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Structural and electronic properties of III-V bismuth compounds

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We have performed *ab initio* self-consistent calculations based on the full potential linear augmented plane-wave method with the generalized gradient approximation to investigate the structural and the electronic properties of the less known bismuth III-V compounds: BBi, AlBi, GaBi, and InBi. Ground state parameters are computed and compared with available theoretical and experimental works. The zinc-blende phase is found to be the most stable for BBi, AlBi, and GaBi, while InBi prefers the tetragonal PbO structure. The relativistic contraction of the 6*s* orbital of Bi has strong effect on the band structure of III-Bi compounds, which exhibits some features that differ considerably from those of typical III-V semiconductors. In particular, we found an inverted band gap, which reflects a semimetallic character of these systems. Their bonding nature is analyzed in terms of valence charge density transfer, showing three different natures of the bond. Besides, the calculated valence charge density for BBi shows an anomalous behavior characterized by a charge transfer toward the cation B atom, while the others III-Bi behave as the typical III-V compounds with a small charge transfer to the anion bismuth atom.

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I. INTRODUCTION

III-V semiconductor compounds have been extensively studied theoretically and experimentally during the last half century. Most of these works, however, have been devoted to materials from the four row constituents, i.e., B, Al, Ga, In, N, P, As, and Sb. The improvement in the epitaxial growth technology, as the metal-organic vapor phase epitaxy (MOVPE) and the molecular-beam epitaxy (MBE) have opened the way to study the remaining III-V elements, bismuth (III-Bi) compounds, which have received less attention.

It is expected that the most III-Bi compounds should have a small or even negative gap.[1,2] Combination of Bi with III-V compounds yields of interesting new III-V semiconductor alloy, containing semiconductor and semimetal compounds. Therefore III-(V-Bi) alloys[3–8] are strong potential candidate materials for the active region of diode laser and photodetectors operating in the infrared and near infrared.

Other example is the quadruple junction solar cell applied in a rapidly expanding range of space and terrestrial applications. The optimal heterostructure for realizing a 40% efficient solar cell with the sequence of band gaps 0.67 eV/1.05 eV/1.42 eV/1.9 eV, GaInP, GaAs, and Ge are ideally suitable lattice matched semiconductors for the top, next to top, and bottom cells. But until quite recently there existed no materials lattice matched to GaAs, with a band gap of 1 to 1.1 eV. The discovery by Weyers *et al.*[9] of the anomalously large band gap bowing in $GaAs_{1-x}N_x$, opened up a new family of such materials. Kondow *et al.*[10] introduced $Ga_{1-x}In_xN_yAs_{1-y}$ as a 1 eV semiconductor, lattice matched to GaAs. However, due to the large size mismatch between N and As, the growth of high quality GaInNAs on GaAs substrate is difficult. In order to overcome this problem, a coalloying approach has been proposed as the quaternary alloys $GaAs_{1-x-y}N_xBi$. Both experimental,[11,12] and theoretical[2] studies demonstrate that this material can have a band gap matching the operating 1 eV lattice matched to GaAs.

Recently Wang and Ye[1] have calculated the lattice structural parameters of the III-Bi family assuming a zinc-blende phase, and Janotti[2] have performed a first-principles band structure calculation for GaBi and InBi in the zinc-blende phase. However less is known about the ground state structure of the III-bismuth groups. To our knowledge the only synthesized compound of the III-Bi group is InBi, and the stable structure phase is the PbO tetragonal structure[13] (*tp*4, space group *P*4/*nmm*). The structural parameters, electronic properties, bonding characteristics, and ground state structure of the III-Bi are therefore unknown. Since the stability of these compounds in conjunction with their electronic properties is critical in promoting alloys, a detailed theoretical investigation of III-bismuth compounds is necessary. In this paper we present a predictive study of the structural and electronic properties of III-Bi by using the state-of-the-art *ab initio* self-consistent full potential linearized augmented plane wave (FPLAPW).

For the remaining parts of this paper, we briefly describe the computational method used in Sec. II. Results for the structural and electronic properties will be presented in Sec. III. Section IV is the conclusion.

