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Effect of the local charge disproportionation on the electronic structure of $BaPb_{1-x}Bi_xO_3$

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We calculate the electronic structure of $BaPb_{1-x}Bi_xO_3$ within a simplified version of a model proposed before for the superconductivity, taking into account the local disproportionation of the Bi atoms in the coherent potential approximation. Three different regimes are obtained as a function of the Bi concentration x: normal metal, metallic with a pseudogap, and insulating phase. This allows a satisfactory explanation of the optical properties, resistivity, Hall, and Seebeck effects. The agreement is improved when the many-body effects due to the covalency of the Bi—O bonding, invoked for the pairing mechanism, are also considered.

I. INTRODUCTION

The perovskitelike system $BaPb_{1-x}Bi_xO_3$ has been the subject of intensive studies since the discovery of superconductivity[1] at $T_c \sim 13$ K, an anomalous high critical temperature for a compound without transition-metal elements. Interest in this system was recently revived by the finding of superconductivity[2,3] up to 30 K in $Ba_{1-x}(K \text{ or } Rb)_xBiO_3$. This value of T_c is of the same order of those found in high-temperature copper oxides. This suggests a common novel pairing mechanism for both copper and bismuth families as they show striking similarities: Both exhibit the same metal-oxygen network and they are poor metals with a low number of carriers. The density of states at the Fermi level is low and the stoichiometric parent compounds are semiconducting. However there are also essential differences between them that would constrain many of the proposed theories if they should apply to both types of systems.

The Bi oxides are three-dimensional compounds instead of the layered structure of all the superconducting copper oxides. The parent cuprate materials are antiferromagnetic insulators, but $BaBiO_3$ is diamagnetic, the Bi ions having zero magnetic moment, and has a doubled unit cell corresponding to a formal charge-ordering $Ba_2Bi^{3+}Bi^{5+}O_6$. In the cuprates the superconductivity occurs as the antiferromagnetism is inhibited introducing a few charge carriers by substituting ions, while in the bismutates—since a cubic perovskite structure is reported[3] for $Ba_{1-x}K_xBiO_3$—it seems that the unit-cell doubling associated with charge ordering is weakened.

In $Ba_{1-x}K_xBiO_3$, with increasing x, holes are added to the parent system but without modifying the underlying BiO lattice. The case of $BaPb_{1-x}Bi_xO_3$ is more complicated as the metal ions themselves are substituted: not only are carriers introduced but also the BiO lattice is modified. However, this latter system has the advantage that a lot of experimental data are available. In particular, the systematic work and the interpretation of the results,[4,5] allow for a description of the underlaying physics which severely restricts the applicability of different theories.

$BaBiO_3$ is semiconducting, the breathing mode is completely softened, and static displacements of the O atoms have been inferred from the crystallographic studies by Cox and Sleight.[6] Although the charge disproportionation has been questioned by x-ray photoemission spectroscopy (XPS) experiments,[7] recent crystallographic[8] and optical[4,5] studies have confirmed the presence of inequivalent Bi sites. However, the magnitude of the charge disproportionation remains open. The resistivity measurements[9] revealed that the metal-insulator (MI) transition takes place at $x \simeq 0.35$.

Resistivity and Hall-coefficient measurements[9] yield the following results. The system is a good metal for $x < 0.2$. For $0.2 < x < 0.35$ the system is metallic but the resistivity shows a semiconductinglike temperature dependence. Superconductivity is observed for $0.05 \lesssim x \lesssim 0.35$ and the maximum T_c is ~ 13 K around $x = 0.25$. The x dependence of carrier concentration n^* follows almost the same x dependence as T_c. The maximum n^* is 4×10^{21} cm^{-3} at $x \sim 0.25$, which is one order of magnitude smaller than those of usual superconductors.

A detailed optical study of this system has been done by Tajima *et al.*[4,5] over a wide energy range and over the hole compositional range. As the Bi concentration x is increased from $x = 0$, the position of the plasma edge shifts to higher energy corresponding to an increase of the electron density contribution of the Bi atoms. With a further increase in x, $x > 0.15$, the spectrum deviates from the usual Drude behavior. From a Kramers-Kronig analysis, the authors inferred that a pseudogap or a minimum in the density of states, develops with x. The pseudogap arises from the trend towards splitting of the Bi-derived band and transforms to a real gap at the MI transition at $x = 0.35$. The optical spectrum shows that $BaPb_{1-x}Bi_xO_3$ has a clear optical gap over the whole semiconducting compositional range, its magnitude increasing with x. Resonant Raman-scattering measurements[5] show that the origin of this gap is a charge disproportionation accompanied by the breathing-mode distortion. The resistivity measurements show that the activation energy, although smaller in magnitude than the optical gap, follows the same x dependence.[5] Since the pioneering work by Rice and Sneddon[10] several theories have been proposed to explain the MI transition. They interpreted the semiconductivity of the $BaBiO_3$ as due to real-space electron pairing which gives rise to the valence configuration $Bi^{3+}Bi^{5+}$. Thus there are effective negative U centers on the Bi sites that are progressively lost by Pb substitution. Finally k-space pairing replaces the real-space pairing, the anomalously high T_c attributed to strong electron-phonon interaction remaining unexplained. Later Jurczek and Rice[11] studied the effect of a broad conduction band on this narrow-band limit theory. Within a Hartree approximation they allowed all O ions to displace according to a breathing-mode charge-density wave (CDW) depending on the *average* energy difference between the two sublattices A and B, since they considered that a coherent potential approximation (CPA) approach would be very complicated. Thus, the effect of local distortions is lost. They have computed the density of states using an orthogonalized moment method. They obtained the persistence of the CDW over a wide range of $x \rightarrow 1$, but the existence of a gap or a pseudogap depends on the method of truncation chosen, rather than on the model parameters.

