Electronic structure of $BaPb_{1-x}Bi_xO_3$

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Electronic-structure calculations have been carried out for representative members of the $BaPb_{1-x}Bi_xO_3$ alloy series with the use of the self-consistent, scalar-relativistic, linear augmented plane-wave (LAPW) method and the virtual-crystal approximation. The study includes LAPW calculations for the high-temperature cubic (x=0, 0.3, 1) as well as the room-temperature tetragonal (x=0.3) and monoclinic (x=1) phases. The cubic results exhibit nearly-rigid-band-like behavior and feature a ten-band O(2p)-[Pb(6s),Bi(6s)] complex near E_F containing a pair of broad (~16 eV) σ -bonding 2p-6s subbands that are approximately centered on nonbonding O 2p states. 6s-2p band overlap and metallic properties are predicted for all x in the cubic phase. The principal features of the cubic band structure survive the tetragonal distortion, predicting a nearly spherical Fermi surface and a low density of states at E_F in the concentration range $0.05 \le x \le 0.30$ where high-temperature superconductivity ($T_c \approx 13$ K) is observed. A strong Fermi-surface instability is shown to occur in the terminal (x=1) BaBiO₃ compound, explaining both the stability of the monoclinic phase as well as its semiconducting properties.

I. INTRODUCTION

The present interest in the perovskite-type $BaPb_{1-x}Bi_xO_3$ system dates back to the discovery by Sleight *et al.*¹ of high-temperature superconductivity $(T_c \approx 13 \text{ K})$ in the composition range $0.05 \le x \le 0.3$ as well as a metal-semiconductor transition at $x \approx 0.35$. These discoveries have stimulated a continuing series of experimental investigations of the physical and electronic properties of this alloy system. Thus far these studies have included superconductivity,²⁻¹² crystallographic,^{3,13-15} transport,^{7,9,12,16-18} specific-heat,¹⁹ optical-absorption,^{3,10,20} electron-tunneling,¹² x-ray photoemission,^{21,22} and Mössbauer²³ measurements.

The results of the more recent superconductivity studies have confirmed the principal features of the original observations of Sleight *et al.*,¹ namely, broad transitions with onset temperatures increasing from about $T_c \approx 9$ K at x = 0.05 to $T_c \approx 13$ K for x = 0.3. Qualitative differences between the results of these independent studies can be easily attributed to materials problems since the earlier measurements involved pressed powders and ceramics while only the most recent investigations^{11,12} have utilized single-crystal samples.

A valuable addition to our understanding of the BaPb_{1-x}Bi_xO₃ system has been provided by the crystallographic studies of Cox and Sleight.¹³⁻¹⁵ Using the combined results of x-ray and neutron measurements, they have mapped out the phase diagram for this alloy system. In particular, they have shown that the room-temperature structure of BaPb_{1-x}Bi_xO₃ changes as a function of increasing x from orthorhombic \rightarrow tetragonal \rightarrow orthorhombic \rightarrow monoclinic. They have shown that superconductivity is confined to the tetragonal phase and the metalsemiconductor transition at $x \approx 0.35$ coincides with the tetragonal \rightarrow orthorhombic phase boundary. The recent report⁸ of superconductivity in BaPbO₃ ($T_c \approx 0.4$ K) indicates that the superconducting region of the phase diagram extends to the orthorhombic structure at x = 0.

Each of these distorted structures shares a number of geometrical features. For example, they each involve a nearly-rigid rotation of neighboring $Pb_{1-x}Bi_xO_6$ octahedral complexes about the cubic [001] (tetragonal phase) or [110] (orthorhombic and monoclinic phases) axes; each distortion leads to a doubling of the primitive unit-cell size from one to two $BaPb_{1-x}Bi_xO_3$ molecular units. In addition to a [110] rotation, the monoclinic distortion also contains a "breathing-mode" component in which the O atoms are displaced so as to produce two inequivalent Bi sites with average Bi(I)-O and Bi(II)-O bond distances differing by $2\delta \approx 0.16$ Å. Although these inequivalent Bi(I) and Bi(II) atoms have been interpreted¹³⁻¹⁵ in terms of an ordered array of Bi³⁺ and Bi⁵⁺ cations, the results of infrared²⁰ and x-ray-photoemission-spectroscopy^{21,22} measurements suggest only marginal differences in the charge distributions at these sites.

The doubling of the unit-cell size produces Brillouin zones of similar shapes and dimensions for each of the distorted phases. These correspond closely to that for an fcc lattice (i.e., one in which the corners R of the simplecubic Brillouin zone are folded back into the zone center Γ). A simple doubling of the unit cell precludes a filledband explanation for the metal-semiconducting transition at $x \approx 0.35$ as well as the observed semiconductor properties for $0.35 \le x \le 1$ in terms of a one-electron gap in the (Pb,Bi) 6s band.¹ However, the results of recent studies²⁴ on ceramic samples do suggest a more complicated phase diagram in this concentration range. In particular, it has been determined that samples in the composition range 0.4 < x < 0.6 show visual evidence for phase separation into two distinctly colored subregions. The results of electron microprobe analysis indicated that these correspond

to distinct domains with local compositions $x \approx 0.35$ and $x \approx 0.60$, respectively.

Additional difficulties arise in regard to understanding the observed properties of the metallic phase. For example, the standard C/T vs T^2 plot of specific-heat data¹⁹ for samples with x = 0.25 is nonlinear, contains no evidence for a specific-heat anomaly at T_c , and extrapolates to a finite intercept at T=0. These data suggest a comparatively small electronic component $\gamma \approx 0.75$ mJ/(mole K²) which is only about $\frac{1}{4}$ that of Pb ($T_c \approx 7.2$ K). Hall-effect measurements⁷ show that $BaPbO_3$ is a semimetal with a carrier concentration $n \approx 10^{21}$ cm⁻³. The replacement of Pb by Bi in these $BaPb_{1-x}Bi_xO_3$ alloys produces a nearly linear increase in n with x, though *n* remains an order of magnitude smaller than that in typical superconductors. Nevertheless, the resistivity increases systematically as a function of x and exhibits⁷ a semiconductorlike temperature dependence for $x \ge 0.25$. Seebeck-effect measurements¹⁷ suggest the presence of two types of carriers, one typically metallic and the other atypically immobile.

This novel combination of high-temperature superconductivity and a metal-semiconductor transition has prompted considerable speculation on the electronic structure of these $BaPb_{1-x}Bi_xO_3$ compounds. According to the rigid-band-type model proposed by Sleight et al.,¹ a partially-filled (Pb,Bi) 6s band overlaps the nearly-filled O 2p bands, thereby leading to semimetallic properties for BaPbO₃ and metallic behavior for x > 0. An unspecified mechanism causes the 6s band to narrow and split as a function of increasing x, ultimately producing semiconducting properties for $x \ge 0.35$. Rice and Sneddon²⁵ have proposed a more sophisticated model which emphasizes the real-space pairing of electrons in the formation of Bi^{3+} and Bi^{5+} rather than Bi^{4+} cations. According to this model, the observed semiconductor-metal transition occurs when Pb substitution dilutes sufficiently the semiconducting Bi³⁺-Bi⁵⁺ lattice.