II. METHOD

The calculations were performed in the framework of density functional theory (DFT). We have employed the full potential linearized augmented plane-wave (FLAPW) method as implemented in the WIEN2K code.[14] The exchange and correlation effects were treated using the generalized gradient approximation (GGA),[15] and the local density approximation (LDA).[16] We expand the basis function up to $R_{MT}K_{MAX}=8$ (R_{MT} is the plane wave radii, K_{MAX} is the maxi-

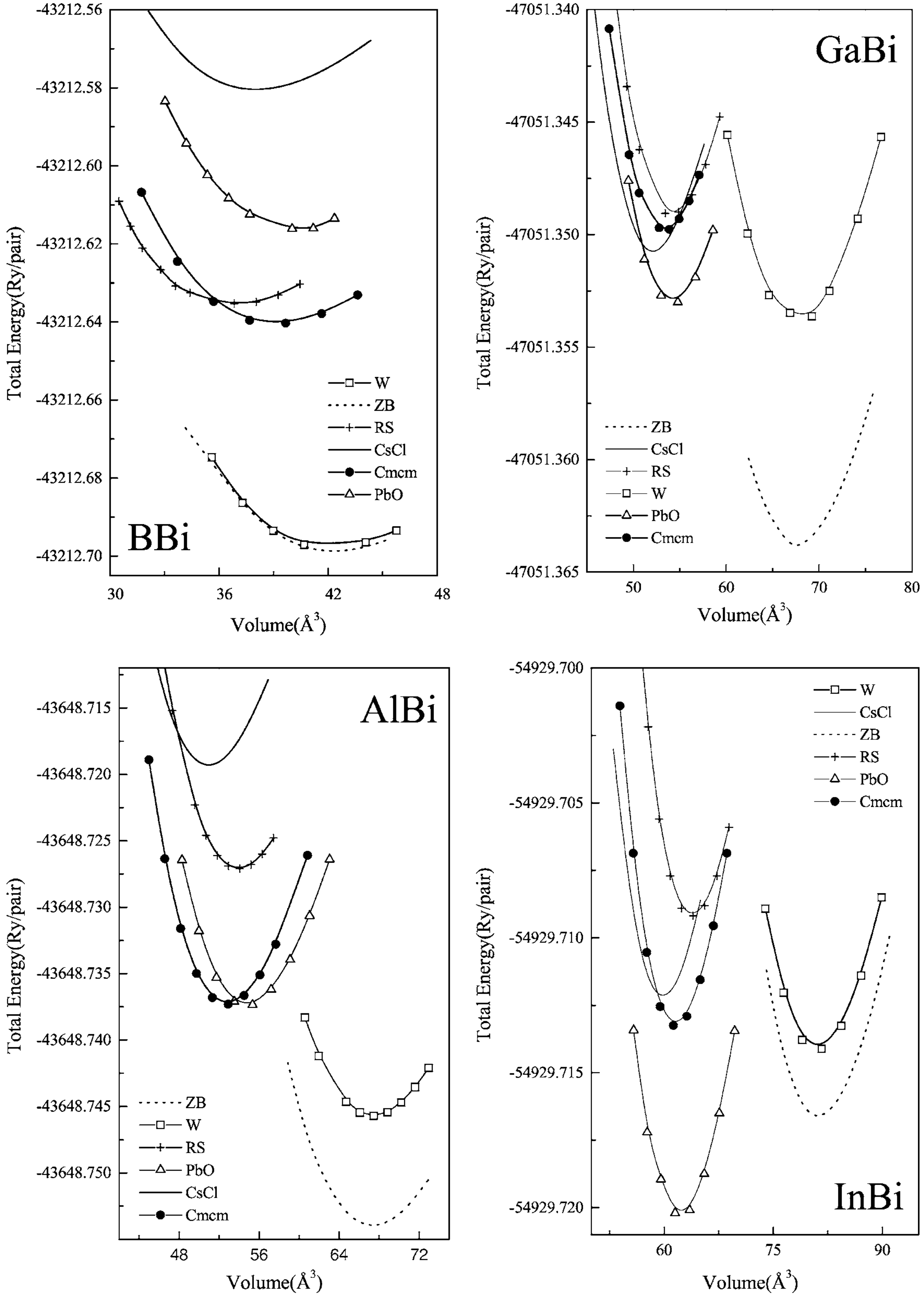

FIG. 1. Total energy versus volume for the zinc-blende (ZB), the wurtzite (W), rocksalt (NaCl), CsCl and *Cmcm* phases of BBi (a), AlBi (b), GaBi (c), and InBi (d).

mum modulus for the reciprocal lattice vectors). The maximum value for partial waves inside atomic sphere is $l=10$. Fully relativistic approximation is used for core electrons, and scalar relativistic approximations are used for valence electrons. Spin-orbit coupling is included using the second-variation method.

