Electronic structure of Ba(Sn,Sb)O$_3$: Absence of superconductivity

D. J. Singh and D. A. Papaconstantopoulos

Complex Systems Theory Branch, Naval Research Laboratory, Washington, D.C. 20375-5000

J. P. Julien and F. Cyrot-Lackmann

*Laboratoire d'Etudes des Proprietes Electroniques des Solides, Centre National de la Recherche Scientifiques,
25 Avenue des Martyrs, Boîte Postale 166, 38042 Grenoble, France*

The electronic structures of BaSnO$_3$, BaSbO$_3$, and BaPbO$_3$, calculated using an extended general-potential linearized augmented-plane-wave method, are reported. The electronic structures of BaSnO$_3$ and its 6s analog BaPbO$_3$ are found to be very different, explaining the absence of superconductivity in the Ba(Sn,Sb)O$_3$ system. These differences are explained by a combination of the relativistic lowering of the 6s states and ion-size effects. Muffin-tin-approximation augmented-plane-wave calculations for BaSnO$_3$ are also reported and the utility of the muffin-tin approximation for this and similar materials is discussed in terms of the differences between the two sets of calculations.

INTRODUCTION

Since the discovery of high critical temperature (T_c) cuprate superconductors,[1] there has been considerable discussion regarding the relationship between these materials and the bismuthate superconductors[2,3] such as Ba$_{0.6}$K$_{0.4}$BiO$_3$ which has $T_c = 30$ K.[3] While the bismuthates lack two-dimensional (2D) structures analogous to the CuO$_2$ planes which are characteristic of the high-T_c cuprate materials, they share many other features with the cuprates. In addition to their high-T_c superconductivity, the bismuthate superconductors, like the cuprates, are characterized by near instabilities in their lattices[4] and by proximity to metal-insulator (MI) transitions.[5,6] Unlike the cuprates whose MI transitions are associated with magnetic phases similar to the 3d transition metal monoxides such as NiO, the MI transitions in the bismuthate materials are thought to be associated with tendencies towards charge disproportionation or structural instabilities.

Superconductivity also occurs in the antimonide,[7] BaPb$_{1-x}$Sb$_x$O$_3$ at a Pb concentration near that for which BaPb$_{1-x}$Bi$_x$O$_3$ has its highest T_c, which is 13 K. In view of the chemical similarity of Bi and Sb, it is remarkable that the highest transition temperature found in the antimonide system is only 3.5 K. We note that rigid-muffin-tin approximation,[8] calculations of the electron-phonon couplings in qualitative agreement with this trend have been reported.[9,10]

Recently, the synthesis of BaSn$_{1-x}$Sb$_x$O$_3$ has been reported.[11] This material may be regarded as the 5s analogue of BaPb$_{1-x}$Bi$_x$O$_3$. This material, however, is not superconducting, and in fact its resistivity is characteristic of an insulator. Cava et al. have proposed that the lack of superconductivity in this system is a result of the conduction band being higher or narrower, possibly as a result of relativistic effects on the 6s series.[11] An alternate explanation is that the somewhat smaller ionic radii of Sn

and Sb as compared to Pb and Bi may lead to a reduction in the stability of the ideal cubic perovskite lattice leading to insulating behavior. This is consistent with the limited range of Sb concentrations for which the compound is stable. In the present study we focus on the former explanation, and report local density approximation (LDA) based electronic structure calculations for the two end points of the alloy system, i.e., BaSnO$_3$ and the hypothetical material BaSbO$_3$. The band structure of BaPbO$_3$ has been calculated by Mattheiss and Hamann[12] using a full potential linearized augmented-plane-wave (LAPW) method as well as by Takegahara and Kasuya[13] and Papaconstantopoulos et al.,[9] both using muffin-tin-approximation augmented-plane-wave (APW) methods. The most notable difference between these calculations is a lowering of the valence Pb(6s)-derived, Γ_1 state in the calculation of Ref. 12 as compared to the calculations of Refs. 9 and 13, leading to a reordering of the bands at Γ. This band, as it disperses away from Γ, is of Pb(6s)-O(2p) character and hence according to the arguments of Ref. 12 may be important for superconductivity. Accordingly, we have performed new, highly converged, calculations for cubic BaPbO$_3$ in order to establish the position of this band.