The purpose of the present investigation is to calculate, with the use of first-principles methods, the electronic structure of representative compounds in the $BaPb_{1-x}Bi_xO_3$ system and to relate these results to the growing body of experimental data that is available for these materials. Two brief reports which focus on the relationship between electronic structure and superconductivity have been published recently.^{26,27}

The present study utilizes a self-consistent, scalarrelativistic formulation of the linear-augmented planewave (LAPW) method²⁸ in which the charge density and potential are expressed in a completely general functional form,²⁹ thereby eliminating all shape approximations. Exchange and correlation effects are treated in the localdensity approximation with the use of the Wigner interpolation formula.³⁰ The LAPW calculations for nonintegral values of x apply the virtual-crystal approximation³¹ in which the Pb_{1-x}Bi_x distribution is replaced by an average atom containing 82 + x electrons. This approximation is known to provide a good description of an *AB* alloy near the limit where the potentials V_A and V_B are equal.³¹ A comparison of the extremely similar energy-band results for cubic BaPbO₃ and BaBiO₃ suggests that this condition is satisfied for the valence bands near E_F in the BaPb_{1-x}Bi_xO₃ system. However, this approximation is expected to be inappropriate for the more tightly-bound (Pb,Bi) 5d core-type states.

The present LAPW calculations have been carried out for cubic BaPbO₃, BaPb_{0.7}Bi_{0.3}O₃, and BaBiO₃, tetragonal BaPb_{0.7}Bi_{0.3}O₃, and monoclinic BaBiO₃. The details of these calculations, including an analysis of the distorted crystal structures, are contained in Sec. II. The results of these calculations, principally energy-band and densityof-states curves as well as valence charge-density contours, are presented in Sec. III. This section also includes comparisons between theory and experiment and a tightbinding estimate of electron-phonon coupling interactions in this alloy system.

II. CALCULATIONAL DETAILS

A. Crystal structures

A reciprocal-space representation of the BaPb_{1-x}Bi_xO₃ phase diagram, as determined by the x-ray and neutron studies of Cox and Sleight,¹³⁻¹⁵ is shown in Fig. 1. The Brillouin zone (BZ) for the simple-cubic high-temperature (750-800 K) phase is shown in the upper part of the figure, using the standard notation to label symmetry points and cross hatching to indicate the irreducible Brillouin zone (IBZ) wedge.

As indicated by the dashed lines, this high-temperature simple-cubic phase leads to a sequence of distorted structures at room temperature. These vary successively from orthorhombic $(O_{\rm I})$ to tetragonal (T) to orthorhombic $(O_{\rm II})$ and finally to monoclinic (M) symmetry as a function of increasing x. The appropriate BZ's for each of these distorted phases are shown in the center portion of the figure. Each has the BZ shape for a slightly distorted fcc lattice. However, the fractional volume of the crosshatched IBZ wedge increases from $\frac{1}{48}$ (cubic) to $\frac{1}{16}$ (T), $\frac{1}{8}$ $(O_{\rm I}$ and $O_{\rm II}$), and $\frac{1}{4}$ (M) as the point symmetry is reduced.

The primitive unit cell for each of these distorted room-temperature phases contains two $BaPb_{1-x}Bi_xO_3$ complexes. As indicated by the solid lines in Fig. 2, its shape is similar to that of a Wigner-Seitz cell for an fcc lattice. Its volume is about twice that of the hightemperature simple-cubic subcell, which is outlined by the dashed lines. The cubic-noncubic transition can be regarded as a transition from a simple-cubic to a rocksalttype lattice in which the nearest-neighbor $Pb_{1-x}Bi_xO_6$ octahedra become in some way inequivalent.

This inequivalence is introduced in the tetragonal distortion by the nearly-rigid rotation about z of neighboring octahedra through alternating angles $\phi \approx \pm 8^\circ$. The result is a lattice of rotated octahedra for which the rotation angles are opposite for [100]-type nearest neighbors but identical for [110]-type second neighbors. Similarly, the cubic-to-orthorhombic and cubic-to-monoclinic distortions in BaPbO₃ and BaBiO₃ involve comparable octahedral rotations ($\phi \approx 8^\circ - 10^\circ$) about the cubic [110] axes. In the case of the tetragonal and orthorhombic distortions, the nearest-neighbor Pb_{1-x}Bi_x sites remain equivalent crystallographically because of the nonsymmorphic char-



FIG. 1. BaPb_{1-x}Bi_xO₃ phase diagram comparing the cross-hatched irreducible wedges of room-temperature Brillouin zones for the orthorhombic (O_{II} and O_{II}), tetragonal (T), and monoclinic (M) phases with that of the high-temperature cubic phase.

acter of the corresponding space groups. However, this crystallographic equivalence is removed by the "breathing-mode" component of the monoclinic distortion.

Cox and Sleight¹⁴ have shown that the space group for tetragonal BaPb_{0.7}Bi_{0.3}O₃ is $D_{4h}^{18}(I4/mcm)$, the same as that observed³² for SrTiO₃ at temperatures below 110 K. The D_{4h}^{18} space group is nonsymmorphic with a body-centered-tetragonal (bct) Bravais lattice. The primitive translation vectors which generate this bct Bravais lattice can be written

$$\vec{t}_{1} = \frac{1}{2}\sqrt{2}a\hat{j} + \frac{1}{2}c\hat{k} ,$$

$$\vec{t}_{2} = -\frac{1}{2}\sqrt{2}a\hat{j} + \frac{1}{2}c\hat{k} ,$$

$$\vec{t}_{3} = \frac{1}{2}\sqrt{2}a\hat{i} - \frac{1}{2}c\hat{k} ,$$
 (1)

where a and c are related to the simple-cubic lattice parameter a_0 by the approximate relations

$$a \approx \sqrt{2}a_0 , \qquad (2)$$
$$c \approx 2a_0 .$$

For convenience, the coordinate axes in Eq. (1) and Fig. 2 have been rotated about z by 45° relative to previous conventions.^{33,34}

The atomic position parameters for the Ba, (Pb,Bi), and O atoms in the bct cell have been determined by Cox and Sleight¹⁴ using several models. In terms of the nonorthogonal lattice vectors of Eq. (1), these position parameters

 $\vec{r}_i = (\xi \vec{t}_1 + \eta \vec{t}_2 + \zeta \vec{t}_3)_i \equiv (\xi, \eta, \zeta)_i$ have been evaluated from the model 1 results of Table III in Ref. 14. The results are presented here in Table I. It is readily shown that the rotation angle ϕ is given by the relation $\phi = \tan^{-1}(1 - 4x) \approx 8^\circ$. The corresponding rotation angle



FIG. 2. Primitive unit cell for the distorted $BaPb_{1-x}Bi_xO_3$ phases, indicating the inequivalent oxygen sites [O(I) and O(II), respectively] and the (dashed) simple-cubic subcell. In the monoclinic structure, the Bi atoms at the center and corners of the cell also become inequivalent.

TABLE I. Summary of structural and atomic position parameters $\vec{r}_i \equiv (\xi, \eta, \xi)_i$ for tetragonal BaPb_{0.7}Bi_{0.3}O₃, as determined by Cox and Sleight (Model 1, Table III, Ref. 14).

Atom	Туре	$(\xi,\eta,\zeta)_i$
Ba	4(<i>b</i>)	$\pm(\frac{1}{4},\frac{3}{4},\frac{1}{2})$
Pb,Bi	4(c)	(0,0,0)
		$(\frac{1}{2}, \frac{1}{2}, 0)$
O(I)	4(a)	$\pm(\frac{1}{4},\frac{1}{4},0)$
O(II)	8(h)	$\pm(x,\frac{1}{2}-x,\frac{1}{2})$
		$\pm(\frac{1}{2}-x,-x,\frac{1}{2}-2x)$

	Model 1	
O(II):	x	0.2161
	а	6.0618 Å
	С	8.6087 Å
	a_0	4.29 Å

The reciprocal-lattice vectors derived from the primitive bct vectors of Eq. (1) are given by

$$\vec{b}_{1} = (\sqrt{2}/2a)(\hat{i} + \hat{j}) + (1/c)\hat{k} ,$$

$$\vec{b}_{2} = (\sqrt{2}/2a)(\hat{i} - \hat{j}) + (1/c)\hat{k} ,$$
(3)

$$\vec{b}_{3} = (\sqrt{2}/a)\hat{i} .$$

These yield the fcc-shaped BZ shown in the center portion of Fig. 1 since the *a* and *c* lattice parameters for BaPb_{0.7}Bi_{0.3}O₃ (see Table I) obey Eq. (2) to within 0.5%. In the case of SrTiO₃, the cubic-to-tetragonal phase transition from the O_h^1 to the D_{4h}^{18} space group involves the freezing in of a soft phonon with R'_{15} symmetry.^{35,36} This causes the simple-cubic *R* point in Fig. 1 to be folded back into the BZ center Γ . A similar mechanism is anticipated in the case of BaPb_{1-x}Bi_xO₃.