Accurate Brillouin zone integrations are performed using the standard special *k* points technique of Monkhorst and

TABLE I. Present results for structural parameters of the ground state phase of III-Bi compounds. *a* and *c* are the lattice constants, *z* is the cell-internal structural parameter, *B* is the bulk modulus, *B′* is the pressure derivative of the bulk modulus, and ΔH is the energy of formation (eV/pair).

			a (Å)	*c* (Å)	*z*	*B* (GPa)	*B′*	ΔH
BBi	(ZB)	This work (GGA)	5.529			72.209	4.73	−8.91
		This work (LDA)	5.416			86.27	4.6	
		LDA[a] (pseudopotential)	5.390			87.7	4.52	
AlBi	(ZB)	This work (GGA)	6.46			39.13	4.31	−7.50
		This work (LDA)	6.31			45.58	4.23	
		LDA[a] (pseudopotential)	6.266			48.2	5.23	
		LDA[b] (FLAPW)	6.341					
GaBi	(ZB)	This work (GGA)	6.47			35.96	4.87	−7.05
		This work (LDA)	6.28			46.37	4.55	
		LDA[a] (pseudopotential)	6.178			46.1	4.57	
		LDA[c] (FLAPW)	6.324			45.1	4.9	
		Expt.[d]	6.33					
InBi	(PbO)	This work (GGA)	4.99	5.03	0.40	39.95	4.79	−7.38
		This work (LDA)	4.81	4.90	0.40	53.70	4.96	
		Expt.[e]	5.00	4.77	0.393			

[a] Reference 1.
[b] Reference 19.
[c] Reference 2.
[d] Reference 7.
[e] Reference 13.

Pack (MP).[17] For the zinc-blende (ZB) and wurtzite (W) phases, we have used $9\times9\times9$ and $9\times9\times4$ MP meshes, respectively. For the CsCl phase we used $10\times10\times10$ MP meshes, for the *Cmcm* phase we used $7\times7\times7$ MP meshes, and for the rock-salt (NaCl) phase we used $11\times11\times11$ MP meshes. The corresponding integrating points over the irreducible Brillouin zone are 56 *k* points for CsCl and NaCl phases, 55 *k* points for the ZB phase, and 48 *k* points for the W and the *Cmcm* phases.

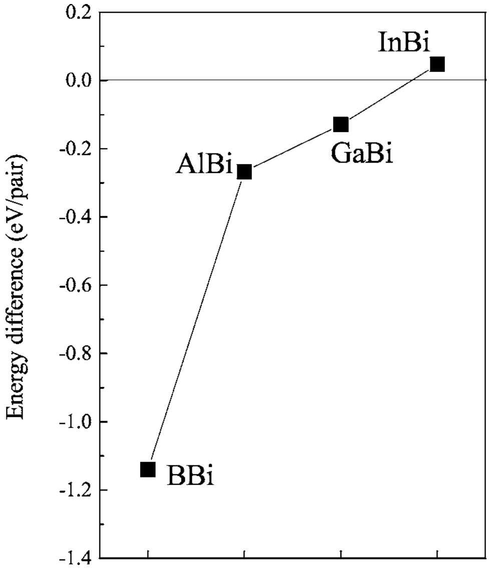

FIG. 2. Total energy difference between ZB and PbO phase for III-Bi group.

III. RESULTS AND DISCUSSION

Total energy versus volume data for the zinc-blende, wurtzite, rock-salt, CsCl, and *Cmcm* phases are shown in Fig. 1 for the III-Bi compounds. The calculated total energies are fitted with the Murnaghan[18] equation of state to obtain structural parameters, which are reported in Table I. The calculated lattice parameters and bulk modulus are, in general, in favorable agreement with the previous calculations. Our calculated LDA lattice parameter for BBi, agrees with the

TABLE II. Calculated elastic constants of cubic BBi, AlBi, and GaBi.