METHOD

The calculations reported here were performed using an extension[14] of the general potential (i.e., no shape approximations) LAPW method.[15] In this approach, variational freedom is enhanced by adding local orbitals to the LAPW basis. This facilitates calculations for systems with extended core states and/or narrow valence bands. In the present study, this extension was used to include the O(2s), Ba(5s), Ba(5p), Sn(4d), and Sb(4d), together with the higher-lying states, in a single energy window. The calculations were performed fully self-consistently using the Hedin-Lundqvist local exchange-correlation

function.[16] The core states were treated relativistically in an atomic approximation, with a semirelativistic approximation being used for the valence bands. Mattheiss and Hamann[12] have discussed the effect of spin orbit on the band structure of BaPbO$_3$. Its effect is small because of the strong hybridization of the Pb(6p) states which is reflected in the bandwidths. The Brillouin zone integrations required to compute the charge density during the iteration to self-consistency were performed using 56 special k points in the irreducible wedge of the zone.[17] For BaSnO$_3$ the experimental lattice parameter of 4.12 Å was used. (Since our interest here is in the electronic structures, we have not performed total energy calculations of the lattice parameters.) BaSbO$_3$ has not been synthesized and was studied in order to compare the effects of substituting Sb for Sn with those of substituting Bi for Pb in the 6s material. Accordingly, the lattice parameter of BaSnO$_3$ was used for this material. BaPbO$_3$ only occurs in the cubic perovskite structure at elevated temperatures. At low temperature its structure is an orthorhombic distortion of the perovskite structure. In the calculations presented here a lattice parameter of 4.267 Å was used. This choice yields the same volume per formula unit as the low-temperature orthorhombic structure. Parallel calculations were performed using a muffin-tin-approximation APW method[18] in order to assess the effects of the muffin-tin (MT) approximation for these materials and thereby facilitate comparison with previous muffin-tin-approximation calculations for related compounds. The computational parameters for the APW calculations are the same as those given in Ref. 9.

RESULTS AND DISCUSSION

The calculated band structure of BaSnO$_3$ is shown in Fig. 1 with the corresponding projected electronic density of states (DOS) in Fig. 2. Selected eigenvalues for BaSnO$_3$ are compared with those of BaPbO$_3$ in Table I.
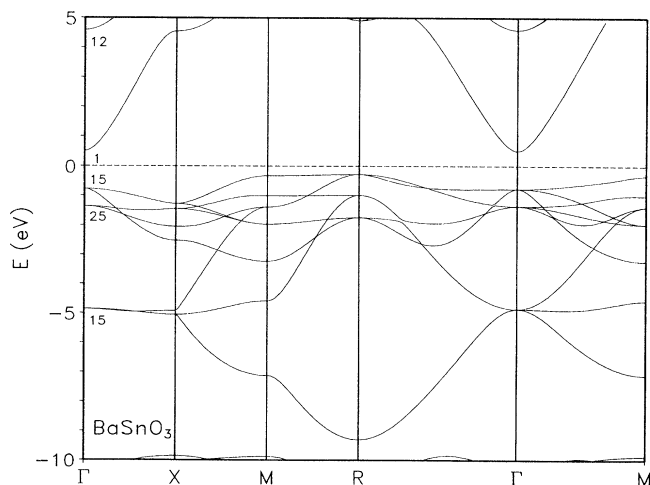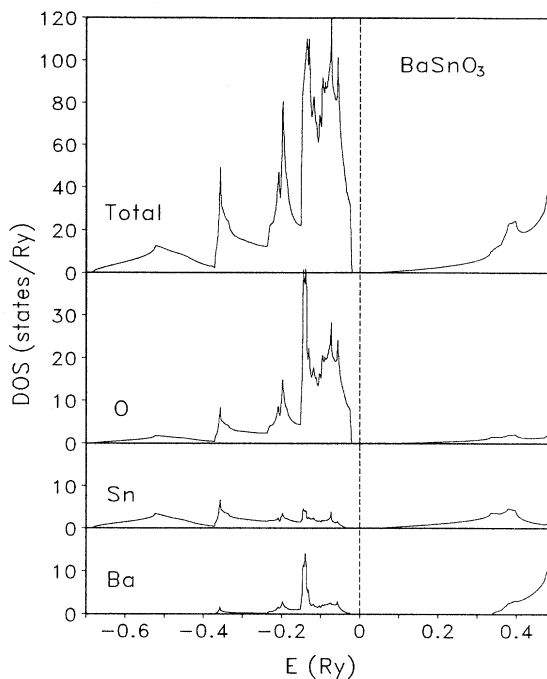

FIG. 2. Projected electronic density of states (DOS) of BaSnO$_3$. The top panel is the total DOS. The lower three panels show the DOS projected onto the Ba, Sn, and O spheres.