A discussion of the symmetry properties of the D_{4h}^{18} space group has been presented³⁴ for states with wave vector \vec{k} which are within the BZ boundaries. As is well known,³³ extra degeneracies can occur for \vec{k} vectors on the BZ boundaries in the case of nonsymmorphic space groups. According to the numerical results presented in Sec. III, the LAPW bands for bct BaPb_{0.7}Bi_{0.3}O₃ exhibit such a degeneracy along the horizontal diagonal of the hexagonal BZ face.

According to Cox and Sleight,^{13,15} the terminal x=1 compound BaBiO₃ becomes rhombohedral at temperatures below about 700 K and monoclinic below 400 K. The monoclinic space group is $C_{2h}^3(C2/m)$. Cox and Sleight have tabulated the monoclinic structural data in terms of a nonprimitive body-centered-monoclinic cell containing four BaBiO₃ molecular units rather than the primitive one-face-centered monoclinic cell which contains only two.

The one-face-centered monoclinic Bravais lattice is determined completely by the four structural parameters a, b, c, and β . This lattice is generated by a pair of equal

basic primitive translations making an arbitrary angle with respect to each other and a third translation which lies in the plane bisecting the angle between the first two. This third vector can have an arbitrary length and can be oriented at an arbitrary angle with respect to the initial pair.³³

For comparing the cubic and monoclinic structures, it is convenient to adopt a coordinate system different from that chosen by Koster³³ to specify the three basic oneface-centered monclinic primitive translation vectors. In particular, we assume that the z axis is parallel to the third translation vector, so that

$$\vec{t}_{1} = Q\hat{i} - R\hat{j} + S\hat{k} ,$$

$$\vec{t}_{2} = R\hat{i} - Q\hat{j} + S\hat{k} ,$$

$$\vec{t}_{3} = c\hat{k} ,$$
(4)

where

$$Q \equiv \sqrt{2}(a \sin\beta - b)/4 ,$$

$$R \equiv \sqrt{2}(a \sin\beta + b)/4 ,$$

$$S \equiv (a \cos\beta + c)/2 .$$
(5)

The x-ray values¹³ for the parameters a, b, c, and β are listed in Table II.

The primitive unit-cell volume $v = \frac{1}{2}abc \sin\beta$ is twice that of the average cubic-cell volume $v_0 = a_0^3$. The relation $v = 2a_0^3$ provides an estimate of the average simple-cubic lattice parameter a_0 which is also included in Table II.

We again define the atomic position vectors \vec{r}_i in terms of projections along the primitive vectors of Eq. (4), $\vec{r}_i = (\xi \vec{t}_1 + \eta \vec{t}_2 + \zeta \vec{t}_3)_i \equiv (\xi, \eta, \zeta)_i$. The transformation

TABLE II. Summary of structural and atomic position parameters $\vec{r}_i \equiv (\xi, \eta, \zeta)_i$ for monoclinic BaBiO₃, as determined by Cox and Sleight (Model 1, Table I, Ref. 13). The lattice parameters are scaled in accordance with their x-ray data.

Atom	Туре	$(\xi, \eta, \zeta)_i$
Ba	4(<i>i</i>)	$\pm(x,x,-x+z)$
Bi(I)	2(a)	(0,0,0)
Bi(II)	2(c)	$(0, 0, \frac{1}{2})$
O(I)	4 (<i>i</i>)	$\pm(x,x,-x+z)$
O(II)	8(j)	$\pm(x+y,x-y,-x+z)$
		$\pm(x-y,x+y,-x+z)$
	Mode	1 1
	Ba: x	0.5045
	Ba: z	0.2468
	O(I): x	0.0604
	O(I): z	0.2608
	O(II): x	0.2613
	O(II): y	0.2552
	O(II): z	-0.0334
	а	6.181 Å
	b	6.136 Å
	С	8.670 Å
	β	90.17°
	<i>a</i> ₀	4.35 Å

MONOCLINIC

BaBiO₃

Bà

from the body-centered-monoclinic to the one-facecentered-monoclinic cell leads to the positional parameters listed in the upper portion of Table II.

The principal features of the monoclinic $BaBiO_3$ unit cell are illustrated in Fig. 3. This figure represents a (100) projection of the individual atoms in the cell. The heights of these atoms above (+) or below (-) the central plane are given in a.u. The lower and upper Bi sites correspond to Bi(I) and Bi(II), respectively. The Bi(I)-O coordination is such that for the inequivalent O(I) and O(II) neighbors, the bond distances are 4.33 and 4.29 a.u., respectively. The corresponding bond lengths for Bi(II) are 3.98 and 4.02 a.u., respectively. Thus the average difference between the Bi(I)-O and Bi(II)-O bond lengths is about 0.3 a.u. or 7%.

The reciprocal-lattice vectors for the real-space monoclinic lattice generated by Eq. (4) are given by

 $\vec{b}_{1} = -2(Q\hat{i} + R\hat{j})/ab \sin\beta ,$ $\vec{b}_{2} = 2(R\hat{i} + Q\hat{j})/ab \sin\beta ,$ $\vec{b}_{3} = [\sqrt{2}S(-\hat{i} + \hat{j}) + a \sin\beta\hat{k}]/ac \sin\beta .$ (6)



FIG. 3. (100) projection of the monoclinic $BaBiO_3$ structure. The heights of individual atoms above or below the central plane are given (a.u.). The average O-Bi(I) and O-Bi(II) bond lengths are 4.3 and 4.0 a.u., respectively.

In order to estimate the approximate orientation of these vectors, we evaluate Q, R, and S of Eq. (5) using the parameters in Table II. It is readily determined that $Q \approx 0$, $R \approx S \approx a_0$ so that the reciprocal-lattice vectors of Eq. (6) are approximately

$$\vec{\mathbf{b}}_{1} \approx -(1/a_{0})\hat{j},$$

$$\vec{\mathbf{b}}_{2} \approx (1/a_{0})\hat{i},$$

$$\vec{\mathbf{b}}_{3} \approx (1/2a_{0})(-\hat{i}+\hat{j}+\hat{k}).$$
(7)

This leads to the monoclinic BZ that is illustrated in the central right-hand portion of Fig. 1.

B. LAPW scheme

The present energy-band results for $BaPb_{1-x}Bi_xO_3$ have been calculated with a self-consistent, scalarrelativistic version of the LAPW method.²⁸ As is well known, this scheme subdivides the crystal into nonoverlapping muffin-tin spheres and an interstitial region. Each LAPW function consists of a plane wave in the interstitial region which joins, with continuous value and slope, onto pairs of numerical radial functions of angular momentum *l* within each muffin-tin sphere. The crystal wave function is expressed as a superposition of LAPW's, with the expansion coefficients determined variationally.

