

Excitonic Pairing in CuO₂- and BiO₃-Based Perovskites

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We study the BiO_m high- T_c oxides and compare them to the CuO_n systems ($m, n = 2$ or 3). Both are described by a general Hamiltonian and studied by perturbation theory in the hopping energy. It is shown that a common polarization mechanism can give rise to pairing of the O holes added to the antiferromagnetic or disproportionated semiconducting states. The necessary conditions are proximity of the M (Cu or Bi) and O levels, a gap in the electronic spectrum of the system, and important nearest-neighbor M -O repulsion.

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The peculiar properties of the new superconducting oxides, particularly their high critical temperature T_c , has led to the consideration of alternative pairing mechanisms.¹ Within the large variety of proposed nonphonon models, there are two major classes: those based on magnetic fluctuations and those based on the electronic polarization of the medium giving rise to pairing between holes. The recent discovery of Ba_{1-x}K_xBiO₃,² with $T_c \sim 30$ K suggests that this compound, as well as BaPb_{1-x}Bi_xO₃ (Ref. 3) with $T_c \sim 13$ K must be considered within the same family of high- T_c superconducting perovskites and favor the second type of mechanism, as there are no magnetic ions in these compounds.

Varma, Schmitt-Rink, and Abrahams⁴ first remarked that a nearest-neighbor repulsion between metallic M (Cu or Bi) and O ions could play an important role, inducing charge fluctuations due to the unusual covalency of the O- M bonds in these perovskites. They proposed that the effective interaction between holes through such polarization could be attractive, leading to high- T_c su-

perconductivity. However, detailed calculations and an understanding of the peculiar properties are needed to test this possibility. Small-cluster calculations⁵ for CuO₂ planes support this mechanism in the perovskites containing magnetic ions, as they point out the relevance of the large on-site repulsion between Cu orbitals. Here we show that a similar excitonic mechanism can also give rise to pairing in the nonmagnetic Bi-based perovskites. The necessary conditions are discussed, analyzing both types of systems within perturbation theory in terms of the hopping t . We compare our results for Cu-based perovskites with those of small-cluster calculations,⁵ obtaining similar conclusions. The same model with parameters appropriate for BaBiO₃ yields a disproportionated insulating ground state and attraction between O holes after a certain amount of doping.

We represent both types of systems by a simple cubic lattice of metal ions ($M = \text{Cu}$ or Bi) in d dimensions ($d = 2, 3$), with an O ion between any two M ions. A common Hamiltonian describing the dynamics of the holes is

$$H = H_0 + H',$$

$$H_0 = \sum_{ijk\sigma} \left\{ \epsilon_M + A \sum_{(l)} S_l (-1)^{i+j+k} \right\} n_{ijk\sigma}^M + \sum_{l\sigma} \epsilon_p n_{l\sigma}^p + u_M \sum_{ijk} n_{ijk}^M n_{ijk}^M + u_p \sum_l n_l^p n_l^p$$

$$+ \sum_{ijk(l)\sigma} \left\{ G - \frac{1}{2} A S_l (-1)^{i+j+k} \right\} n_{ijk\sigma}^M n_{l\sigma}^p + \sum_l B S_l^2, \quad (1)$$

$$H' = t \sum_{ijk(l)\sigma} (c_{ijk\sigma}^M p_{l\sigma} + \text{H.c.}),$$

where ijk labels the M positions and l denotes the O sites. The first term in H_0 represents the energy of the M orbitals [$3d(x^2 - y^2)$ if $M = \text{Cu}$, $6s$ if $m = \text{Bi}$]. The second is the energy of the O p orbitals directed towards their nearest-neighbor M ions. The third and fourth terms describe on-site Coulomb energies; the fifth represents the intersite Coulomb repulsion between M and O ions. The last term of H_0 accounts for the elastic energy loss when some O atoms are displaced along the nearest-neighbor lines. Each displacement modifies the on-site and intersite M -O energies of the two neighboring M ions in an opposite way. For simplicity, we consider only three positions for the O ions, $S_l = 0, \pm 1$. We

also assume that $A < B < 2A$, $S_l = 1(-1)$ for all l corresponds to a breathing distortion. H' represents the hopping between nearest-neighbor M and O ions (the phases of the atomic orbitals were chosen to have $t > 0$ for all directions).