In addition, band energies, calculated using a muffin-tin APW method, are given in Table I (a comparison of the muffin-tin and full-potential results is given below). The band structure of BaSbO$_3$ is shown in Fig. 3. The band structure of BaPbO$_3$ is quite similar to the one calculated by Mattheiss and Hamann[12] using a similar approach and accordingly is not shown here.

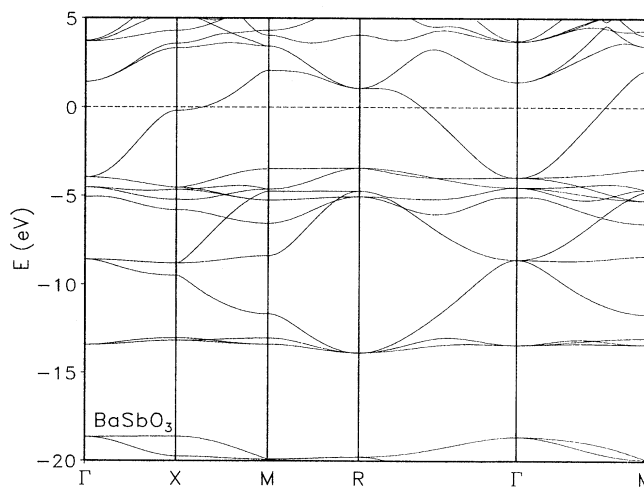FIG. 1. Band structure of BaSnO$_3$. The dashed line indicates the Fermi energy.

FIG. 3. Band structure of the hypothetical material BaSbO$_3$ at a lattice parameter equal to that of BaSnO$_3$. The dashed line indicates the Fermi energy.

TABLE I. Comparison of the band energies (in eV relative to the Fermi energy) of BaSnO$_3$ and BaPbO$_3$. MT denotes calculations performed using a muffin-tin APW method (see text). For the MT calculations on insulating BaSnO$_3$ the position of the Fermi energy in the gap was set such that the conduction band minimum was the same as for the general potential calculation. E_g denotes the band gap.

	BaSnO$_3$	BaSnO$_3$ (MT)	BaPbO$_3$	BaPbO$_3$ (MT)
Γ_{15} Ba $5p$	-10.24	-10.26	-10.23	
Γ_{15}	-4.86	-5.04	-4.21	-3.95
Γ_{25}	-1.29	-3.10	-0.96	-2.19
Γ_{15}	-0.77	-2.07	-0.58	-1.35
Γ_1	0.51	0.51	-1.62	-1.70
Γ_{12}	4.59	3.18	4.70	3.88
R_1	-9.30	-8.90	-9.46	-8.86
R'_{25}	-1.74	-2.11	-1.30	-2.57
R_{12}	-0.99	-1.52	-0.03	-0.13
R'_{15}	-0.28	-3.41	0.07	-1.33
R_{15}	4.91		4.85	5.07
E_g	0.79	2.03	Metallic	Metallic

The band structure of BaSbO$_3$ may be related in a crude way to that of BaSnO$_3$ by raising the Fermi energy of the latter material into the conduction bands. Thus Sb is apparently an electron donor in this system. In addition, significant nonrigid band effects are present as may be expected in an ionic material. These are gap closings and a narrowing of the bands. The differences between the band structures of BaSbO$_3$ and BaBiO$_3$ (see Refs. 12 and 19 for general potential calculations of the band structure of BaBiO$_3$) are less pronounced and probably less significant than those between the corresponding Sn and Pb materials, which we focus on in the following discussion.

Several differences between the electronic structures of BaSnO$_3$ and BaPbO$_3$ (see Ref. 12) are apparent from Figs. 1 and 2. The most significant of these is that the former material is an insulator with a fairly substantial indirect band gap of 0.79 eV while the latter is a metal. This in itself explains the absence of superconductivity in the Ba(Sn,Sb)O$_3$ system, and is consistent with the suggestion of Cava et al.[11] BaPbO$_3$ is a metal and doping with Bi leads to shifts of the Fermi energy accompanied by some nonrigid band effects.[12] The substantial gap found for BaSnO$_3$ and the resistivities measured in Ref. 11 are consistent with a picture in which doping BaSnO$_3$ with Sb leads to the formation of an impurity band which broadens with increasing Sb concentration An examination of Fig. 2 reveals that the upper valence bands are of O(2p) character. The small Sn and Ba components visible in the projected DOS in this energy range are due to the extended tails of the O(2p) states extending into neighboring spheres. The states near the conduction band minimum are of Sn(5s) character, with the lowest noncore Ba states occurring about 4 eV above the Fermi energy. The situation in the 6s material, BaPbO$_3$, is quite different. The bands are broader and the O(2p) and metal(s) states, which are separated by the band gap in the 5s material, overlap. Mattheiss and Hamann have

pointed out that the resulting hybridized O(2p)-(Pb,Bi)(6s) bands may be strongly coupled to phonons which modulate the O-(Pb,Bi) bond length and have speculated that this may be responsible for the high-T_c superconductivity of the bismuthates.

