigma}\rightarrow 1-n_{i\sigma}$, $q_i\rightarrow -q_i$, leaves it invariant except for irrelevant additive terms.

On completing the square, one obtains

$$H_i=\frac{p_i^2}{2M}+\frac{1}{2}K\left[q_i+\frac{\alpha}{K}n_i\right]^2+U_{\rm eff}n_{i\uparrow}n_{i\downarrow}-\frac{\alpha^2}{2K}n_i , \tag{2}$$

with

$$U_{\rm eff}=U-\frac{\alpha^2}{K} , \tag{3}$$

so that the equilibrium value of the coordinate depends on the site occupation

$$q_{n_i}=-\frac{\alpha}{K}n_i . \tag{4}$$

For that value of q_i, the energy per carrier has been reduced by the polaron binding energy $\varepsilon_p=-\alpha^2/2K$. In addition, the electron-phonon coupling has caused a reduction of the electron-electron repulsion from U to $U_{\rm eff}$.

The small-polaron (self-trapped) regime occurs when the lattice deformation follows the motion of the carriers from site to site. In that regime the effective hopping amplitude for a small polaron at zero temperature is

$$t_h=tS^2 , \tag{5a}$$

$$S=e^{-\alpha^2/4K\hbar\omega} , \tag{5b}$$

with t the bare hopping amplitude for a carrier and $\omega=\sqrt{K/M}$ the vibrational frequency. This antiadiabatic regime can only occur if the condition

$$t_h<\hbar\omega \tag{6}$$

is satisfied, so that the lattice deformation instantaneously adjusts to the motion of the carrier. Pairing in this model will arise if the condition

$$U_{\rm eff}<0 \tag{7}$$

is satisfied. From Eqs. (3), (5), and (7), we obtain

$$t_h<te^{-U/2\hbar\omega} . \tag{8}$$

It can be seen that the resulting hopping amplitude is unphysically small, for a typical vibrational frequency of $\hbar\omega\sim 1000K$, and electron-electron repulsion U of the order of electronvolts.

Nevertheless, one may consider the occurrence of superconductivity in this model. If $|U_{\rm eff}|<t_h$ (and $U_{\rm eff}<0$), it will be described by the usual weak-coupling BCS theory. This requires extreme fine-tuning of parameters due to the smallness of t_h and the fact that $U_{\rm eff}$ [Eq. (3)] is the difference of two large quantities. In the more likely case of $|U_{\rm eff}|\gg t_h$, superconductivity will arise through Bose condensation of preexisting pairs (bipolarons) above T_c.[12] In the former case, T_c is proportional to t_h and in the latter case to $t_h^2/|U_{\rm eff}|$. In both cases, but particularly in the latter one, Eq. (8) indicates that the magnitude of the resulting critical temperatures would not be relevant for real systems.

One may consider more general models than Eq. (1) involving intersite phonons and intersite pairing. However, the basic difficulty remains: Electron-phonon interactions that are strong enough to overcome the local static Coulomb repulsion between carriers will generally lead to localization of the pairs[23] rather than superconductivity except at unphysically low temperatures.

III. PAIRING OF ELECTRON-HOLE ASYMMETRIC POLARONS

We denote by $|n\rangle$ the ground state of the site oscillator with n carriers at the site and define

$$S=\langle 0|1\rangle , \tag{9a}$$

$$T=\langle 1|2\rangle . \tag{9b}$$

The Hamiltonian [Eq. (1)] leads to

$$S=\exp\left[-\frac{K}{4\hbar\omega}(q_0-q_1)^2\right] , \tag{10a}$$

$$T=\exp\left[-\frac{K}{4\hbar\omega}(q_1-q_2)^2\right] , \tag{10b}$$

so that $S=T$ since $q_0-q_1=q_1-q_2=\alpha/K$. This is due to the fact that the Hamiltonian is electron-hole symmetric. Any perturbation that breaks particle-hole symmetry will lead to $S\neq T$. In that case the hopping amplitude for a carrier in the absence of other carriers is

$$t_h = S^2 t \ , \tag{11a}$$

while if another carrier is present at the site the first carrier is hopping to or from