		C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
BBi	This work (LDA)	163.8	28.3	86.3
	LDA[a] (pseudopotential)	160.2	51.5	87.4
AlBi	This work (LDA)	76.8	30.4	68.8
	LDA[a] (pseudopotential)	72.2	36.2	33.4
GaBi	This work (LDA)	81.6	28.1	59.7
	LDA[a] (pseudopotential)	73	32.7	36.3

[a] Reference 20.

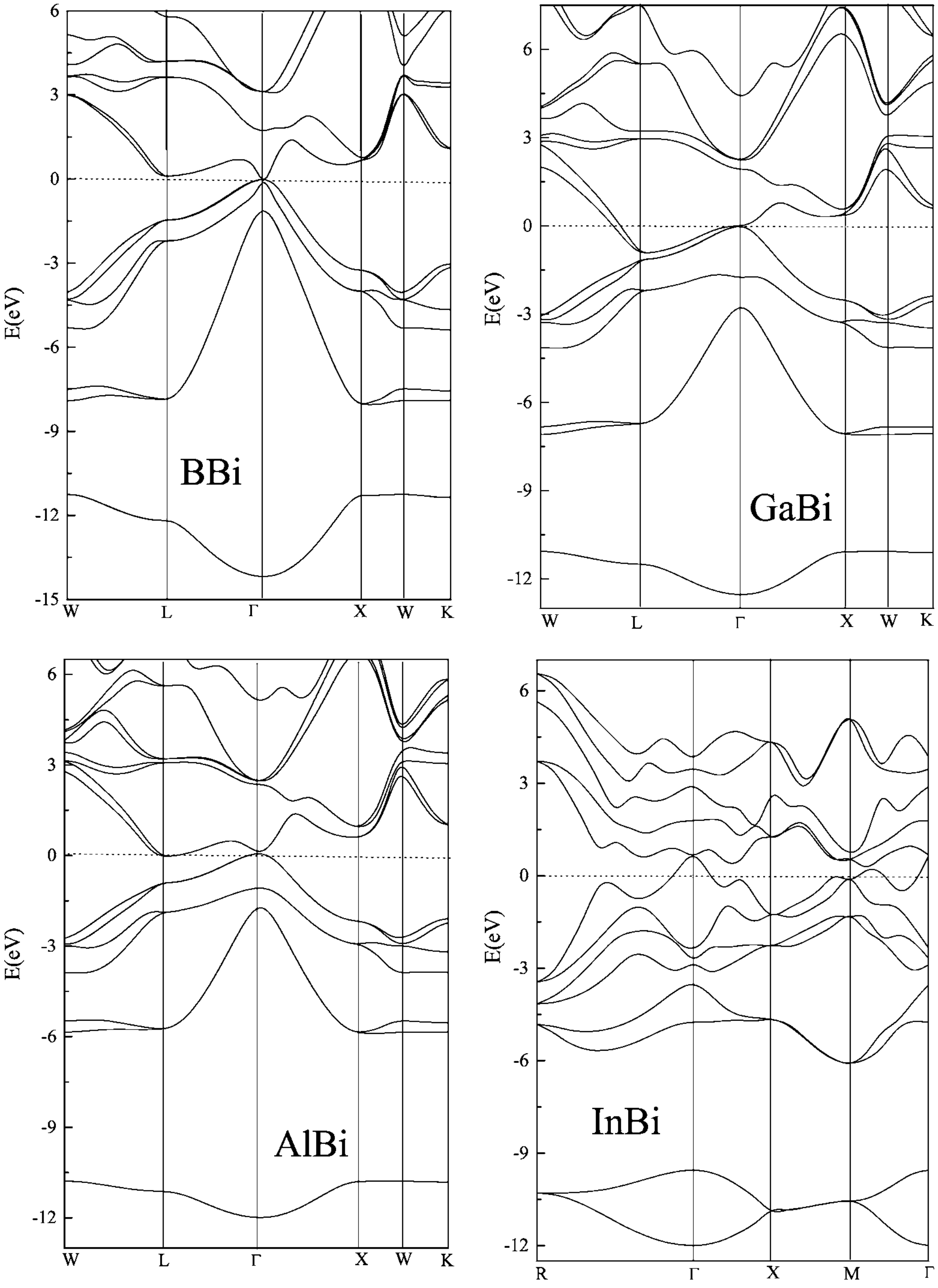

FIG. 3. Calculated relativistic band structure of BBi (a), AlBi (b), GaBi (c), and InBi (d).