In seeking an explanation for the differences in the electronic structures of the 5s and 6s materials, we note, as did Cava et al.,[11] that Sn and Pb are very similar from a chemical point of view, as are Sb and Bi, apart from relativistic shifts which lower the valence s states in the 6s systems relative to the corresponding 5s systems. Since the important Γ_1 state, which drops into the O(2p) manifold in BaPbO$_3$ but not in BaSnO$_3$, is primarily of (Pb,Sn)(s) character, this relativistic shift may provide an explanation of the difference between the two materials. Relativistic atomic calculations show that the 6s level in Pb is 0.9 eV lower than the 5s level in Sn and that this difference increases to 1.8 eV for the 4+ ions. On the other hand, the lowering of the Γ_1 state relative to the center of the O(2p) manifold at Γ on going from BaPbO$_3$ to BaSnO$_3$ is 2.5 eV, which is significantly larger than the expected effect of the relativistic lowering of the 6s state in the Pb ion. In view of the strong coupling of the electronic structure to phonons, such as the breathing mode, which modulate the Pb-O separation,[12] and the larger than expected lowering of the Γ_1 state in the 6s material, it is interesting to study the role of the differing metal-O bond lengths in the 5s and 6s materials.

BaSnO$_3$ and BaPbO$_3$ consist of tetravalent cations in a BaO$_3$ cage. In the 6s material the cage is expanded to accommodate the larger Pb ion, and as a result the important Pb-O bond length is 0.07 Å larger than the Sn-O separation in the 5s material. The difference in ionic radii between 4+ Pb and Sn ions is 0.19 Å,[20] which is almost three times larger than this. Thus it seems that the BaO$_3$ cage partially suppresses the expansion of the lattice arising from the larger Pb ion. On the other hand, the radial extent of the 5s orbital in Sn and the 6s orbital in Pb is

similar, due to the relativistic contraction in Pb. Thus the valence s orbital experiences a lower effective pressure in the $6s$ material, because of the larger lattice parameter.

In order to investigate the role of different ionic radii in determining the position of the Γ_1 state in these materials, we have performed additional self-consistent electronic structure calculations The first of these was for $BaSnO_3$ with the lattice parameter reduced by 4%. This was done to understand the role of the BaO_3 cage which prevents the lattice from contracting as much as would be expected from the difference in the ionic radii, when Sn is substituted for Pb. The principal result of this calculation is that the Γ_1 state is raised relative to the $O(2p)$ manifold under pressure, yielding an increase in the band gap. For a 4% reduction in the lattice parameter, the indirect gap (which remains between R and Γ) is increased to 2.5 eV while the separation between the uppermost $O(2p)$ band at Γ and the Γ_1 state increases to 2.9 eV. This result motivated calculations for $BaSnO_3$ using the lattice parameter of $BaPbO_3$, which is approximately 3.5% larger than the equilibrium lattice parameter, and for $BaPbO_3$ with the $BaSnO_3$ lattice parameter. These were performed in order to determine to what extent the differences in the metal-O bond lengths can explain the differences in the band structures of the two materials. This is reasonable because the radii of the valence s orbitals of Pb and Sn are practically identical, so that increasing the lattice parameter of $BaSnO_3$ to that of $BaPbO_3$ simulates reducing the effective "pressure" on the $Sn(5s)$ orbital to a value similar to that on the $Pb(6s)$ orbital in that later material. We find that when $BaSnO_3$ is expanded to the $BaPbO_3$ lattice parameter, the Γ_1 state drops below the valence band maximum at R, yielding metallic behavior. Unlike the situation in $BaPbO_3$, however, this state remains above (by 0.1 eV) the uppermost $O(2p)$ band at Γ. The separation between the Γ_1 state and the center of the $O(2p)$ manifold is 1.5 eV, as compared to 2.8 eV at the equilibrium lattice parameter and 0.3 eV for $BaPbO_3$. Conversely, when $BaPbO_3$ is compressed to the lattice parameter of $BaSnO_3$, the Γ_1 state is pushed up in energy to 1.6 eV above the center of the $O(2p)$ manifold and 0.15 eV above the uppermost $O(2p)$ band at Γ. (This is still below the Fermi energy, so that the compressed material remains metallic.) Thus when either material is compressed from the equilibrium lattice parameter of $BaPbO_3$ to that of $BaSnO_3$ the important Γ_1 state is raised by 1.3 eV with respect to the $O(2p)$ states. The fact that the shift is the same in both materials reflects the similarity of the $Pb(6s)$ and $Sn(5s)$ orbitals. This allows us to conclude that the shift of the Γ_1 state due to the differing lattice parameters of the two materials is 1.3 eV, and that the remaining shift of 1.2 eV is due to the relativistic lowering of the $Pb(6s)$ orbital. This value of 1.2 eV is consistent with atomic calculations, discussed above. The combination of these two effects is responsible for the insulating character of $BaSnO_3$ and the absence of superconductivity in the $Ba(Sn,Sb)O_3$ system.