$$t_h' = STt \ . \tag{11b}$$

The resulting effective Hamiltonian is then

$$H_{\text{eff}} = -\sum_{\substack{\langle ij \rangle \\ \sigma}} [t_h + \Delta t(n_{i-\sigma} + n_{j-\sigma})][c_{i\sigma}^{\dagger} c_{j\sigma} + \text{H.c.}] + U_{\text{eff}} \sum_i n_{i\uparrow} n_{i\downarrow} \ , \tag{12}$$

to first order in the intersite hopping t, with

$$\Delta t = tS(T - S) \ . \tag{13}$$

(Strictly speaking, another term appears that applies to hopping processes where three particles are at the two sites involved, but it is irrelevant in the dilute regime of interest here.) We have studied this Hamiltonian extensively elsewhere.[24] It gives rise to superconductivity in the dilute carrier concentration regime provided the parameters satisfy the condition

$$\frac{\Delta t}{t_h} > \left[1 + \frac{U_{\text{eff}}}{2zt_h} \right]^{1/2} - 1 \tag{14}$$

(z = number of nearest neighbors to a site) or, equivalently,

$$\frac{T}{S} > \left[1 + \frac{U_{\text{eff}}}{D_h} \right]^{1/2} , \tag{15}$$

with

$$D_h = 2zt_h \ , \tag{16}$$

the single-carrier bandwidth.

For $T = S$, the condition Eq. (15) reduces to Eq. (7). However, for $T > S$ pairing will occur in the presence of an on-site repulsion. The binding energy for pairs arises from the gain in kinetic energy of pairs compared to single carriers caused by the hopping interaction Δt. For sufficiently large T/S, pairing will occur even if the on-site repulsion is considerably larger than the single-carrier bandwidth. The optimal situation occurs for $T = 1$, i.e., when the oscillator wave functions with one carrier and two carriers at the site are the same. In that case, Eq. (15) yields

$$\frac{U_{\text{eff}}}{D_h} \leq \frac{1}{S^2} - 1 \tag{17a}$$

or, in terms of the bare bandwidth $D = 2zt$,

$$\frac{U_{\text{eff}}}{D} \leq 1 - S^2 \ . \tag{17b}$$

It is clear that for a given value of the Coulomb repulsion U this condition will be satisfied for values of the electron-phonon coupling α substantially smaller than required by the condition $U_{\text{eff}} < 0$; thus, the single-carrier hopping amplitude t_h can be substantially larger. Additionally, the effective hopping amplitude for pairs is larger than for single carriers in this model, as can be seen intuitively from Eq. (12) and is discussed in detail in Ref. 25. A major objection to bipolaronic superconductivity is thus removed.

IV. GENERALIZED HOLSTEIN MODELS

We consider various generalizations of the Holstein model [Eq. (1)] that give rise to electron-hole symmetry-breaking terms. For definiteness, we work in a hole representation, i.e., n_i (2, 1, or 0) is 2 minus the number of electrons at the site. Assume the various parameters in the Hamiltonian [Eq. (1)] depend on the site carrier density n_i:

$$H_i = \frac{p_i^2}{2M(n_i)} + \frac{1}{2} K(n_i) q_i^2 + \alpha(n_i) q_i n_i + U n_{i\uparrow} n_{i\downarrow} \tag{18}$$

(allowing for n_i dependence of U does not lead to any new physical effect). The ground-state oscillator wave function with n holes at the site is (we omit the site index)

$$\Psi_n(q) \equiv \langle q | n \rangle = \left[\frac{K(n)}{\pi \hbar \omega(n)} \right]^{1/4} \exp\left[-\frac{K(n)}{2\hbar\omega(n)} (q - q_n)^2 \right] , \tag{19}$$

with

$$q_n = -\frac{\alpha(n)}{K(n)} n \ , \tag{20a}$$

$$\omega(n) = \left[\frac{K(n)}{M(n)} \right]^{1/2} , \tag{20b}$$

and the overlap matrix element of two such wave functions with occupation numbers n and n' is

$$\langle n | n' \rangle = \int dq \Psi_n^*(q) \Psi_{n'}(q) = \left[\frac{2(a_n a_{n'})^{1/2}}{a_n + a_{n'}} \right]^{1/2} \times \exp\left[-\frac{a_n a_{n'}}{2(a_n + a_{n'})} (q_n - q_{n'})^2 \right] , \tag{21a}$$

$$a_n = \frac{K(n)}{\hbar \omega(n)} \ , \tag{21b}$$

so that $\langle 0 | 1 \rangle$ and $\langle 1 | 2 \rangle$ will, in general, be different when the parameters are n dependent. For the particular case where only the coupling constant α depends on n, Eq. (21) reduces to Eq. (10). We now consider some specific examples.