A simpler model proposed by Yoshioka and Fukuyama[12] considers a binary alloy of two components, one of which has two conduction electrons and the other none. The presence of an on-site attraction, treated in the Hartree-Fock approximation, leads to a small gap in the electronic structure. However, this model assumes a large disproportionation and neglects half of the lattice with the upper Bi band, which, in fact, lies closer to the Pb band according to Refs. 4 and 5 and our results. The above-mentioned models neglect the O bands.

Extensive band-structure calculations have been done by Mattheiss and Hamann.[13] According to these studies the undistorted cubic $BaPb_{1-x}Bi_xO_3$ alloys possess a single broad conduction band that comes from the σ-antibonding mixture of Pb-Bi ($6s$) and O ($2p$) states. This band is gradually filled in rigid-band fashion with increasing x until it is half-filled in $BaBiO_3$, where a combination of Fermi-surface nesting and the strong coupling of the conduction-band states near the Fermi-level ε_F to breathing-mode O displacements leads to a commensurate CDW gap. But it remains to be explained why the semiconducting properties of $BaPb_{1-x}Bi_xO_3$ are extended up to a concentration of 65% Pb. This persistence of the gap clearly favors a local rather than a CDW description.

In this work we calculate the electronic structure of $BaPb_{1-x}Bi_xO_3$ within a simplified version of a model proposed before to explain the superconductivity of these Cu-free systems. The excitonic pairing mechanism was studied by perturbation theory in the Bi-O hopping[14] and by exact diagonalization in small systems.[15] We consider a three-dimensional simple cubic lattice of metal ions (there is an oxygen between any two sites). Each metal site can be occupied by a Bi or a Pb atom. While Pb atoms have a charge near 4+, Bi atoms show a tendency to disproportionate towards Bi^{3+} and Bi^{5+} and the origin of this property is the first point to discuss. From spectroscopic data[16] one finds that the ionization energy difference between a pair of disproportionated Bi^{3+} and Bi^{5+} and two Bi^{4+} is $U_M \sim 10.7$ eV. This value is smaller but comparable to the corresponding intra-atomic repulsion energy for Cu, $U_M \sim 17$ eV. These values are certainly reduced by screening in the compounds, but an additional mechanism is needed in order to get an effective on-site attraction in the bismuth case. Although nonlinear screening effects have been invoked,[17] we found we can relate it more naturally to phonons as they have been observed.

Neglecting screening effects, which should be poor in the semiconducting phase, and considering spectroscopic data,[16] the change in Madelung's energy of the undistorted structure[6] when Bi^{4+} ions disproportionate into Bi^{3+} and Bi^{5+} states is -5.7 eV. The corresponding change when the six O^{-2} ions move 0.08 Å towards their nearest-neighbors[6] Bi^{5+} ions is -6.0 eV. Their sum overcomes U_M by 1.0 eV. This difference is decreased if the elastic energy loss is considered, but enlarged when the electron-phonon interaction originated from the distance variation of the hopping integrals is included.[18]

A characteristic of the experimentally observed breathing mode in the parent $BaBiO_3$ compound is that it leads to an effective attraction for half of the Bi sites, while it costs more energy to add one particle on the other half of the Bi sites. This makes it possible that the added holes go to O sites or to different unoccupied Bi sites depending on the respective energies.

In analogy with the high-T_c copper oxides for which there is evidence that the added holes have O character,[19] we have obtained that, for reasonable values of the parameters, this is also the case for the bismuth oxides.[14,15] Experimental support for this picture comes from Seebeck measurements[20] which show two types of carriers: electrons, which can be attributed to $6s$ Pb states, and heavier objects of hole character, which we attribute to "biexcitons"—two added O holes are attracted by the charge transfer of two Bi holes into neighboring O [see Fig. 6 or Fig. 3(d) of Ref. 14 in the hole representation]—responsible for the high T_c. Although in our opinion the O bands then have a fundamental role in the superconductivity of these systems, we neglect them in this calculation in which we focus on the effect of the local disproportionation of the Bi atoms. The influence of the O states is discussed later.