Finally, we remark on the accuracy of the results obtained using the muffin-tin approximation. Based on the close correspondence of our calculated band structure for $BaPbO_3$ and that of Mattheiss and Hamann,[12] we believe that the different band ordering at Γ found in Refs. 9 and 13 results from the use of the muffin-tin approximation, and that the ordering of Ref. 12 and the present study is the correct LDA ordering. In the case of $BaSnO_3$, we find that the calculated band structures using the general potential LAPW method and the muffin-tin APW method are qualitatively similar and that the ordering of the bands at Γ is the same using the two approaches. Both methods predict $BaSnO_3$ to be an insulator with the APW method predicting a larger band gap of 2.0 eV (note, however, that band gaps are often underestimated in LDA based calculations). However, the ordering of bands at the R point differs. This is significant because the valence band maximum is at R. In both calculations the valence band maximum is of primarily $O(2p)$ character. However, the symmetries differ. The muffin-tin calculation predicts that the uppermost valence band is an R_{12} state while the general potential calculation yields an R'_{15} valence band maximum. In both calculations the gap is indirect with the conduction band minimum having Γ_1 symmetry. Thus while the muffin-tin approximation preserves the trends found in the general potential calculations, it appears that the use of this approximation changes some potentially important details in the energy bands and to a lesser extent in the electronic DOS of these materials.

In perovskite structure oxides the dominant interactions between the ions arise from the Coulomb (i.e., the Madelung energy) interaction and the repulsion between the ion cores. Both these interactions may be expected to be well described in a MT approximation. (The general agreement of the MT and full-potential band structures, presented here, indicates that the ionicity is correctly described by MT calculations.) Thus it may be expected that the lattice parameters obtained using a MT approximation method will be in reasonable agreement with those obtained using more sophisticated approaches. On the other hand, the lattice dynamics and structural stability of these materials are strongly influenced by the high polarizability of the O ions. Accordingly, it may be expected that the MT approximation will be inadequate for studying these properties.

There have been calculations of electron-phonon coupling strengths for the $(Ba,K)BiO_3$, $Ba(Pb,Bi)O_3$, and $Ba(Pb,Sb)O_3$ systems which have reproduced the experimental trends in the superconductivity of these materials.[9,10] These calculations were based on band structures which were calculated using the muffin-tin approximation. In these systems the superconducting phases occur when the materials are doped such that the Fermi energy falls at a position above that in $BaPbO_3$. Thus in the superconducting materials the Fermi level occurs in the highly dispersive metal$(6s)$-$O(2p)$ hybridized conduction band. A comparison of the full-potential band structures of $BaSbO_3$ (Fig. 3), $BaPbO_3$, and $BaBiO_3$ (Ref. 9) with the muffin-tin-approximation band structures of Refs. 9 and 10 reveals this band is not strongly affected by the muffin-tin approximation. This lends credibility to the electron-phonon calculations of Refs. 9 and 10.

CONCLUSIONS

Electronic structures of $BaSnO_3$, $BaSbO_3$, and $BaPbO_3$ have been calculated within the LDA. Unlike $BaPbO_3$, $BaSnO_3$ is found to be an insulator. This difference can be understood as due to a combination of the relativistic lowering of $6s$ levels in Pb relative to the $5s$ levels in Sn, combined with ion-size effects.

ACKNOWLEDGMENTS

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