A. Dependence of coupling constant on n

For $\alpha(n)$ varying with n, we have

$$q_0 - q_1 = \frac{\alpha(1)}{K} \ , \tag{22a}$$

$$q_1 - q_2 = \frac{2\alpha(2) - \alpha(1)}{K} \ , \tag{22b}$$

and $S \neq T$ if $\alpha(1) \neq \alpha(2)$. A possible parametrization is

$$\alpha(n) = \alpha + \frac{\alpha'}{2}(n-1) , \tag{23}$$

so that

$$\alpha(1) = \alpha , \tag{24a}$$

$$\alpha(2) = \alpha + \frac{\alpha'}{2} , \tag{24b}$$

and

$$q_0 - q_1 = \frac{\alpha}{K} , \tag{25a}$$

$$q_1 - q_2 = \frac{\alpha + \alpha'}{K} . \tag{25b}$$

For α and α' of opposite sign, the coupling Eq. (23) becomes weaker as holes are added. We believe that this is the appropriate physical choice (in an electron rather than hole representation, it would correspond to α and α' of the same sign). The Hamiltonian [Eq. (18)] becomes

$$H_i = \frac{p_i^2}{2M} + \frac{1}{2}Kq_i^2 + \alpha q_i n_i + (U + \alpha' q_i) n_{i\uparrow} n_{i\downarrow} , \tag{26}$$

so that a nonzero α' can also be interpreted as arising from a dependence of the on-site Coulomb repulsion on the lattice deformation. This Hamiltonian has previously been considered by Pincus.[26] The choice α and α' of opposite sign in the hole representation can be seen to correspond to the physical effect that when electrons are added to the site the electron-electron repulsion is reduced if the lattice is allowed to relax to its new equilibrium position. This choice leads through Eq. (10) to $S < T$ and hence to a tendency for holes to pair.

B. Dependence of force constant on n

It is reasonable to expect a dependence of the stiffness K on the number of carriers at the site. As electrons are added to an ion, the electrostatic force between ions is reduced, leading to smaller K values. This corresponds to the general physical fact that as bands in a solid become filled, the lattice becomes less stiff, phonon modes soften, and eventually a lattice instability can occur. It is also associated with the fact that the higher-energy states in a band are antibonding like while the lower ones are bonding like. Thus, for our case, we expect K to be a decreasing function of the number of electrons at the site or, equivalently, in the hole picture to be an increasing function of n.

There are two competing effects associated with the variation of K with n. As K increases with increasing n, the harmonic-oscillator wave function becomes more compact due to the increase in the factors in the exponent of Eq. (19), which would tend to lead to a reduction of overlap matrix elements. However, another effect is that the change in the equilibrium displacement [Eq. (20a)] becomes smaller as $K(n)$ increases, leading to an increase in the overlap of wave functions with different n values. The latter effect is found to always dominate, leading again to $S < T$ and tendency for holes to pair.

C. Dependence of mass on n

Just as inescapable as the change in electrostatic forces with n is the fact that the ionic mass will increase as electrons are added to the ion, so that $M(n)$ is a decreasing function of n = number of holes. This leads to an increasing phonon frequency with n and a more widely spread out oscillator wave function and, hence, to an increase in overlap matrix elements and $S < T$ (the equilibrium position of the oscillator is not affected by changes in M). Of course, this will be a quantitatively small effect due to the smallness of electronic compared to ionic masses; nevertheless, it is interesting to note that the effect is of the same sign as in the other cases.