The crystal potential and charge density are expressed in a general functional form and are free of any shape approximations.²⁹ They are expanded in terms of a Fourier series in the interstitial region and lattice harmonics within the muffin-tin (MT) spheres. The latter expansions each consist of a sum of terms involving products of radial functions of angular momentum l and symmetrydetermined linear combinations³⁷ of spherical harmonics with $-l \le m \le l$.

Values for the MT radii $R(Pb,Bi) \approx 2.14$ a.u. and $R(O) \approx 1.83$ a.u. have been chosen to yield nearly-touching (Pb,Bi)-O spheres along the [100] axes and to equalize approximately the convergence of the (Pb,Bi) 5d and O 2p energy-band states. The radius of the Ba spheres is less critical and the value $R(Ba) \approx 2.99$ a.u. has been used in each of the present LAPW calculations. This radius is about 20% smaller than the maximum possible value.

Calculations for the cubic $BaPb_{1-x}Bi_xO_3$ compounds have included approximately 270-300 LAPW's with wave vectors $(\vec{k} + \vec{G})^2 \le 10$ a.u., where \vec{G} is a primitive vector of the reciprocal lattice with integer coefficients n_i ,

$$\vec{G} = 2\pi (n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3) .$$
(8)

Limited studies indicate that this basis of about 55-60 LAPW's per atom yields energy eigenvalues which are converged to about 0.03 eV.

Computer-memory limitations have resulted in a more restricted LAPW basis for the noncubic compounds, where the number of atoms in the primitive cell has doubled. The corresponding wave vectors for these LAPW's are determined by the condition $(\vec{k} + \vec{G})^2 < 7.6$ a.u. and involve 380–390 LAPW's. This reduced LAPW basis of about 38 functions per atom increases the convergence errors by about an order of magnitude to about 0.3 eV.

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The calculations apply a frozen-core approximation in scalar-relativistic which atomic charge densities the Ba $\cdots 4d^{10}5s^2$, are utilized to represent (Pb,Bi) $\cdots 5s^2 5p^6$, and O $1s^2$ core states. Test calculations were performed in which the more tightly-bound valence states [i.e., those with (10-25)-eV binding energies] were added to the frozen core, including the Ba 5p [(10-12)-eV],(Pb,Bi) $5d \quad [(15-23)-eV],$ and 0 2s[(16-18)-eV] states. These simplified treatments caused key energy-band states near E_F to shift by as much as 1-2 eV and consequently were not pursued.

The Fourier expansion of the charge density and potential in the interstitial region of the unit cell included approximately 2300 and 3200 plane waves for the cubic and noncubic (body-centered-tetragonal and monoclinic) LAPW calculations, respectively. The corresponding lattice-harmonic expansions inside the muffin-tin spheres generally included all terms with angular momentum $l \leq 4$. For the simple-cubic and body-centered-tetragonal structures, this led to a maximum number of 4 and 9 terms, respectively, in this expansion. In the monoclinic calculation the expansion was limited to $l \leq 3$ and nevertheless included as many as 16 terms.

The charge density for the simple-cubic calculations has been evaluated with the use of four special \vec{k} points³⁸ to determine the average of the charge density over the occupied BZ volume. These four special points correspond to 64 points in the full BZ. During each iteration, the charge density is applied to calculate the corresponding crystalline potential, with exchange-correlation effects included via the Wigner interpolation formula.³⁰ In each calculation, a total of five iterations was sufficient to reduce the average difference between the final input and output potentials to a fraction of the maximum deviation, ~0.1 eV.

A similar mesh density of special \vec{k} points was applied in the corresponding calculations for tetragonal BaPb_{0.7}Bi_{0.3}O₃ and monoclinic BaBiO₃, respectively. The folding of the simple-cubic BZ to form an fcc-type zone decreases the full BZ sampling from 64 to 32 points. This reduces ultimately to a total of three and ten special \vec{k} points in the IBZ for the tetragonal and monoclinic calculations, respectively. Both calculations converged at a rate comparable to those for the cubic materials, yielding maximum deviations of ~0.1 eV between the fifth and final input and output potentials.

The sensitivity of the tetragonal BaPb_{0.7}Bi_{0.3}O₃ results to this special-points averaging procedure was checked by carrying out an additional iteration in which the full BZ sampling was increased to $\frac{1}{2}(6)^3 = 108$ points, with ten special points in the IBZ. The result was a minor (~10%) increase in the average difference between the input (three-point sampling) and output (ten-point sampling) potentials, the value of which remained less than 0.1 eV.

III. RESULTS AND DISCUSSION

The LAPW energy bands near E_F for simple-cubic BaPbO₃ and BaBiO₃ are shown in Figs. 4 and 5, respectively. In both materials, the Fermi energy cuts through the upper portion of a ten-band complex that evolves from



FIG. 4. LAPW energy bands for cubic BaPbO₃.

the (Pb,Bi) 6s and O 2p manifolds. The low-lying corelike bands near the bottom of each figure correspond to Ba 5p states while the uppermost cluster of unoccupied bands are derived primarily from Ba 5d states with some (Pb,Bi) 6p admixture.

The more tightly bound (Pb,Bi) 5d and O 2s bands occur at lower energies and are not shown. These bands are nearly degenerate in BaPbO₃, producing a strongly-



FIG. 5. LAPW energy bands for cubic BaBiO₃.

hybridized eight-band manifold with a 5-eV bandwidth which is centered approximately 15.5 eV below E_F . A 6-eV increase in the Bi 5d binding energy in BaBiO₃ leads to nonoverlapping O 2s and Bi 5d subbands centered at about -17.5 and -23.5 eV, respectively, in this compound.

The ten-band complex that is centered slightly below E_F in Figs. 4 and 5 consists of a pair of broad (~16 eV) σ -bonding 6s-2p subbands which are roughly centered about a narrower cluster (~2-4 eV) of nonbonding O $2p_{\perp}$ states. These nonbonding states are derived from O 2p orbitals which are oriented perpendicular to the nearest-neighbor Pb,Bi bond directions. The pair of broad bonding-antibonding subbands results from the strong $(sp\sigma)$ interaction between (Pb,Bi) 6s and O $2p_{\parallel}$ orbitals oriented along nearest-neighbor bond directions.

The lower Γ_1 state in Figs. 4 and 5 has predominantly (Pb,Bi) 6s character. Its position relative to the top of the nonbonding O $2p_{\perp}$ bands $[E(R_{15'})]$ and E_F in Fig. 4 determines whether BaPbO₃ is semimetallic $[E(\Gamma_1) < E_F]$ or semiconducting $[E(\Gamma_1) > E_F]$. In the latter case the reversed ordering of the Γ_1 and Γ_{15} states would modify the connectivity of the conduction band and yield an indirect-gap semiconductor with a minimum gap $E_g \approx E(\Gamma_1) - E(R_{15'})$.

As shown in Fig. 4, this lower Γ_1 state falls about 2 eV below $E(R_{15'})$, thereby predicting semimetallic behavior for BaPbO₃ with a carrier density of about 0.7×10^{21} cm⁻³. Atomic estimates³⁹ show that the Pb 6s binding energy is increased by about 2.5 eV as a result of the combined effects of the Darwin and mass-velocity corrections. Therefore, this 6s-2p band overlap and the resulting semimetallic properties of BaPbO₃ are a direct consequence of relativistic effects.

The increased binding of the Bi 6s state lowers Γ_1 in BaBiO₃ by an additional 2.5 eV relative to the O $2p_{\perp}$ bands, as shown in Fig. 5. This shifts the center of gravity of the pair of broad $6s \cdot 2p_{\parallel}$ subbands to lower energies. As a result, the extra valence electron per cell raises E_F relative to the O $2p_{\perp}$ bands more slowly than expected in terms of a rigid-band model.