We model the local disproportionation in $BaBiO_3$ by subdividing the three-dimensional metal lattice in two interpenetrating fcc sublattices of inequivalent Bi sites. When Bi is substituted by Pb, the diagonal energies on each sublattice site are modified, depending on their occupancy by a Bi or a Pb atom and on the number of nearest-neighbor (on the other sublattice) Pb atoms. The system is solved in the CPA approximation. The electronic structure obtained presents a real gap for a wide compositional range and then a pseudogap persists in the metallic phase allowing to explain the experimental results discussed before. A better agreement is obtained when the O states are considered.

The model which takes into account the local disproportionation of the Bi atoms is presented in Sec. II. The numerical results are shown in Sec. III. In Sec. IV we discuss the effect we expect from inclusion of the O bands and from the many-body effects proposed for the superconductivity, in the complete electronic structure of $BaPb_{1-x}Bi_xO_3$. A detailed comparison with experiment is done in Sec. V. The conclusions are contained in Sec. VI. A brief account of this work has been presented previously.[21]

II. THE MODEL

The model is a simplified version of the one proposed before to study the pairing mechanism in the different perovskites.[14,15] We explain it first for the case of $BaBiO_3$ (without Pb). The Ba atoms are considered only as donors of electrons. The Bi ions occupy a simple cubic lattice and the O ions lie between any two Bi ions. The Bi lattice is subdivided in two fcc interpenetrating sublattices, A and B, in such a way that the six nearest neighbors of an A atom (atom of sublattice A) lie in sublattice B and vice versa. As observed in the real material,[6,8] the O ions are displaced a distance δ from the midpoint towards their nearest-neighbor B atom. Consistent with this distortion, the B atoms are more positively charged than the A atoms as a consequence of the electron-electron repulsion. According to our physical picture, this disproportionation and the local breathing-mode distortion are neither cause nor effect, but can only exist simultaneously.

When Bi is substituted by Pb, we assume that any O atom lying between two Bi ions remains displaced by the same distance δ, while the distortion of an O atom is removed if at least one of its nearest neighbors is a Pb atom. Each displaced O atom makes the electronic energy at its nearest-neighbor B atom (second-nearest-neighbor A atom) increase (decrease) by a constant amount Δ.

In order to investigate the effects of local distortion disproportionations on the electronic structure, keeping the mathematics tractable, we first neglect the covalency of the O-metal bonding; its influence, which we believe is crucial for the superconductivity, will be discussed in Sec. IV. As the important physics lies on the effect of the local distortions on the on-site Bi energies, we take for simplicity the on-site repulsion (minus disproportionation Madelung's energy correction) at the metal sites $U_M=0$. With these simplifications the problem is reduced to the following Hamiltonian describing the dynamics of the metallic 6s electrons:

$$H=\sum_{i\in A,\sigma}\varepsilon_i^A a_{i\sigma}^{\dagger}a_{i\sigma}+\sum_{i\in B,\sigma}\varepsilon_i^B b_{i\sigma}^{\dagger}b_{i\sigma} \\ +t\sum_{i\in A,\langle j\rangle\in B,\sigma}(a_{i\sigma}^{\dagger}b_{j\sigma}+\text{H.c.})\ . \tag{1}$$

Here $m\in\gamma$ specifies that site m belongs to sublattice γ (A or B), and $\langle j\rangle$ means the nearest neighbor of site i.

The first and the second terms denote the on-site energy at site i of sublattices A and B, respectively. The third term represents the nearest-neighbor hopping between metallic sites mediated by the in-between O^{-2} ions. The total number of 6s electrons in the system is directly given by the Bi concentration x. (This is true as long as the O 2p states remain fully occupied. In the covalent case, the statement remains valid if the 6s states are replaced by the antibonding 6s-2p states and if there is no overlap with the bonding 6s-2p and nonbonding O 2p states. At the MI transition, many-body effects become crucial as explained in Sec. IV.) If site i of sublattice $A(B)$ is occupied by a Bi atom and n of its nearest neighbors are also Bi atoms, then $\varepsilon_i^A=\varepsilon_{\rm Bi}-n\Delta(\varepsilon_i^B=\varepsilon_{\rm Bi}+n\Delta)$. Assuming that the occupation probabilities are uncorrelated, the probabilities that the energy at a site i has any of these values are given by

$$\begin{aligned} &p(\varepsilon_i^A=\varepsilon_{\rm Pb})=p(\varepsilon_i^B=\varepsilon_{\rm Pb})=p_0=1-x\ ,\\ &p(\varepsilon_i^A=\varepsilon_{\rm Bi}-n\Delta)=p(\varepsilon_i^B=\varepsilon_{\rm Bi}+n\Delta)\\ &\qquad\qquad=p_n=\begin{bmatrix}6\\ n\end{bmatrix}x^{n+1}(1-x)^{6-n}\ . \end{aligned} \tag{2}$$

The coefficient of the last expression in the number of ways of picking up n elements out of 6.

Neglecting the correlations between energies at neighboring sites, the problem can be viewed as that of an alloy of eight different elements in a lattice with two inequivalent sites per unit cell. The concentration of each component is given by the respective probability in Eq. (2). We solve this problem using the single-site coherent-potential approximation of Velicky *et al.*,[22] generalized for the case of two sites per unit cell and a multicomponent system. The results are shown in Sec. III.