D. Anharmonicity

As mentioned in the Introduction, the possibility of anharmonic lattice effects playing an important role in high-T_c oxides has been discussed by several authors.[16–20] It is reasonable to expect that in a soft lattice that may arise for the case of nearly full bands, anharmonic effects will become particularly important (this is related to the smaller values of the stiffness K alluded to earlier). We consider then a potential as in Eq. (18) with a small anharmonic term added:

$$V(q) = \tfrac{1}{2}Kq^2 + \beta q^4 + \alpha q n . \tag{27}$$

To lowest order in β, the equilibrium position of the oscillator is now given by

$$q_n = -\frac{\alpha}{K} n + \frac{4\beta\alpha^3}{K^4} n^3 , \tag{28}$$

so that the relative displacements are

$$q_0 - q_1 = \frac{\alpha}{K} - \frac{4\beta\alpha^3}{K^4} , \tag{29a}$$

$$q_1 - q_2 = \frac{\alpha}{K} - \frac{28\beta\alpha^3}{K^4} . \tag{29b}$$

Once again, the relative displacement decreases as holes are added (note that $\beta > 0$ for stability), leading to an increasing overlap matrix element ($S < T$) and a tendency for holes to pair.

Let us now consider some quantitative examples of these effects. The change in coupling constant with n is, from Eqs. (24), (22), and (10),

$$\frac{\alpha(2) - \alpha(1)}{\alpha(1)} \equiv \frac{\Delta\alpha}{\alpha} = \frac{\alpha'}{2\alpha} = -\frac{1}{2}\left[-\left[1 - \frac{\ln T/S}{\ln 1/S} \right]^{1/2} \right] . \tag{30}$$

For definiteness, let us assume that the polaronic reduction of the bandwidth S^2 is a factor of $\frac{1}{10}$. From the condition Eq. (15), we have that when the effective repulsion U_{eff} equals the hole bandwidth D_h, superconductivity will occur if $T/S > \sqrt{2}$. Replacement in Eq. (30) yields a

minimum value of $\Delta\alpha/\alpha=8.2\%$. For $U_{\rm eff}$ twice the hole bandwidth, the required change is $\Delta\alpha/\alpha=13.8\%$. These values are further reduced if the polaronic mass enhancement factor is larger, as seen from Eq. (30). Thus it can be seen that a rather small dependence of coupling constant on occupation is enough to give rise to superconductivity in the presence of appreciable hole-hole repulsion and only moderate polaronic mass enhancement.

For a change in the stiffness with n, if we take only into account the effect in the equilibrium position of the oscillator, we obtain an expression of the form Eq. (30), with $\Delta K/K$ replacing $\Delta\alpha/\alpha$

$$\frac{\Delta K}{K}=\frac{K(2)-K(1)}{K(2)} . \tag{31}$$

However, this does not include the effect of the change in the width of the oscillator wave function with $K(n)$. To obtain a numerical estimate, we assume a mass $M=16$ a.u. (corresponding to an oxygen atom) and

$$\hbar\omega=1000K , \tag{32a}$$

a typical optical frequency. We then have

$$K=28.6\ \text{eV}/\text{Å}^2 , \tag{32b}$$

and assuming a polaronic reduction factor $S^2=\frac{1}{10}$,

$$\alpha=3.37\ \text{eV}/\text{Å}^2 . \tag{32c}$$

We find using Eq. (21) that the required changes in stiffness for given $U_{\rm eff}/D_h$ are slightly larger than given by Eq. (30): For $U_{\rm eff}/D_h=1$, $\Delta K/K=8.6\%$, and for $U_{\rm eff}/D_h=2$, $\Delta K/K=14.5\%$. Again, we note that these rather modest changes in stiffness with occupation are likely to occur in real systems.

Finally, we consider the effect of anharmonicity as given by the potential Eq. (27). The dimensionless anharmonicity parameter is given by

$$\frac{\beta\hbar\omega}{K^2}=\frac{1-[1-(\ln T/S)/(\ln 1/S)]^{1/2}}{96\ln 1/S} , \tag{33}$$

and for $U_{\rm eff}/D_h=1$ and 2, this yields $\beta\hbar\omega/K^2=0.15\%$ and 0.25%, respectively, for $S^2=\frac{1}{10}$ [the bare parameter β is $\beta=14$ and 24 eV/Å^4, respectively, for the parameters in Eq. (32)]. Thus we find that a very small degree of anharmonicity in the potential is sufficient to satisfy the condition for superconductivity for large values of the effective Coulomb repulsion.