The corresponding cubic LAPW results for the intermediate compound $BaPb_{0.7}Bi_{0.3}O_3$ are indicated by the solid lines in Fig. 6. These results are derived from the so-called virtual-crystal approximation³¹ in which the random distribution of Pb,Bi atoms is replaced by an average atom with atomic number 82.3. As a comparison with the results for BaPbO₃ and BaBiO₃ (Figs. 4 and 5, respectively) indicates, this approximation provides, for intermediate values of x, a smooth interpolation of the energy-band results for the end members of this alloy series.

The principal features of these energy-band results can be understood in terms of a simple tight-binding (TB) model.^{26,27} The dotted bands shown in Fig. 6 are derived from a three-parameter TB model involving the orbital energies $E_{6s} = -4.1$ eV, $E_{2p} = -1.9$ eV, and the nearestneighbor two-center interaction $(sp\sigma)=2.2$ eV. In this approximation the nonbonding O $2p_{\perp}$ bands are degenerate and perfectly flat. The characteristic features of the LAPW bonding-antibonding subbands are reproduced by this model, except in those energy ranges where the con-



FIG. 6. LAPW energy bands (solid lines) for cubic $BaPb_{0,7}Bi_{0,3}O_3$ compared with those derived from simple tightbinding (TB) models involving three (dotted lines) and five (dashed lines) TB parameters, respectively.

nectivity of the LAPW results is changed by band overlap.

One can systematically improve the accuracy of this TB model by including additional orbitals and/or interactions. For example, the dashed lines in Fig. 6 are derived from an expanded TB model in which interactions with the unoccupied (Pb,Bi) 6p states have been incorporated by means of two added parameters: the orbital energy $E_{6p}=3.5$ eV and the nearest-neighbor two-center parameter $(pp\sigma)=2.7$ eV, assuming for simplicity that $(pp\pi) = -(pp\sigma)/3$.⁴⁰ These $6p-2p_{||}$ interactions improve noticeably the overall fit between the LAPW and TB bands. They clearly contribute to the stability of these compounds by lowering the one-electron energy of the lower Γ_{15} subband by about 3.5 eV in the ΓXM plane.

The effect of the cubic-tetragonal and cubic-monclinic phase transitions on the energy-band results for $BaPb_{0.7}Bi_{0.3}O_3$ and $BaBiO_3$ are illustrated in Figs. 7 and 8, respectively. Here, the noncubic LAPW results are denoted by the dots while the solid lines correspond to cubic bands which have been folded back into the reduced tetragonal and monoclinic IBZ's shown in the insets. The cross-hatched band regions denote energy ranges where the folded bands are dense and complicated. The foldedcubic results in Figs. 7 and 8 have been calculated with a restricted LAPW basis such that the number of LAPW's per atom and therefore the overall convergence is comparable to that of the corresponding noncubic results.

A comparison of these folded cubic results with those shown in Figs. 5 and 6 indicates that these convergence errors are of the order of 0.3 eV. The principal effect of this reduced convergence is to lower the broad $6s-2p_{11}$



FIG. 7. Comparison of LAPW energy bands for cubic (solid lines) and tetragonal (dotted lines) $BaPb_{0.7}Bi_{0.3}O_3$ along symmetry lines of the body-centered-tetragonal Brillouin zone (see inset).



FIG. 8. Comparison of LAPW energy bands for cubic (solid lines) and monoclinic (dotted lines) BaBiO₃ along selected lines of the monoclinic Brillouin zone (see inset).

manifold and E_F by about 0.3 eV relative to the nonbonding $2p_{\perp}$ states.

The folded-cubic and tetragonal results in Fig. 7 are aligned so their Fermi energies are equal. The bands are plotted along typical symmetry lines in the IBZ which are equivalent in the cubic phase. Individual symmetry points are labeled in the inset, with the use of a notation analogous to that for an fcc lattice. Where necessary, primes are introduced to distinguish cubic symmetry points which become inequivalent in the tetragonal phase.

Overall, the cubic-to-tetragonal phase transition produces rather small changes in the cubic energy-band results. Typical band shifts or splittings are of the order of 0.1 eV. It is noted that the nonsymmorphic character of the tetragonal $D_{4h}^{18}(I4/mcm)$ space group produces a "sticking together" or degeneracy along the W'L lines, which is lifted along the WL lines on the hexagonal face of the Brillouin zone.

Density-of-states (DOS) curves derived from the cubic and tetragonal LAPW energy-band results for BaPb_{0.7}Bi_{0.3}O₃ (Figs. 6 and 7, respectively) are compared in Fig. 9. These curves have been calculated by means of the tetrahedral method,⁴¹ with the use of LAPW eigenvalues and wave functions at 84 (100) uniformly distributed \vec{k} points in the IBZ wedge of the cubic (bct) BZ. This mesh corresponds to 1728 (864) \vec{k} points in the entire cubic (bct) BZ. It is estimated that this mesh is adequate to yield cubic DOS curves which are accurate to within a few percent near E_F , where the bands are fairly linear.



FIG. 9. LAPW density-of-states results near E_F for (a) cubic and (b) tetragonal BaPb_{0.7}Bi_{0.3}O₃, including projections of the O 2p (dashed) and Pb,Bi 6s (dot-dashed) contributions.

Reduced accuracy is expected in the bct DOS results, particularly for states near the hexagonal BZ faces in Fig. 7. The reason is that that tetrahedral integrations have been extended beyond these faces to span the full simpletetragonal (rather than the bct) IBZ wedge. This can lead to band-folding-induced connectivity errors near the BZ faces and produce unexpected inaccuracies in the bandby-band linear-interpolation aspect of the tetrahedral method.

The dashed and dot-dashed lines in Fig. 9 correspond to projected DOS results in which the total DOS is weighted by the squares of the O 2p and (Pb,Bi) 6s LAPW wavefunction coefficients within the corresponding O₃ and Pb,Bi muffin-tin spheres. Although the relative weights of the LAPW 2p and 6s wave-function components depend on the assumed values for the O and Pb,Bi muffintin radii, the present LAPW projections are consistent with the model TB results. As shown in Fig. 9, the electrons near E_F in BaPb_{0.7}Bi_{0.3}O₃ have predominantly O 2pcharacter. The (Pb,Bi) 6s orbitals dominate if the O 2pcontribution per oxygen site is considered.

The cubic-to-tetragonal phase transition produces rather modest changes in the cubic DOS curve near E_F . A noticeable effect is the addition of some apparent "noise" to the relatively smooth cubic results. A second change is represented by the splitting of the cubic DOS peak located about 1.5 eV above E_F . It is clear from Fig. 7 that this peak arises from the bands near the hexagonal BZ faces and the splitting of this DOS peak in Fig. 9(b) ($\sim 0.5 \text{ eV}$) is larger than a typical energy-band shift or splitting in this energy range. It is believed that both effects are due in part to the above-mentioned limitations of the bct DOS calculations. The 0.3-eV difference in the onset energy of the sharp O $2p_{\perp}$ DOS peak 1.0–1.3 eV below E_F in Fig. 9 is due primarily to previously described differences in the convergence of the cubic and tetragonal BaPb_{0.7}Bi_{0.3}O₃ results in Figs. 6 and 7, respectively.