The model is equivalent to the one discussed before,^{4,5} but with inclusion of O displacements. It can also be considered as a way of generalizing the model of Rice and Sneddon⁶ to covalent M -O binding. As correlations are essential, we solve the interaction Hamiltonian H_0 exactly and include H' as perturbation. We define

$$\Delta = \epsilon_p - \epsilon_M; \quad \bar{u} = u_M - z(2A - B), \quad (2)$$

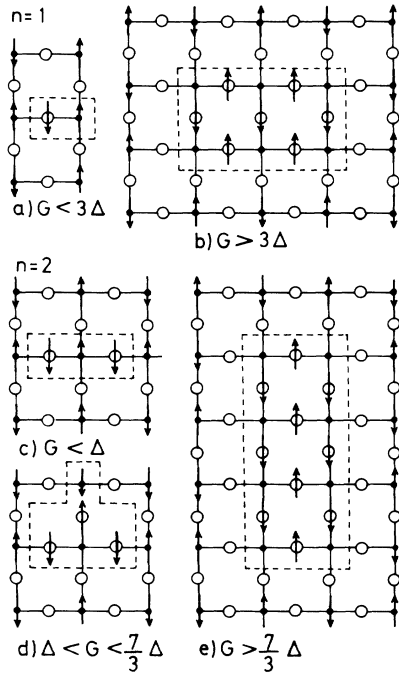


FIG. 1. Schematic representation of the ground state for the Cu oxides with $N+n$ holes for different G values. The indicated limits corresponds to $t=0$. Filled circles denote metal sites and open circles O sites.

where $z=2d$ is the coordination number of the M ions. We represent $|g,n\rangle(|g_0,n\rangle)$ by the ground state of $H(H_0)$ for n holes added to the undoped system. If we assume for the moment that $\Delta > 0$, $|g_0,0\rangle$ depends on the sign of \tilde{u} . If $\tilde{u} > 0$, $|g_0,0\rangle$ has one hole in each M ion and the O ions are undistorted. If instead $\tilde{u} < 0$, a disproportionation accompanied by a breathing-mode distortion takes place and $|g_0,0\rangle$ consists of alternating doubly occupied and empty M sites. We believe that in layered Cu oxides, $\tilde{u} > 0$, while in BaBiO₃-based compounds, because of the larger dimensionality ($z=6$) and the lower magnitude of the s - s intra-atomic Coulomb repulsion, $\tilde{u} < 0$. This is also consistent with the O breathing mode observed in BaBiO₃ (Ref. 3) but not in the Cu-based compounds.

We start considering the Cu-based oxides for which \tilde{u} and $\Delta > 0$. Figure 1 shows several states when $n=1$ or 2

holes are added to $|g_0,0\rangle$. If $u_M > 7\Delta$ and $u_p > 2\Delta$, these states represent $|g_0,n\rangle$ for different values of G . Some of them have been already considered.⁵ We calculate the energy taking into account all degenerate states of H_0 which mix up to order t^2 , except those states which differ from $|g_0,0\rangle$ in two holes without a common nearest neighbor. We find that, among all possible linear combinations of these states, $|g,n\rangle$ is always given by those of highest symmetry. The energies of the states represented by Fig. 1 are given in Table I, in the simplest case $u_M, u_p \rightarrow +\infty$ for $z=4,6$. Here $E_i = E(N+i) - E(N)$. Figure 2 shows, for $z=4$, the resulting binding energy defined as

$$E_b = E_2 - 2E_1. \tag{3}$$

An effective attraction between O holes occurs for large enough G . For $G < G^c$, $E_b > 0$. For $t \rightarrow 0$, we obtain $G^c/\Delta = 0.54 + 0.07(3-z/2)$. This value is reduced if more delocalized wave functions for two added O holes are considered, but in any case a finite G is necessary to have pairing. For larger t , G^c increases when $(H')^4$ terms are neglected.

The key of the pairing mechanism between O holes is that when the second hole is added sufficiently near the first, a reorganization of the charges, lowering the total energy, becomes possible. A similar process cannot take place if in $|g,2\rangle$ only the M sites are occupied. This leads to a minimum u_M for excitonic pairing. For $t \rightarrow 0$, we obtain $u_M^c/\Delta = 2.42 + 0.15(3-z/2)$. As for G^c , u_M^c decreases if more complex $N+2$ hole states are considered, but always $u_M^c > \Delta + 2G^c$. The interval of G for which $E_b < 0$ shrinks when u_M decreases. For $t=0$ and $u_M < 5\Delta$, $E_b < 0$ only for $G < -\Delta + 2u_M/3$. For finite t this upper bound increases.

For large G/Δ , H' in second order always favors pairing, and more strongly for $z=6$. For small G/Δ and t/Δ , E_b is also smaller for larger z .

In summary, the range of G for which pairing is obtained decreases with increasing Δ , in agreement with previous results,⁵ and a minimum u_M is necessary for this excitonic mechanism. This value increases with Δ .