For completeness, we also give a numerical estimate for the effect of the change in ionic mass due to the nonzero electron mass. For the parameters discussed above, we find $T/S=1.000\,018$, leading to superconductivity in the presence of a repulsive interaction of up to $U_{\rm eff}/D_h=3.6\times10^{-5}$. Thus, even if all other electron-hole symmetry-breaking terms are assumed to be absent, the fact that electrons have a positive mass would lead to pairing of holes in the presence of a repulsive $U_{\rm eff}$ in this model.

In a real system, presumably a combination of all these electron-hole symmetry-breaking perturbations will exist. The fact that they are all of the same sign, and that they lead to pairing in the presence of appreciable Coulomb repulsion, leads us to conclude that there is no justification for ignoring them in treatments of polaronic superconductivity as has been done in the past.

V. ISOTOPE EFFECT

There have been several reported observations of a change in the critical temperature of high-T_c oxides upon substitution of ^{16}O by a heavier isotope.[27] In the model discussed here, the dependence of overlap matrix elements on phonon frequency leads to an isotope effect. We use the weak-coupling approximation to the critical temperature for the effective Hamiltonian [Eq. (12)]:[24]

$$T_c=1.13zt_{\rm eff}\sqrt{n(2-n)}e^{-a/b} , \tag{34a}$$

$$a=[1+k(1-n)]^2 , \tag{34b}$$

$$b=2k(1-n)+k^2\left[1-n+\frac{n^2}{2}\right]-u , \tag{34c}$$

$$k=\frac{\Delta t}{t_{\rm eff}} , \tag{34d}$$

$$u=\frac{U_{\rm eff}}{2zt_{\rm eff}} , \tag{34e}$$

and we have

$$\Delta t=tS(T-S) , \tag{35a}$$

$$t_{\rm eff}=t_h+n\Delta t . \tag{35b}$$

The isotope exponent is given by

$$\alpha=-\frac{d\ln T_c}{d\ln M} , \tag{36}$$

and it is $\frac{1}{2}$ in the conventional weak-coupling electron-phonon theory. Here α is nonuniversal. Contributions to it arise from changes in the prefactor and the exponent in Eq. (34a). The prefactor decreases as the ionic mass increases, leading to a positive contribution to α, which is the dominant effect; the exponent a/b decreases in most of the density range, leading to a negative contribution to α that somewhat offsets the effect of the prefactor. At high densities, however, the exponent increases with increasing ionic mass, leading to an increasingly larger α as the hole density increases.

For a quantitative estimate, we take $t=0.5$ eV (which corresponds to the free-electron mass for the actual oxygen-oxygen spacing in high-T_c oxides) and a polaronic mass enhancement factor of 10 as in the previous section. We choose the electron-hole asymmetry parameter $\Delta\alpha/\alpha$ to give rise to a maximum T_c of 100 K, for the representative cases $U_{\rm eff}/D_h=2$ and 4 as examples. Figure 1 shows T_c versus n for $U_{\rm eff}/D_h=2$ and ionic masses of 16 and 17 a.u., and Fig. 2 shows the isotope exponent α versus n for $U_{\rm eff}/D_h=2$ and 4. It can be seen that the obtained isotope exponent is larger than the conventional value $\frac{1}{2}$ and much larger than what is found experimentally in high-T_c oxides.[27]