III. NUMERICAL RESULTS

The average on-site Green's function in sublattice γ (A or B) is given by

$$G_\gamma(\omega)=\frac{\gamma-\Sigma_{\bar\gamma}(\omega)}{R}g_0(R)\ , \tag{3}$$

where $\bar\gamma=A(B)$ if $\gamma=B(A)$ and

$$R=\{[\omega-\Sigma_A(\omega)][\omega-\Sigma_B(\omega)]\}^{1/2}\ . \tag{4}$$

$g_0(\omega)$ is the Green's function of a tight-binding Hamiltonian for a simple cubic structure [$x=0$ in Eqs. (1) and (2)] and Σ_A and Σ_B are determined by the following CPA self-consistency equations:

$$\sum_{n=1}^{8}p_n\frac{\varepsilon^\gamma(n)-\Sigma_\gamma(\omega)}{1-[\varepsilon^\gamma(n)-\Sigma_\gamma(\omega)]G_\gamma(\omega)}=0\ , \tag{5}$$

where $\varepsilon^\gamma(n)$ and p_n are the energies and corresponding probabilities given in Eq. (2).

For simplicity we have taken

$$g_0(\omega)=\frac{2}{W^2}[\omega-(\omega^2-W^2)^{1/2}]\ . \tag{6}$$

With this choice, the density of states for $x=0$ has a semi-elliptical form of half-width W, given by the imaginary part of $g_0(\omega)$ and the van Hove singularities, which are unimportant for our discussion, are lost.

For the numerical calculations we assume $\varepsilon_{\mathrm{Pb}}-\varepsilon_{\mathrm{Bi}}=W=3$ eV, independent of x, and we take $\Delta=4W/30$ in order to reproduce the observed reflectivity gap[5] for $x=0.8$.

Figure 1 shows the resulting total density of states as a function of the Bi concentration x. With this value of Δ the MI transition is seen to occur for x slightly larger than 0.25. As it will be discussed later, many-body effects would shift the transition composition to larger values of x. For larger values of Δ the semiconducting region increases and for $6\Delta \gg t$ and intermediate values of x, the density of states shows 14 different peaks near the energies $\varepsilon_{\mathrm{Pb}}$ and $\varepsilon_{\mathrm{Bi}} \pm n\Delta$ $(n=0$ to $6)$. As Δ/t or x decrease, the width of the peaks increases with respect to the distance between two consecutive ones, and the peaks begin to fuse among them. An intermediate situation is shown in Fig. 1 for $x=0.8$, where only a few isolated peaks remain in the gap. They come mainly from Bi atoms occupying A sites with a small number of nearest-neighbor Bi atoms. This can be inferred from Fig. 2 where the Bi and Pb density of states at A sites is displayed. Figure 3 shows the same densities at a B site.

Neglecting the biexcitonic states,[14] the MI transition occurs when for decreasing x, the lower band constituted mainly of Bi states at A sites touches an upper band of mixed Pb and sublattice B Bi states. Since for $x \rightarrow 0$, sublattices A and B are equivalent, for x sufficiently near but different from zero, the system should be metallic for any choice of the other parameters. For $x=0$, since the $6s$ conduction electrons, are provided by the Bi ions, one has an empty Pb band and the system is semiconducting. (In the real system, a small overlap of the O—Pb bonding and antibonding bands can lead to a poor metal, as proposed by Cox and Sleight[6].)

The number of carriers increases with the Bi concentration x until the disproportionation becomes important. Then a pseudogap develops in the electronic structure (see Figs. 1–3 for $0.10<x<0.25$) until for x large

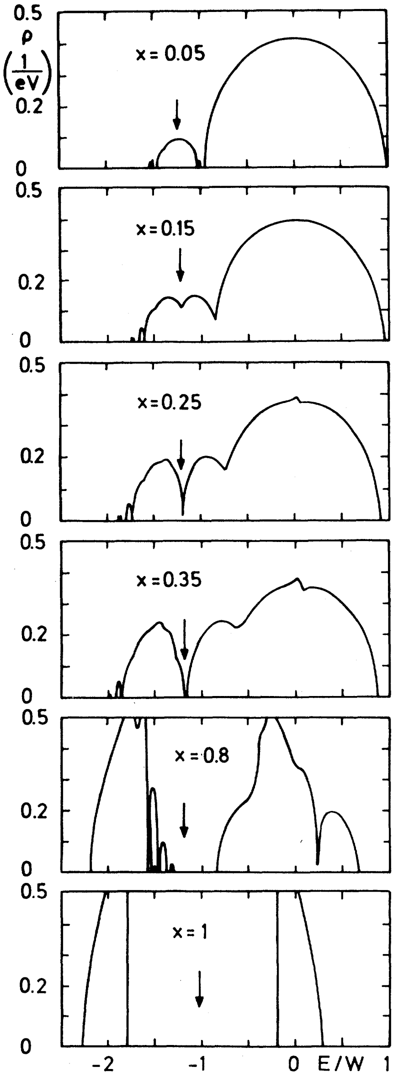

FIG. 1. Evolution of the density of Pb+Bi states in $\mathrm{BaPb}_{1-x}\mathrm{Bi}_x\mathrm{O}_3$ for $\varepsilon_{\mathrm{Pb}}-\varepsilon_{\mathrm{Bi}}=W$ and $\Delta=4W/30$, as a function of the concentration x. The arrows indicate the position of the Fermi level ε_F. Three different physical regimes are obtained: metallic, metallic, with a disporportionation pseudogap and insulating.