Note that while in the undoped compounds the anti-ferromagnetic alignment of two M spin is favored by an energy $[t^4/(\Delta+G)^2][1/u_M + 2/(2\Delta+u_p)]$, terms of order $(H')^2$ favor a local ferromagnetic alignment when

TABLE I. Energies of the states represented in Fig. 1 up to second order in H' .

$$\begin{aligned} \text{(a)} \quad E_1 &= \epsilon_0 + 2G + 2t^2[z/(\Delta+G) - 2(z-1)\Delta] \\ \text{(b)} \quad E_1 &= \epsilon_0 + 6\Delta + 2t^2[3z/(\Delta+G) - 4/(G-\Delta) - 3/(2G-\Delta)] \\ \text{(c) and (d)} \quad E_2 &= 2\epsilon_0 + (7G+\Delta)/2 - R + t^2[7z/(\Delta+G) - 5(z-1)/\Delta]/2; \\ R &= \{[\Delta - G + t^2[z/(\Delta+G) - (z-1)/\Delta]]^2/4 + 3(z-2)t^2\}^{1/2} \\ \text{(e)} \quad E_2 &= 2\epsilon_0 + 8\Delta + 4t^2\{2z/(G+\Delta) - 2/(G-\Delta) - 3/(2G-\Delta)\} \end{aligned}$$

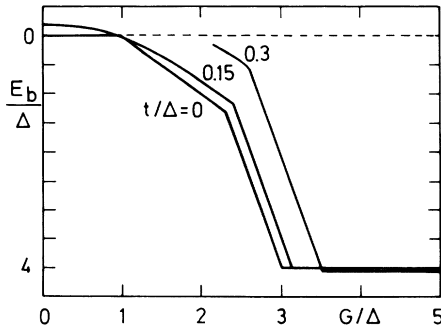


FIG. 2. Binding energy for a pair of holes as a function of G for $\tilde{u}, u_p \rightarrow \infty, d=2$, and indicated values of t/Δ .

holes are added. The antiferromagnetic order is progressively destroyed with doping.

We consider now a different range of parameters which we believe correspond to the nonmagnetic Bi-based compounds: $\tilde{u}, \Delta, A' - u_p$, and $E_{BP} < 0$, where

$$E_{BP} = u_M - 2\Delta - zA', \quad (4)$$

and $A' = 2A - B$. In this case $|g_0, 0\rangle$ is the distorted disproportionated ground state proposed previously for $\text{Ba}_2\text{Bi}^{3+}\text{Bi}^{5+}\text{O}_6$.³ In the range of parameters considered, the added holes go preferentially to the O sites, as shown in Fig. 3. The respective energies in order t^2 , obtained as before, are given in Table II. Here also $|g, n\rangle$ has the highest possible symmetry. In $d=3$, e.g., for two added holes, there are 15×2 states built with four holes, zero total spin in different O atoms, and a common nearest-neighbor M [Fig. 3(d)]. $|g, 2\rangle$ for large G is a mixture of the four linear combinations that transform like the representation Γ_1 of the point group O_h .

The resulting binding energy for $z=6$ is plotted in Fig. 4. As before, for $G > G^c$ we find attraction between O holes. G^c increases with Δ and t . A lower limit of E_b is E_{BP} , i.e., the binding energy of a bipolaron. Excitonic pairing occurs when $|g, 2\rangle$ has the form of Fig. 3(d): The charge reorders the breaking of a bipolaron at a doubly occupied M site, decreasing the interatomic Coulomb energy. For $t=0, G^c = -(E_{BP} + 2A')/4$.

In order $t^2, |g, n\rangle$ has spin degeneracy. When terms of order t^4 are considered, the state of minimum total

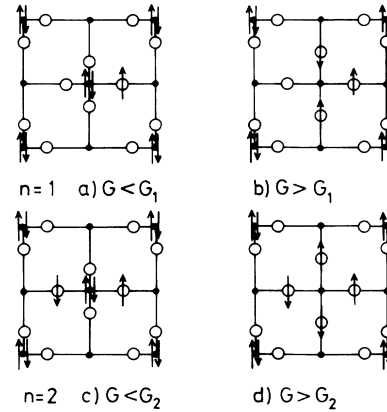


FIG. 3. Same as Fig. 1 for the Bi oxides, $G_1 = (|E_{BP}| - A')/2, G_2 = (|E_{BP}| - 2A')/4$.

spin of the O holes with a common M nearest neighbor is favored. In particular, $|g, 2\rangle$ is a singlet. This agrees with susceptibility measurements in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$.²

For $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$, where the metal ions themselves are substituted, we have the following physical picture. For large x , the Pb 6s states are filled with holes. As x decreases, the number z of distorted O ions also decreases. This implies that $|E_{BP}|, G^c$, and the energy E_2 of the state of Fig. 3(d) all decrease. When the Pb 6s band becomes wide enough, it would attract electrons from the Bi^{3+} sites, but we have shown that it costs less energy to build the structure of Fig. 3(d). This process makes the system metallic and provides the necessary holes for pairing (in the case of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, doping directly provides holes). The disproportionation, being a local effect, remains present for larger amounts of Pb. This agrees with the two types of carriers of different sign and mobility seen in the Seebeck measurements.⁷ A detailed study of the electronic structure of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$, consistent with the optical results,⁸ will be published elsewhere.