As the results in Fig. 8 indicate, the cubic-tomonoclinic phase transition for BaBiO₃ produces energyband shifts and splittings near E_F which are significantly those exhibited by the tetragonal larger than BaPb_{0.7}Bi_{0.3}O₃ bands in Fig. 7. It is important to note that the largest splittings occur near E_F , particularly along the W'L - WL' lines and near the K, K' points of the IBZ shown in the inset. These splittings, which have a nearly constant value of about 1 eV, are nearly sufficient to open up an energy gap at E_F . This would be consistent with the observed¹ semiconducting properties of monoclinic BaBiO₃, which is estimated to have a 0.2-eV band gap. In fact, the LAPW results for monoclinic BaBiO₃ exhibit a small (~0.1 eV) band overlap involving states at W-W'and L'. It is believed that this deficiency in the calculation is due either to limitations of the local-density method or convergence errors. The latter are of the same order ($\sim 0.3 \text{ eV}$) as the band overlap.

The fact that the largest splittings occur in the immediate vicinity of the BaBiO₃ Fermi energy E_F provides a textbook explanation for the occurrence of the cubicmonoclinic phase transition at reduced temperatures. Namely, the distortion-induced 1-eV splittings cause a decrease in the average one-electron energies for states near E_F and thereby enhance the stability of the monoclinic phase at low temperatures.

As described in Sec. II A, the cubic-monoclinic distortion consists of two components: (i) a nearly-rigid rotation of BiO₆ octahedra about [110]; (ii) a "breathingmode" distortion that changes the average Bi(I)–O and Bi(II)–O bond distances by 2δ =0.16 Å=0.30 a.u. (see Fig. 3). As shown below with the use of simple TB arguments, the 1-eV splittings at E_F in Fig. 8 are due primarily to the breathing-mode component of the monoclinic distortion. The rigid rotation of BiO₆ octahedra about the [110] axes is expected to produce comparatively small band shifts and splittings, similar to those shown in Fig. 7 for tetragonal BaPb_{0.7}Bi_{0.3}O₃.

Because of the low point symmetry of the monoclinic phase, it is not practical to map out the BaBiO₃ band structure in full detail along each inequivalent BZ line. The results in Fig. 8 summarize the bands along only a few representative symmetry directions. The similarity of the results along formerly equivalent cubic symmetry lines suggests that, to a reasonable approximation, $E(\vec{k})$ retains the full-cubic point symmetry, though band degeneracies and crossings are consistent with the reduced symmetry of the monoclinic structure.

A much emphasized feature^{13,15,25} of monoclinic BaBiO₃ is the presence of two inequivalent Bi sites in the primitive unit cell. These sites, which are labeled Bi(I) and Bi(II), respectively, in Fig. 3, become inequivalent as a result of the breathing-mode component of the cubic-monoclinic distortion which changes the average Bi(I)–O and Bi(II)–O bond distances by $2\delta \approx 0.30$ a.u. In particular, these sites have been associated with the existence of two Bi oxidation states, Bi³⁺ and Bi⁵⁺, in this and other compounds.^{13,15}

This degree of charge transfer between the Bi(I) and Bi(II) ions is unlikely in a compound such as BaBiO₃, where the bonding is covalent and the nearest-neighbor Bi(6s)-O(2p) interaction is sufficiently strong to produce an overall 16-eV valence-conduction bandwidth. In estimating the magnitude of this charge transfer, one should compare this 16-eV bandwidth with the \sim 1-eV splittings at E_F that result from the cubic-monoclinic distortion, as shown in Fig. 8.

This expectation of limited charge transfer between the inequivalent Bi(I) and Bi(II) is consistent with LAPW charge-density results, as shown in Fig. 10. Here, we compare the valence charge density in pseudocubic {100} planes for tetragonal BaPb_{0.7}Bi_{0.3}O₃ [Fig. 10(a)] and monoclinic BaBiO₃ [Fig. 10(b)]. In each case the plotting plane has been chosen to pass through the corner Pb,Bi sites. Those O atoms which lie above, within, and below these planes are indicated by $+, \cdot$, and -, respectively. The orientation of these planes is readily established with the assistance of Figs. 2 and 3, respectively.

The charge-density results in Fig. 10 illustrate that the rotation angles involved in the tetragonal and monoclinic distortions are comparable. More importantly, there is no significant difference in Fig. 10(b) between the valence charge-density contours surrounding the Bi(I) and Bi(II) sites at the centers and corners of the plotting areas, respectively. The main effect of the 2δ change in the



FIG. 10. LAPW charge-density contour plots in pseudocubic $\{100\}$ -type planes for (a) tetragonal BaPb_{0.7}Bi_{0.3}O₃ and (b) monoclinic BaBiO₃. Charge densities are expressed in units electrons/(a.u.)³ and adjacent contours increase by a factor of 2.

average Bi(I)–O and Bi(II)–O bond distances is to decrease the value of the minimum charge density along the stretched Bi(I)–O bonds by ~0.1 electrons/(a.u.)³ (10%) and produce a corresponding 10% increase in the minimum value along the compressed Bi(II)–O bond directions. These $\pm 10\%$ changes in the charge-density minima cause noticeable differences in the widths of the 0.08 electrons/(a.u.)³ contours along these nearest-neighbor directions.

In setting up the LAPW calculations, identical radii have been assigned to the muffin-tin spheres at the Bi(I) and Bi(II) sites, despite these differences in the nearestneighbor Bi(I)-O and Bi(II)-O bond lengths. This allows us to compare directly the integrated LAPW valence charge within the Bi(I) and Bi(II) muffin-tin spheres in the monoclinic phase. For $R(Bi) \approx 2.12$ a.u., the integrated Bi(I) and Bi(II) valence charge densities correspond to 10.85 and 10.84 electrons per atom, respectively. The total valence charge density in the interstitial region corresponds to about 14.4 electrons (out of a total of 82 electrons per monoclinic cell). As a result, it is not possible to assign a specific charge to the atoms at the Bi(I) and Bi(II) sites. However, it is reasonable to expect that the difference between the Bi(I) and Bi(II) oxidation states is accurately represented by the calculated 0.01-electron difference within the Bi(I) and Bi(II) MT spheres.

Another measure of possible Bi(I)-Bi(II) valency differences can be derived from the core-region potentials surrounding these atoms. In a typical calculation the spherical average of such a potential is nearly identical to that of the atom shifted by a constant. In such cases, an accurate prediction of the core levels in the solid can be made with the use of atomic eigenvalues which are shifted by the same constant. The core levels predicted for Bi(I) and Bi(II) by this method are found to differ by only 0.1 eV in monoclinic $BaBiO_3$. This is another indication of very small Bi(I)-Bi(II) charge transfer. It is noted that the relative positions of these core levels is determined by the charge distribution in the entire unit cell, not just that in the Bi muffin-tin spheres.

This prediction of limited charge transfer in monoclinic BaBiO₃ is consistent with the results of XPS studies on the Bi 4f core levels. The XPS 4f spectral lines are broadened but unsplit in the room-temperature monoclinic phase.^{21,22} A similar conclusion had been reached previously by de Hair and Blasse²⁰ on the basis of vibrational studies using infrared spectroscopy.

Equally small differences are calculated for the integrated charge density at the inequivalent O(I) and O(II) sites in monoclinic BaBiO₃. In this case, the core-region potentials differ by about 0.01 eV and the integrated MT charges are 5.64 and 5.65 electrons, respectively, in oxygen spheres of equal radius $R \approx 1.83$ a.u.

A useful experimental overview of the $BaPb_{1-x}Bi_xO_3$ valence bands is provided by the XPS spectra²² for BaPbO₃, BaPb_{0.75}Bi_{0.25}O₃, and BaBiO₃. These data are dominated by two prominent x-independent peaks which originate from the O $2p_1$ bands and the corelike Ba 5p levels. They also contain two less-pronounced x-dependent features, one of which falls below and the other above the O $2p_1$ bands. The lower-energy hump can be interpreted in terms of a density-of-states peak that arises²⁶ from bands near the lowest M_1 states in Figs. 4–6. Although this peak is not particularly high, its prominence in the XPS spectra is enhanced by the fact that half its weight involves Pb,Bi 6s 6p states whose photoelectric cross sections are estimated⁴² to be about 4 times larger than that of the O 2p states.