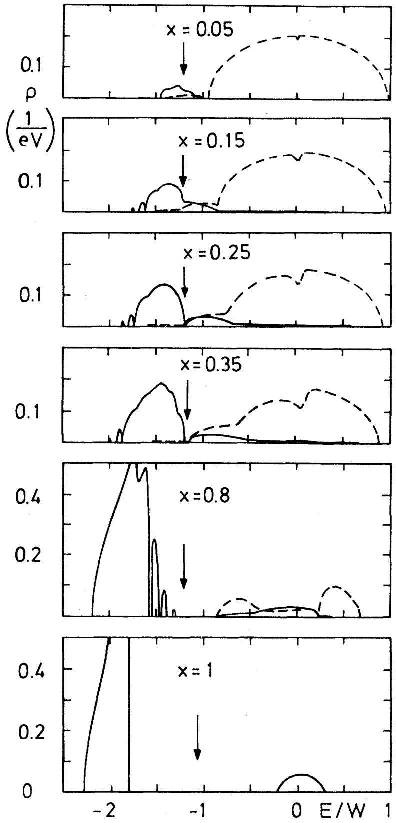

FIG. 2. Contribution of the Bi (solid line) and Pb states (dashed line) to the density of states of an atom of sublattice A, for different Bi concentrations x, indicated inside each figure. Other parameters as in Fig. 1. The arrows indicate the Fermi energy.

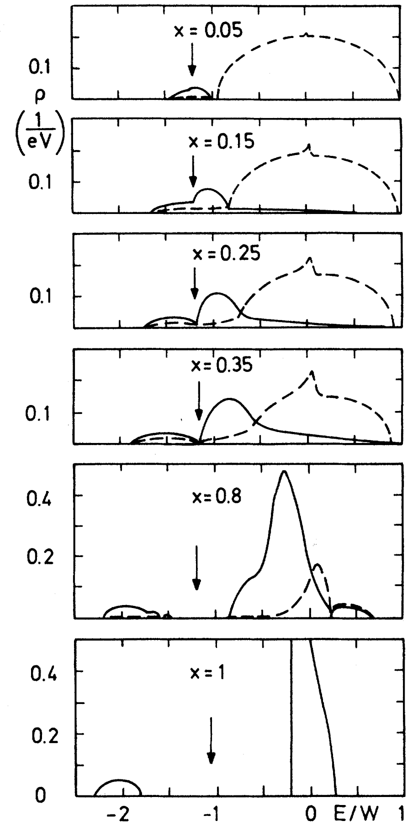

FIG. 3. Same as Fig. 2 for an atom of sublattice B.

enough a real gap appears. This behavior is illustrated by the density of states at the Fermi level shown in Fig. 4.

Finally in Fig. 5 we show the valence of the Bi ions in both sublattices as a function of x. For $x \rightarrow 0$ the oxidation state of all Bi ions lies between $+4$ and $+5$. The exact value depends on $\varepsilon_{\mathrm{Pb}} - \varepsilon_{\mathrm{Bi}}$. We must point out that with the assumption that the O ions between two Bi atoms are always displaced by the same distance δ, independently of x, we are overestimating the disproportionation for $x \rightarrow 0$. The degree of disproportionation as x increases depends on the ratio Δ/t. For the parameters we have chosen, for $x \rightarrow 1$ we obtain an important effect. Experimentally the exact value of the charge disproportionation is controversial.

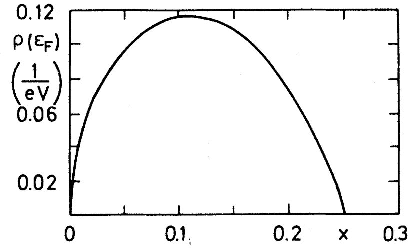

FIG. 4. Density of states at the Fermi level for $\mathrm{BaPb}_{1-x}\mathrm{Bi}_x\mathrm{O}_3$ as a function of the Bi concentration x, neglecting the contribution of many-body effects due to Bi-O covalency. Parameters as in Fig. 1.

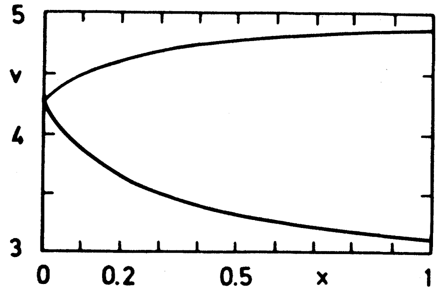

FIG. 5. Oxidation state of the Bi atoms in the two inequivalent sites as a function of the Bi concentration x. Parameters as in Fig. 1.