To conclude, we have shown that a similar mechanism can be responsible for pairing in both types of oxides. This comes from a model Hamiltonian in which we have just included well known features of the undoped semiconducting systems. Doping induces pairing between

TABLE II. Energies of the states represented in Fig. 3 up to second order in H' .

(a)	$E_1 = \epsilon_0 + 2G + A' + t^2\{2z/\Delta_1 + z/(\Delta_2 + 2G) - 3(z-1)/(2\Delta - \Delta_2 - u_M) - 1/(2\Delta - \Delta_2 - u_M + u_p)\}$
(b)	$E_1 = \epsilon_0 + 2\Delta - u_M + zA' + t^2\{2z/\Delta_1 - 3/\Delta_2 - 3(z-2)/(2G - \Delta)\}$
(c)	$E_2 = 2\epsilon_0 + 4G + 2A' + 2t^2\{z/\Delta_1 + 1/(\Delta_2 + G) - 2(z-2)/\Delta_3 - 1/(\Delta_3 + u_p)\}$
(d)	$E_2 = 2\epsilon_0 + \Delta - u_M + zA' + 2t^2\{z/\Delta_1 + 1/\Delta_2 - (z-3)/(3G - \Delta)\}$;
	$\Delta_1 = \Delta + G + zA' - u_M; \Delta_2 = \Delta - (z-1)A'; \Delta_3 = \Delta_1 - 2(A' + G)$

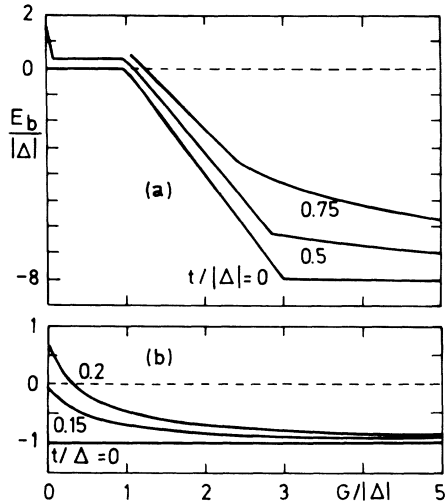


FIG. 4. Binding energy as a function of G for \tilde{u} , $\Delta < 0$, $d=3$, and indicated values of t/Δ . (a) and (b) correspond to $-E_{BP} > 2A'$ and $-E_{BP} \leq A'$, respectively. Other parameters are (a) $u_M = u_p = A' = 2|\Delta|$, (b) $u_M = 3|\Delta|$, $u_p = 2|\Delta|$, and $A' = |\Delta|$.

holes for large enough G , inhibiting the spin or charge instabilities.

Features common to both types of systems which appear as necessary conditions to have this polarization mechanism are the following: (1) quasidegeneracy of the metal and O levels; (2) a gap in the excitation spectrum, i.e., $E(N+1) + E(N-1) - 2E(N) > 0$; and (3) large enough repulsion between nearest-neighbor M and O orbitals.

We have considered states with only up to $N+2$ holes. The long-range Coulomb energies, absent in our model, prevent a local accumulation of charge when more holes are added to the system.

A difference between both types of systems is that the excitonic pairing mechanism involves only one electron-hole pair in the cuprates but two in the bismuth oxides. It can be shown that the mobility of the excitonic states for two added holes is low for $t \ll G$. It increases with t and decreases strongly with G . For $\tilde{u} < 0$, the mobility of the bipolarons is in any case lower than that of the structure of Fig. 3(d) (a bipolaronic regime will appear

when doping with electrons). The O distortion slightly reduces both mobilities. For a typical breathing-mode frequency $\omega \sim 15$ THz and a distortion $\delta = 0.08 \text{ \AA}$,³ the hopping matrix elements that are accompanied by a distortion are reduced by about 5%. Instead, direct O-O hopping and higher z enhance the mobility.

Although the binding energy E_b increases with G , it is perhaps the region for G just above G^c which is relevant to superconductivity. One has in fact smaller binding energy but considerably higher mobility. Although pairing does not necessarily mean superconductivity, the pairs that we obtain have s -wave symmetry.

The value of t for real systems could be beyond the range of validity of our perturbation calculation. Based on the results of Ref. 5 and our preliminary small cluster calculations for Bi-O chains, we believe that our conclusions remain valid for larger values of t .

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