For very low hole densities, the weak-coupling expres-

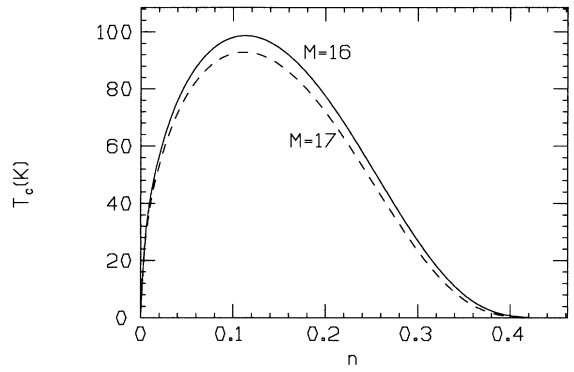

FIG. 1. Critical temperature vs occupation for two values of the ionic mass: $M=16$ (solid line) and 17 (dashed line) a.u. Other parameters are $\hbar\omega=1000K$, $t=0.5$ eV, $S^2=\frac{1}{10}$, $U_{\rm eff}/D_h=2$, and $\Delta\alpha/\alpha=24.6\%$.

sion for T_c [Eq. (34)] becomes inaccurate as the system approaches the strong-coupling limit. The isotope coefficient in the strong-coupling limit is easily obtained from the strong-coupling expression for T_c:[28]

$$T_c=\frac{1-n}{2\ln[(2-n)/n]}\varepsilon_b\ , \tag{37a}$$

$$\varepsilon_b=\left[\frac{U_{\rm eff}^2}{4}+4z\Delta t^2\right]^{1/2}-\frac{U_{\rm eff}}{2}\ . \tag{37b}$$

The resulting α is 0.73 and 0.60 for the two cases above, respectively, somewhat smaller than the weak-coupling expression results as $n\to 0$ (0.96 and 0.68). The actual value of α in this limit is in between these two estimates and can be obtained from the numerical solution of the BCS equation for T_c in this model.

It is interesting to note that the usual bipolaronic model ($S=T$, $U_{\rm eff}<0$) leads to a negative isotope effect in the weak-coupling regime: The prefactor in Eq. (34a) decreases as the ionic mass increases, but the exponent also decreases due to the increasing density of states, and the latter effect dominates. The behavior is different in the model discussed here because the coupling constant $k=\Delta t/t_{\rm eff}$ changes less rapidly than u due to the fact that both Δt and $t_{\rm eff}$ depend on overlap matrix elements. On the other hand, in the usual bipolaronic model in strong coupling the isotope effect is positive, because the Bose condensation temperature is inversely proportional to the pair effective mass, which increases as the ionic mass increases.

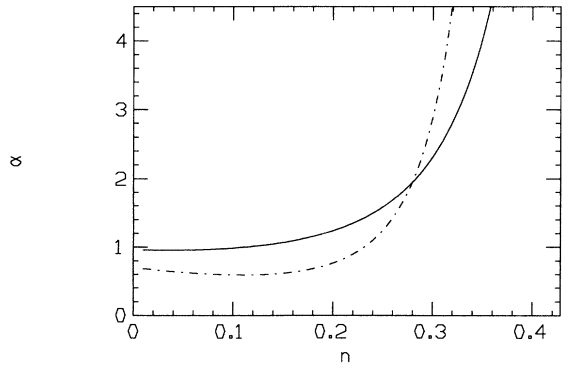

FIG. 2. Isotope exponent [Eq. (36)] vs occupation for two sets of parameters that give rise to a maximum T_c of 100 K. Solid line, same parameters as in Fig. 1; dot-dashed line, $U_{\rm eff}/D_h=4$, $\Delta\alpha/\alpha=42.4\%$; other parameters as in Fig. 1.

VI. SOME FURTHER REMARKS

We address here two other points in connection with the class of models discussed in the previous sections.

A. Inclusion of nearest-neighbor Coulomb repulsion

A nearest-neighbor Coulomb repulsion can be included in the model Hamiltonian [Eq. (12)] and the condition for superconductivity [Eq. (15)] is easily extended.[24] The net effect of doing this for the considerations in this paper may be rather small for the following reasons.

(i) We have only considered here contributions to Δt arising from the on-site dynamics and the single-particle hopping. Another contribution to Δt will arise from the "hybrid" matrix element of the Coulomb interaction between electrons at neighboring sites.[29] This contribution should be included if the direct nearest-neighbor repulsion is included and will tend to cancel the effect of the nearest-neighbor repulsion.