IV. ROLE OF THE OXYGEN STATES AND MANY-BODY EFFECTS

As we have said in the Introduction, we think that oxygen holes are important in the superconducting region. Their presence has been confirmed in doped CuO_2 high-temperature superconductors[19] and there is some indication from Seebeck measurements[20] that holes are present also in $\mathrm{BaPb}_{1-x}\mathrm{Bi}_x\mathrm{O}_3$. According to our physical picture the O holes begin to appear at the MI transition as we are going to show below. As even in the metallic phase this system presents a low number of carriers,[9] the screening length is rather small, and the nearest-neighbor Coulomb repulsion is important. Thus, when O holes are considered, many-body effects must also be included. Unfortunately we cannot include these correlations retaining all the physical ingredients of the detailed electronic structure we have calculated before. However we can qualitatively discuss the effect of these correlations analyzing the strong-coupling limit $t \rightarrow 0$. In this limit the ground state for $x = 1$ corresponds to doubly occupied A sites (Bi^{3+}) and empty B sites (Bi^{5+}). The relevant configurational average energies calculated within the model of Ref. 14 are the following:

(i) The average energy necessary to add an electron in the orbital aligned along the Bi-O-Bi direction of an O site,

$$E_p = \varepsilon_p + 2G + U_p/2 , \tag{7}$$

where G is the nearest-neighbor Coulomb repulsion between metal and O electrons and U_p the on-site O Coulomb repulsion. Taking into account the balance between nuclear charges and electrons we assume that E_p is independent of x. Although Pb has one less conduction electron than Bi it also has one less nuclear charge.

(ii) The energy necessary to add the second $6s$ electron on a Bi site of sublattice A

$$E_{\mathrm{Bi}}^{A} = \varepsilon_{\mathrm{Bi}} + U_M - 6x\Delta + 12G , \tag{8}$$

where U_M is the on-site Coulomb repulsion of the Bi sites.

(iii) The energy necessary to add the first $6s$ Bi electron in sublattice B,

$$E^{B}_{\mathrm{Bi}} = \varepsilon_{\mathrm{Bi}} + 6x\Delta + 12G \ . \tag{9}$$

(iv) Half the energy necessary to add the two 6s electrons on a Bi site of sublattice A,

$$\tilde{E}^{A}_{\mathrm{Bi}} = \varepsilon_{\mathrm{Bi}} + \frac{U_M}{2} - 3x\Delta + 12G \ . \tag{10}$$

(v) Half the energy necessary to add two 6s electrons on a Bi site of sublattice B

$$\tilde{E}^{B}_{\mathrm{Bi}} = \varepsilon_{\mathrm{Bi}} + \frac{U_M}{2} + 3x\Delta + 12G \ . \tag{11}$$

(vi) The energy necessary to add two holes building the biexcitonic structure of Fig. 6. This state takes advantage of the energy gain in interatomic Coulomb repulsion by reordering the charges,

$$E_{\mathrm{biexc}} = 2\varepsilon_{\mathrm{Bi}} - 4\varepsilon_p + U_M + 6x\Delta - 4U_p \ . \tag{12}$$

From these energies we can derive the following information:

(i) The gap between Bi states is related to

$$\Delta E = \min(E^{B}_{\mathrm{Bi}}, \tilde{E}^{B}_{\mathrm{Bi}}) - \max(E^{A}_{\mathrm{Bi}}, \tilde{E}^{A}_{\mathrm{Bi}}) \ . \tag{13}$$

If $6x\Delta > U_M$, Eq. (8) gives a lower value than Eq. (9) with $\Delta = 0$. This means that it is more convenient to distort the O ions, and Eq. (13) giving the disproportionation gap simplifies to

$$\Delta E = \tilde{E}^{B}_{\mathrm{Bi}} - \tilde{E}^{A}_{\mathrm{Bi}} = 6x\Delta \ (\text{if } 6x\Delta > U_M) \ . \tag{14}$$

The gap vanishes for $x < x_d$ with $x_d = U_M/6\Delta$.

(ii) When holes are added to the system (or if electrons are transferred to the Pb band), the necessary condition to have holes with oxygen character, even if $E_p < \tilde{E}^{A}_{\mathrm{Bi}}$ is

$$2\tilde{E}^{A}_{\mathrm{Bi}} + E_{\mathrm{biexc}} < 0 \ , \tag{15}$$

i.e.,

$$4(\varepsilon_{\mathrm{Bi}} - \varepsilon_p) + 2U_M - 4U_p + 24G < 0 \ . \tag{16}$$

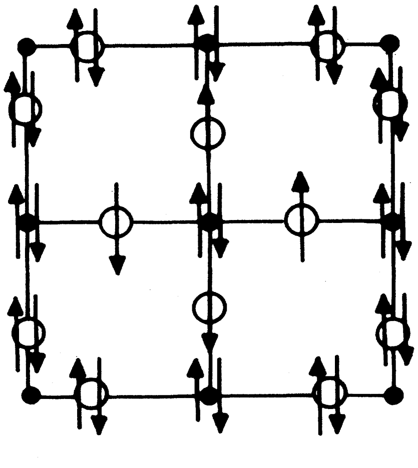

FIG. 6. Schematic representation of the biexcitonic structure proposed as responsible for pairing in BiO_3 superconductors (Refs. 14 and 15).