The energy scales of the individual XPS spectra have been adjusted to align the Ba 5p peaks. Relative to the BaBiO₃ Fermi level, the observed binding energy of the lower x-dependent feature varies between about 9.0, 10.0, and 10.7 eV for x = 0, 0.25, and 1, respectively. These values are in excellent agreement with the calculated binding energies of the M_1 -derived DOS peak, namely 9.0, 9.8, and 10.8 eV for x = 0, 0.3, and 1, respectively. A similar comparison of the XPS-LAPW binding energies for the corresponding O $2p_{\perp}$ peaks yields comparable agreement (3.3, 3.7, and 3.1 eV vs 2.8, 3.0, and 2.8 eV, respectively). The upper XPS shoulder arises from the partial filling of the antibonding $6s-2p_{\parallel}$ subband above the nonbonding O $2p_{\perp}$ DOS peak. Its observed width of about 1–2 eV in BaBiO₃ is comparable to that shown in Fig. 5.

The principal XPS-LAPW discrepancy involves the Ba 5p binding energy. The calculated value is systematically about 1.7 eV above the center of gravity of the spin-orbit-split XPS value (~12 vs 13.7 eV below E_F). We believe that this discrepancy is due principally to the difference between local-density functional eigenvalues and excitation energies, which become important for localized, corelike states. An upper bound to the size of the correction we could expect from this effect is given by the difference between the 5p eigenvalue in the Ba atom and the 5p ioni-

zation potential computed with the transition-state approximation, 4.5 eV.

It is useful to consider how the present scalarrelativistic energy-band results near E_F would be modified if spin-orbit coupling were included in a fully-relativistic calculation. In general, these changes are expected to be small since the $BaPb_{1-x}Bi_xO_3$ valence and conduction bands are derived primarily from O 2p and (Pb,Bi) 6s states. The principal source of spin-orbit effects is the admixture of (Pb,Bi) 6p states that is implied, for example, five-parameter tight-binding model for bv the $BaPb_{0.7}Bi_{0.3}O_3$ (Fig. 6). The LAPW wave function for the lower Γ_{15} state in Fig. 6 contains a (Pb,Bi) 6p component $f_p \approx 0.1$, where f_p is the square of the 6p admixture coefficient within the (Pb,Bi) muffin-tin sphere. A comparable (Pb,Bi) 6p admixture is present throughout this split-off Γ_{15} subband and also near the R_{15} state above E_F in Figs. 4 - 6.

An atomic estimate of the Pb 6p spin-orbit parameter, $\xi_{6p} \approx 1.0$ eV, can be obtained from the calculated difference between the $6p_{3/2}$ and $6p_{1/2}$ eigenvalues of the Dirac equation.³⁹ Including a symmetry-dependent factor of 1.5 for the threefold-degenerate Γ_{15} state, this yields a total estimated splitting of about $1.5f_p\xi_{6p} \approx 0.15$ eV for the lower Γ_{15} state as a result of (Pb,Bi) 6p covalent mixing. Elsewhere in the Brillouin zone where the prefactor is 1.0, the estimated spin-orbit-induced band splittings or shifts are reduced to $f_p\xi_{6p} \approx 0.1$ eV.

Spin-orbit effects are not expected to remove the 0.1-eV band overlap at E_F that is exhibited by the scalarrelativistic results for monoclinic BaBiO₃ in Fig. 8. The reason is that the monoclinic structural distortion changes the Bi 6s and 6p admixture components $(f_s \text{ and } f_p,$ respectively) for the bands bordering this gap in such a way that the interband spin-orbit interaction is essentially zero. For example, typical admixture components at the $\operatorname{Bi}(I)$ site for the lower and upper bands near E_F are $f_s \approx 0.1$, $f_p \approx 0$, and $f_s \approx 0$, $f_p \approx 0.05$, respectively. The corresponding wave-function components at the Bi(II) site are $f_s \approx 0$, $f_p \approx 0.03$, and $f_s \approx 0.16$, $f_p \approx 0$, respectively. Thus, at each Bi site, the 6p weight is concentrated either in the lower (nearly-filled) band [Bi(II) site] or the upper (nearly-empty) band [Bi(I) site]. As a result, the interband spin-orbit interaction is expected to be negligibly small.

The Dirac solutions for the Pb atom³⁹ also provide a simple means for estimating possible errors in valenceelectron energies that are caused by the scalar-relativistic treatment of core-electron wave functions and charge densities. In the case of the Pb 6s state, a comparison of the scalar-relativistic and Dirac eigenvalues yields agreement to within 0.05 eV. A similar comparison between the center of gravity of the $6p_{1/2}$ and $6p_{3/2}$ energies and the scalar-relativistic 6p eigenvalue produces comparable (~0.1-eV) agreement, suggesting that these errors are small.

A precise experimental characterization of the electronic states near E_F in these BaPb_{1-x}Bi_xO₃ compounds is presently lacking. The specific-heat data of Methfessel *et al.*¹⁹ exhibit non-Debye behavior and suggest a relatively small electronic contribution γ . Their plot of C/T vs T^2 for superconducting x = 0.25 samples ($T_c = 11.1$ K) is nonlinear, exhibits no anomaly at T_c , and extrapolates to a finite intercept at T=0. Neglecting electron-phonon enhancement effects, the density of states at E_F estimated from the T=0 intercept corresponds to 0.15 "states/eV spin Pb,Bi atom."⁴³ According to Fig. 9, this is comparable to the calculated cubic (0.12) and bct (0.15) values obtained from a rigid-band interpolation to x=0.25. Since superconductivity in BaPb_{1-x}Bi_xO₃ can be suppressed by the application of magnetic fields of reasonable (~50-kG) strength,⁷ a reliable determination of γ is both possible and desirable. In conjunction with the present value for the band-structure DOS at E_F , this would permit a determination of the electron-phonon-coupling constant λ for these materials.

Suzuki *et al.*¹⁰ have carried out optical transmission measurements on sputtered $BaPb_{1-x}Bi_xO_3$ films. The results exhibit a minimum in the absorption coefficient at about 2.2 eV followed by a rapid rise. The data have been interpreted¹⁰ in terms of direct transitions involving filled states at E_F and unoccupied bands about 2.4 eV above. The present energy-band results in Figs. 4–6 provide no strong candidates for interpreting this 2.4-eV transition.

An implicit assumption of the present theoretical treatment of the $BaPb_{1-x}Bi_xO_3$ system is that of considering these materials to form a homogeneous alloy series. Evidence supporting a contrary view has been summarized recently by Methfessel and Methfessel.²⁴ In particular, they have argued that sample inhomogeneities may play a crucial role in determining the electronic, transport, and superconducting properties of these materials, resulting in the possible presence of impurity clustering, phase separation, superconducting granules, etc.

A related issue concerns the potential existence of ordered alloy phases for integral values of $x^{-1}=2$, 3, 4, etc. Of particular interest in regard to superconductivity are samples with the composition x=0.25. According to the single-crystal measurements by Batlogg *et al.*¹² the data for x=0.25 samples show that not only is $T_c \approx 12$ K a maximum at this composition, but also that the width of the transition is narrow (less than 0.3 K) only in this concentration range and broadens ($\sim 3-4$ K) at neighboring compositions. This suggests²⁴ the possibility that superconducting is actually limited to the composition near x=0.25. Its apparent occurrence over the $0.05 \le x \le 0.30$ concentration range may be an artifact of stoichiometric inhomogeneities.