(ii) We have treated the hopping between sites only to first order here. Second-order contributions give rise to a nearest-neighbor attraction between antiparallel spin carriers[30] that also tends to offset the direct nearest-neighbor Coulomb repulsion. The most important second-order processes here involve "vertical" transitions at the two sites involved, giving a contribution proportional to $t^2/\hbar\omega$ with t the *bare* hopping amplitude. These terms can be important as they are not offset by the polaronic band reduction factor. An example of the importance of these terms for a related spin model can be seen in Fig. 1 of Ref. 30 (the difference between the curves labeled 1 and 2 in that figure).

The combination of these two effects should make the net effect of including a direct nearest-neighbor Coulomb repulsion rather small, in particular with respect to the condition on the magnitude of the particle-hole symmetry breaking necessary to give rise to superconductivity.

B. Nature of the phase transition

In the usual bipolaronic pairing mechanisms, the transition to the superconducting state occurs through Bose condensation of preexisting pairs.[12] This is because the pair mobility is much smaller than the pair binding energy. In the models discussed here, the pair mobility is usually larger than the pair binding energy and the transition is of the usual BCS type except for extremely low density of holes.[28,31]

The situation is illustrated most simply in the strong-coupling limit, where the polaron mass is so large that single polarons are essentially localized and two polarons

delocalize upon pairing. This limit should be applicable to high-T_c oxides in the low-hole-concentration regime.[32] The relation between pair binding energy ε_b and pair mobility t_p is found to be[28,25]

$$\varepsilon_b = 2zt_p - V \tag{38}$$

in this limit. Here V is the nearest-neighbor Coulomb repulsion. Equation (38) expresses the fact that pairing is driven by the kinetic-energy gain of delocalization ($2zt_p$) in this model, while it is opposed by the static Coulomb repulsion. The size of the pair in this limit is a single lattice spacing. The pair mobility is found to be[28]

$$t_p = \frac{2(\Delta t)^2}{U_{\text{eff}} - V} , \tag{39}$$

for $\Delta t \ll U_{\text{eff}} - V$, which should be quite generally valid. It is clear from Eqs. (38) and (39) that t_p can be much larger than ε_b (as V increases, ε_b approaches zero, while t_p remains finite). In that regime, which we believe is applicable to high-T_c oxides, the superconducting state containing pairs of small spatial extent is destroyed by the unbinding of these pairs rather than Bose decondensation as the temperature is raised.

VII. APPLICABILITY TO HIGH-T_c OXIDES

We have argued in Sec. II that the usual small bipolaronic model is inapplicable to describe superconductivity in high-T_c oxides (or any other real system) due to the fact that the large energy difference between the local Coulomb repulsion and the phonon frequency leads to an extremely large carrier effective mass for the values of electron-phonon coupling required to make the interaction attractive. This difficulty does not occur in the extensions of the model discussed here.

Nevertheless, it does not seem possible to describe high-T_c oxides with a purely phononic small-polaron model. One problem is the isotope effect, which as seen in Sec. V is much larger than observed experimentally. Another problem arises from the condition on the parameters for small polarons to exist in the first place.[10] Comparison of the energy of a carrier that moves without distorting its background and a small-polaron carrier leads to the condition

$$zt(1-S^2) < \frac{\alpha^2}{2K} , \tag{40}$$

for the small-polaron carrier to be energetically favored. Thus the largest bare hopping t for which small polarons will form satisfies the equality in Eq. (40). The effective bandwidth is then

$$D_h = 2zt_h = 2\hbar\omega \ln(1/S^2)\frac{S^2}{1-S^2} . \tag{41}$$

The largest D_h occurs for $S \to 1$, $D_h = 2\hbar\omega$, yielding $D_h = 0.17$ eV for a typical optical-phonon frequency $\hbar\omega = 1000K$. Even this value of D_h is too small compared with the estimated effective bandwidth in high-T_c oxides $D_h \sim 0.5$ eV. Since the polaronic bandwidth reduction factor S^2 is expected to be considerably smaller than 1, Eq. (41) indicates that the energy scale $\hbar\omega$ involved is considerably larger than optical-phonon frequencies and hence likely to be of electronic origin.