(iii) In the case of $BaPb_{1-x}Bi_xO_3$, in contrast to $Ba_{1-x}K_xBiO_3$ where holes are provided by Ba substitution, in order to have biexcitons, two electrons must be transferred into the Pb band or to the Bi B subband. Assuming that the inequality (16) is satisfied, the conditions are, respectively,

$$f(x) = 2(\varepsilon_{\mathrm{Pb}} + 12G) + E_{\mathrm{biexc}} < 0 \tag{17}$$

or

$$g(x) = 2\tilde{E}^{B}_{\mathrm{Bi}} + E_{\mathrm{biexc}} < 0 \ . \tag{18}$$

The latter relation can be written as

$$g(x) = 4(\varepsilon_{\mathrm{Bi}} - \varepsilon_p) + 2U_M + 12x\Delta + 24G - 4U_p < 0 \ . \tag{19}$$

Both functions $f(x)$ and $g(x)$ increase with the Bi concentration x [see Eq. (12)] and the MI transition occurs when

$$\min[f(x_c), g(x_c)] = 0 \ , \tag{20}$$

where according to experiment,[9] $x_c = 0.35$ for $BaPb_{1-x}Bi_xO_3$. The necessary conditions for our picture on the biexcitons to be valid are that Eq. (20) and the unequalities (16) and $\varepsilon_p < \tilde{E}^{A}_{\mathrm{Bi}}$ must be satisfied in the range $x_1 < x < x_c$ where $x_1 \sim 0.1$. These conditions can be satisfied for a wide range of reasonable values of the parameters.[14,15]

V. COMPARISON WITH EXPERIMENT

In contrast with previous work that only obtained a pseudogap,[11] or a gap[13] for $x \to 1$, we obtain semiconducting behavior for $x > x_c' \sim 0.25$. This critical concentration for the MI transition, obtained with the Δ value taken to reproduce the optical gap,[5] approaches the experimental one[9] $x_c \simeq 0.35$ $(x_c > x_c')$ when the many-body effects discussed in Sec. IV are considered. In fact, we believe that due to interatomic correlations, for $x \sim 0.3$ it is more convenient to transfer electrons from the O ions to the band above the gap forming the biexcitonic structure responsible for pairing.[14,15] This pushes the MI transition to higher x values.

In agreement with experimental results[5] for $x < 0.7$, the optical gap decreases with x. For $x > 0.7$ it seems that the experimental gap remains constant, but as the method employed to prepare the samples was changed just at this concentration—and as the properties of $BaPb_{1-x}Bi_xO_3$ are known to be sensitive to the preparation treatment[8]—this point requires further study.[5] The extended states of lower weight that appear in the gap for large x (see Fig. 1, $x = 0.8$) could explain why the observed resistivity gap is smaller than the optical one.[5] As we have discussed in Sec. III and as it can be inferred from Figs. 2 and 3, these peaks come mainly from A-Bi atoms (with oxidation state near 3+) surrounded by some nearest-neighbor Pb atoms.

The optical studies by Tajima *et al.*[4,5] show that the reflectivity spectra for the samples of $x = 0$, 0.05, and 0.125 can be fitted fairly well to the calculated ones using the Drude equation. However, when the Bi content increases, for $x > 0.15$, the plasma edge still shifts towards higher energy, while the reflectivity in the lower-energy region is reduced and the deviation from the Drude curve becomes accordingly more remarkable. The spectrum seems to change gradually from the metallic to the semiconducting phase, and from the optical behavior, the boundary composition between these two phases is not quite clear. It is likely that the effect of the disproportionation begins for $x > x_d \simeq 0.15$ and the behavior is continuous: A pseudogap appears, the density of states at the Fermi level decreasing for increasing x down to the opening of a real gap at $x_c \sim 0.35$. This behavior is well reproduced by the calculated curves (see Figs. 1–3). The value of x_c' increases with decreasing Δ. The presence of a pseudogap before the transition is also indicated by the semiconductorlike temperature behavior of the resistivity for $x \simeq 0.25$, that is the resistivity increases as the temperature goes down, also in the metallic phase.[4]

The carrier density n^* estimated from the Hall effect[9] varies linearly with x up to $x \sim 0.15$ where it becomes larger than expected, up to a maximum around $x \sim 0.2$, and then n^* decreases. The Seebeck coefficient[20] seems to consist of two contributions: one from ordinary electrons and the other from additional carriers with hole character and fairly low mobility. While the former contribution increases linearly with x up to $x \sim 0.15$, the hole part shows a maxima around $x \sim 0.20$, near the value where T_c also becomes maximum. The x dependence that we obtain for the density of states at the Fermi level ε_F (see Fig. 4) which can be related to n^*, follows the general features of the above results. The effect of small amounts of Bi substitution in $BaPbO_3$ is to increase linearly with x the number of carriers, as Bi has one conduction electron more than Pb. However for $x \sim 0.1$ the Bi atoms begin to disproportionate, a pseudogap develops at ε_F and the lower band takes the donated conduction electrons, so decreasing the average number of carriers. The additional increase in carrier concentration experimentally observed[9] around $x \sim 0.2$ can be explained again by the effect of the O-metal covalency. The heavier-hole character carriers seen in Seebeck measurements[20] would then correspond to the biexcitonic structure (see Fig. 6 and Refs. 14 and 15), the concentration of which would have the same x dependence.