One can construct a possible ordered arrangement of Pb,Bi atoms with a 3/1 ratio by considering a simplecubic superlattice with dimension $a = 2a_0$. If one locates the Bi atoms at the body-centered sites and the Pb atoms at the remaining simple-cubic sites, then the primitive bcc-type cell would have the composition Ba₄Pb₃BiO₁₂ and contain a total of four octahedral complexes. Clearly, additional structural studies for x = 0.25 single-crystal samples are called for in order to determine the possible existence of superlattice effects in this alloy system.

Because of their low carrier density and low DOS at E_F , the novel occurrence of high- T_c superconductivity in these BaPb_{1-x}Bi_xO₃ compounds has led to speculation^{9,24} concerning the potential existence of a new mechanism for superconductivity in these materials, involving possibly excitons,⁴⁴ plasmons,⁴⁵ bipolarons,⁴⁶ real-space pairing,²⁵ etc. On the other hand, arguments favoring the conventional electron-phonon-coupling mechanism have been presented.^{26,27} According to the latter point of view, unexpectedly strong electron-phonon-coupling effects exist in these materials. These originate from the distance modulation of the dominant ($sp\sigma$) interaction between neighboring (Pb,Bi) 6s and O $2p_{||}$ orbitals at E_F .

It should be noted that even the "conventional" electron-phonon mechanism has somewhat unconventional features in this alloy system. For example, Weber⁴⁷ has shown that the dominant contribution to phonon anomalies and strong electron-phonon coupling in high- T_c superconductors often can be traced to a "dormant" interaction involving electron states near E_F . These correspond to orbital interactions which are zero or dormant as a result of symmetry cancellation when the atoms are in their equilibrium positions but then increase with a large gradient as the atoms are displaced. In terms of this criterion, the distance modulation of the nearest-neighbor $(sp\sigma)$ interaction is not expected to be important for superconductivity in these materials.

Although it is possible to calculate phonon frequencies from first principles via frozen-phonon calculations,⁴⁸ the present analysis^{26,27} regarding soft phonons and electronphonon coupling in these compounds is based on the three-parameter TB model that has been described earlier in this section. The simplicity of the TB approach is important in view of the complicated band structures that result from frozen-in $R_{15'}$ (Fig. 7) and $R_{15'} + R_1$ (Fig. 8) phonons.

This model TB representation of the BaPb_{0.7}Bi_{0.3}O₃ band structure is denoted by the dotted lines in Fig. 6. Because each of the distorted room-temperature $BaPb_{1-x}Bi_{x}O_{3}$ phases has a BZ shape similar to that for an fcc lattice (see Fig. 1), it is interesting to fold and replot these model TB bands in this reduced BZ. The folded simple-cubic TB bands for BaPb_{0.7}Bi_{0.3}O₃ are represented by the dashed lines in Fig. 11. A remarkable feature of these results is that a rigid-band filling of the conduction band leads to the prediction of a zero-gap semiconductor with $E_F = 2.5$ eV for x = 1 (BaBiO₃). This results from the perfect nesting of identical electron and hole Fermisurface sheets centered at the Γ and R points of the simple-cubic BZ, respectively. The shape of these surfaces is shown in Fig. 12. A comparison of these model TB results and the corresponding folded cubic LAPW bands in Figs. 7 and 8 reveals that this nesting becomes imperfect in the LAPW results. In particular, the band degeneracies that occur precisely at E_F (along WL and near K) in the model TB results of Fig. 11 are distributed over a 1-eV range in Fig. 8. The same is true for the improved fiveparameter TB model, whose bands are denoted by the dashed lines in Fig. 6.

This three-parameter TB model for $BaPb_{1-x}Bi_xO_3$ has been applied to estimate the "deformation" potentials resulting from some of the more characteristic distortions of perovskite-type compounds. These include a "rigidrotation" of the Pb,BiO₆ octahedra, breathing-mode displacements of O atoms, and "ferroelectric"-"antiferroelectric" displacements of Pb,Bi atoms. The dependence



FIG. 11. Comparison of folded simple-cubic TB bands (dashed lines) with those incorporating a frozen-in "breathing-mode" displacement of O atoms (solid lines).

of the nearest-neighbor $(sp\sigma)$ interaction on bond length has been estimated from the ~1-eV splittings along the *W'L* and *WL'* lines in Fig. 8. Here, the average Bi(I)–O and Bi(II)–O bond lengths differ by $2\delta \approx 0.30$ a.u., and this leads to the determination that $(sp\sigma)_{-\delta}=2.4$ eV and $(sp\sigma)_{+\delta}=2.0$ eV for the decreased and increased bond lengths, respectively.

The TB bands for a rocksalt-type structure with a frozen-in breathing-mode displacement of O atoms [i.e., one that changes the Bi(I)—O and Bi(II)—O bond lengths by 2δ] are shown by the solid lines in Fig. 11. This distortion yields conduction-band splittings and shifts which are a maximum on the BZ boundary and decrease as one moves toward the center of the zone. Similar splittings, though smaller in magnitude by a factor of about 3, are produced by an antiferroelectric displacement of Pb,Bi atoms. Analogous model TB calculations for ferroelectric Pb,Bi displacements and a rigid rotation of Pb,BiO₆ octahedra about the cubic [001] axis yield smaller splittings and shifts which are a maximum at the BZ center and small at the zone boundaries.

The results of these model calculations are summarized in Fig. 13 where we plot the shift in the TB conductionband energy ΔE_c vs \vec{k} for each of these frozen-in distortions. The atomic displacement $\delta \approx 0.08$ Å is identical for each distortion so one can compare directly the corresponding "deformation" potentials $\Delta E_c / \delta$. The appropri-



FIG. 12. Sketch of electronlike Γ -centered simple-cubic Fermi surface predicted by the three-parameter TB model for BaBiO₃. This electron surface nests perfectly with an identical hole surface centered at the Brillouin-zone corner (R).



FIG. 13. Plot of the TB conduction-band energy shifts $\Delta E_c(\vec{k})$ and $\Delta E_c(\vec{k})/\delta$ ($\delta = 0.0784$ Å = 0.148 a.u.) originating from (a) "breathing-mode" O displacements; (b) "antiferroelectric" Pb,Bi displacements; (c) "ferroelectric" Pb,Bi displacements; (d) "rigid rotation" of Pb,BiO₆ octahedra.

ate scales for these are shown to the right. The small anisotropies in Figs. 13(b)-13(d) reflect the noncubic symmetry that results from these frozen-in distortions.

The deformation potentials for the breathing-mode displacements are about 6 eV/Å near the BZ boundary and decrease to ~1 eV/Å at E_F for $x \approx 0.3$. A similar value of ~1 eV/Å is achieved by the ferroelectric modes at E_F for small x. This suggests that the phonon modes that are likely to be important for superconductivity in these materials involve ferroelectric displacements of Pb,Bi atoms and breathing-mode displacements of O atoms.

In conclusion, we have carried out a comprehensive study of the electronic structure of the BaPb_{1-x}Bi_xO₃ system using a combination LAPW and TB methods. The results predict that the superconducting electrons for $0.05 \le x \le 0.3$ have predominately O $2p_{||}$ character, with comparable Pb,Bi 6s admixture. LAPW and model TB results demonstrate the existence of a Fermi-surface-

induced instability at x = 1 (BaBiO₃) which explains both the cubic-monoclinic structural transition as well as the semiconducting properties of the distorted phase. A TB analysis suggests that the phonon modes which are important for superconductivity are those which modulate the nearest-neighbor ($sp\sigma$) interaction. The most likely candidates include "ferroelectric" displacements of Pb,Bi atoms (Γ_{15} symmetry) and breathing-mode displacements of O atoms (R_1 symmetry).

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