We conclude that for small polarons to be energetically favored requires an electronic polaron mechanism to obtain a bandwidth compatible with observations in high-T_c oxides. Such a mechanism could arise from distortion of the electronic charge cloud in oxygen anions by the conducting holes, as discussed, for example, in Ref. 9. In Ref. 9, this physics was described by an effective spin model, but it may be equally well describable by the electron-hole asymmetric Holstein models discussed in this paper. Taking into account also the oxygen ionic motion would then result in a combined electronic-phononic small-polaron model, with the effective overlap matrix elements [Eq. (9)] being

$$S = S_1 S_2 , \tag{42a}$$

$$T = T_1 T_2 , \tag{42b}$$

where the indices 1 and 2 refer to the overlaps of the electronic and phononic parts of the site wave functions, respectively.

In such a model, the polaron binding energy would be provided principally by the electronic part of the polaron, for which the constraints resulting from Eqs. (40) and (41) are easily satisfied with an electronic energy scale $\hbar\omega$. With a resulting bandwidth of $D_h \sim 0.5$ eV, the constraint of being in the antiadiabatic regime for the phonon degrees of freedom is still approximately satisfied [Eq. (6) with ω an optical-phonon frequency]. The considerations of the previous sections concerning electron-hole asymmetry would still apply, with S and T resulting from the combined effects as in Eq. (42). The degree of phononic contribution to the polaron may be inferred empirically by the observed isotope effects. The results obtained in Sec. V for a purely phononic polaron compared to experimental observations[27] indicate that the phononic component of the small polaron would be rather small.

VIII. CONCLUDING REMARKS

Because of the complex nature of real solid-state systems, physicists strive to study simple models that contain the essential physics of the phenomena of interest. The correct treatment of symmetries has often played an important role in the progress of physics. If the real system under study possesses a certain symmetry, it is usually not useful to study model Hamiltonians to describe the system that lack this symmetry, as essential physics could be missed. By the same token, it is likely not to be very useful to confine one's attention to model Hamiltonians where a certain symmetry is present if the real systems that the Hamiltonians are intended to describe do not possess that symmetry.

Real solid-state systems, and in particular those systems for which small-polaron models are used, are not electron-hole symmetry, ultimately due to the basic fact that electrons and protons have vastly different masses. Thus to confine one's attention to Hamiltonians that are

electron-hole symmetric is not justifiable in our opinion. We have seen in this paper that a variety of generic electron-hole symmetry-breaking perturbations to the Holstein model are likely to exist in real systems and that they give rise to qualitative changes in the resulting physics. Furthermore, we have argued that all these symmetry-breaking perturbations have the same sign and thus will act cooperatively. In the presence of these perturbations, we have seen that superconductivity can exist in these systems under conditions on the parameters that are vastly less restrictive than in the electron-hole symmetric case.

It is interesting to note that one of the motivations for Bednorz and Müller[33] to search for superconductivity in oxides was to look for possible bipolaronic superconductors as proposed earlier by Chakraverty.[11] This paper, as well as our previous work, suggests that such bipolarons, albeit electron-hole asymmetric ones, may indeed play an important role. As discussed in Sec. VII, however, it appears that rather than purely phononic, the dominant component of the polarons may be electronic.

In connection with conventional materials, Alexandrov[34] has argued that "strong-coupling" superconductors, which are assumed[35] to have dimensionless electron-phonon coupling λ larger than 1, should be described by small-polaron theory rather than by the conventional Eliashberg theory.[35] If one were to accept this point of view, the discussion in this paper suggests that those superconductors should exhibit predominantly hole conduction, which is in agreement with the empirical observation of Chapnik.[36] Of course, a purely electronic polaronic mechanism could also provide an explanation for Chapnik's observation.[37]

We conclude by emphasizing two key differences between the electron-hole asymmetric polaronic superconductors discussed here and the conventional ones.[12] (1) The transition to the normal state occurs here through pair unbinding rather than Bose decondensation so that (essentially) no pairs exist above T_c. (2) Spectral weight in the optical conductivity is transferred from high to low frequencies upon entering the superconducting state.[38] This does not occur in the absence of electron-hole asymmetry. These differences should help to experimentally distinguish between electron-hole symmetric and asymmetric polaronic superconductors.

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