Since the discovery of superconductivity[1] in $BaPb_{1-x}Bi_xO_3$ the bismuth valence state, considered a crucial parameter for the comprehension of the physical properties of this perovskitelike compound, has been a matter of controversy. However, recent detailed neutron-diffraction studies[8] for the end member $BaBiO_3$ have confirmed the initial finding by Cox and Sleight[6] of two crystallographically inequivalent sites for the Bi cations, with two significantly different Bi-O distances for the *A* and *B* sites (and have explained some differences in previous work by the sample dependence on the preparation method). Furthermore, Chaillout *et al.*[8] evaluate the effective valences using Zachariasen's formula, finding values around 3.40 and 4.40 for the two different Bi sites. In Fig. 5 the valence of the Bi ions in both sublattices is plotted as a function of x. For the parameters we have chosen we obtain a larger effect. As we have already said, the Bi valence as $x \rightarrow 0$ depends on the ratio $(\varepsilon_{\rm Pb} - \varepsilon_{\rm Bi})/W$, and by taking the same distortion for all O ions between two Bi atoms independently of the environment we are overestimating the effect of the charge transfer for small values of x; the ratio Δ/t controls the increase of the disproportionation with x.

VI. CONCLUSIONS

A local, rather than a CDW description for $BaPb_{1-x}Bi_xO_3$ is strongly suggested by the persistence of the semiconducting behavior up to 65% Pb, and the properties of the metallic phase near the MI transition. We have then studied the effect of the disproportionation of Bi atoms combined with local O distortions, on the electronic structure of this system. It has been shown that in the coherent potential approximation, three regimes are obtained as a function of the Bi concentration x: metallic, metallic with a pseudogap, and insulating.

Our picture of the MI transition is the following: For $x \sim 1$ there are two bands of mainly Bi character, one is full and the other one empty, and another empty band of mainly Pb states with weight $(1-x)$. As larger amounts of Pb replace Bi atoms, the Pb band broadens, the number of distorted O ions and then, the energy difference between Bi states in both sublattices, decrease. Since the weight of the lower Bi band coincides with the number of conduction electrons in the system x, the system remains semiconducting until for $x = x_c$ the difference between the top of the lower Bi band and the bottom of the Pb or upper Bi band is zero, or low enough, so that biexcitons can be formed. For $x < x_c$ the system is metallic but the disproportionation is not yet completely inhibited and a pseudogap persists also in this phase for $x > \sim 0.1$.

This evolution of the electronic structure with the Bi concentration x allows us to understand the continuous behavior of the optical properties in spite if the MI transition at $x_c = 0.35$. Other properties as the resistivity and the x dependence of the Hall coefficient also give support to this picture.

We have also discussed how interatomic correlations arising from the covalency of the O-metal bonding, proposed as the origin of the pairing mechanism,[14,15] would yield a better agreement. We think, in fact, that although the present calculation is consistent with the experimental results, these many-body effects must be included to have a completely satisfactory description. We have proposed that O holes appear after considerable amount of Pb substitution, due to the interatomic correlations. The Coulomb repulsion between nearest-neighbor Bi and O atoms then becomes a relevant parameter giving rise to pairing of the O holes by the charge transfer of the two holes of the common neighboring Bi^{5+} site. The heavier hole-character carriers, with maximum concentration for the maximum T_c, seen in Seebeck measurements[20] would then correspond to this biexcitonic structure. This can explain the additional increase of the Hall coefficient[9] and would push the MI transition to a higher x_c value than the one obtained considering only the Bi-disproportionation.

This scenario seems also consistent with recent isotope effect studies in BiO superconductors, suggesting that pairing is mediated by electronic excitations which involve atomic displacements as a result of charge redistribution.[23] The existence of biexcitons could also explain the curious x dependence of the intensity of the 100-cm^{-1} mode observed by Raman scattering,[24] which clearly also correlates with the magnitude of T_c. This mode could be due to movements of the O^{-1} ions of a biexciton that keep unaltered the Bi-O distance. Raman experiments in ^{18}O-substituted samples could clarify this possibility.

To conclude, within a model that allows a common pairing mechanism for the CuO_2 and BiO_3 superconductors, we have calculated the electronic structure of $BaPb_{1-x}Bi_xO_3$ obtaining a satisfactory explanation of the available experimental results.

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