recent LDA fist-principles pseudopotentiel calculations.[1] For AlBi and GaBi, our LDA lattice parameter is closer to the recent FLAPW[2,19] than with the pseudopotentiel[1] LDA calculations. The small differences between the two FLAPW calculations are due to the different *k* points sampling. Our results show the usual trends of LDA and GGA, with respect to LDA, the GGA increases the lattice constant. The arithmetic average of the LDA and GGA lattice constant of GaBi(6.37 Å) agrees well with the recent measured value of 6.33±0.06 Å.

The zinc-blende phase is found as the ground state structure of BBi, AlBi, and GaBi. In the case of InBi, we found that the PbO tetragonal phase is the ground state structure, which is in agreement with the experimental findings. Our calculated structural parameters for this structure agree favorably with the experimental structural parameters values.

In Fig. 2, we present the total energy difference (ΔE_{ZB}-PbO) between the ZB and the PbO phase for the III-Bi groups. The total energy difference increases as the anion(Bi) becomes heavier (i.e., from BBi to TlBi). Hence the PbO phase is stabilized over the zinc-blende as the *X*-Bi compounds become heavier. The PbO structure is a likely candidate for the structural ground state stability for the heavy III-V compounds: TlSb, TlBi, and InBi.

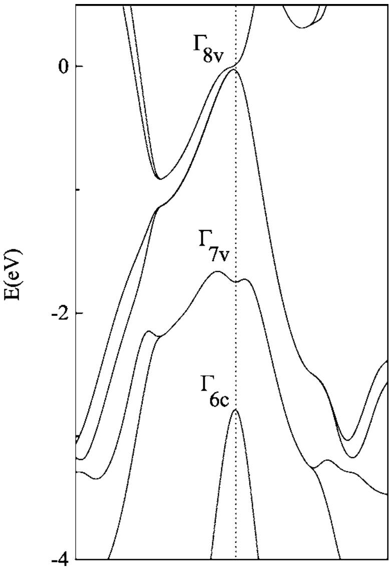

FIG. 4. Calculated relativistic band structure of GaBi between −4 eV and 0 eV.

In order to check the absolute stability of the ground phase of the III-Bi, we calculate the formation energy from the ground state total energies of the crystals $E_{X\mathrm{Bi}}$ and the free atoms E_X, E_{Bi} as follows:

$$\Delta H(\mathrm{bulk}) = E_{X\mathrm{Bi}}(\mathrm{bulk}) - [E_X(\mathrm{bulk}) + E_{\mathrm{Bi}}(\mathrm{bulk})],$$

where X stands for B, Al, Ga, and In. The total energies of the free atoms include the spin polarization energies. The values for the cohesive energy are reported in Table II for the series of the III-Bi group. These results predict the thermodynamic stability of these compounds. Since BBi, AlBi, and GaBi have never been synthesized, it is important to study the mechanical stability of these compounds. The mechanical stability for a cubic crystal implies the following restriction: $C_{11}-C_{12}>0$, and $C_{44}>0$, where C_{11}, C_{12}, and C_{44} are the elastic constants. The elastic constants were obtained by fitting the total energy of the strained crystals. Three types of strain, the volume change, volume conserved tetragonal and rhombohedral shear strains were considered. The calculated elastic constants are given in Table II, indicating that these compounds are stable against elastic deformation.

The thermodynamic and mechanical stability of BBi, GaBi, and AlBi in the zinc-blende phase, allow the possibility of pseudomorphic growth of a cubic III-V-Bi alloy, as it was demonstrated recently on the epitaxial growth of good crystal quality of cubic GaAsBi by MBE.[8] However alloying InBi with III or V atoms seems to be problematic, while cubic InAsBi has been grown by MOVPE.[2] This alloy has a large miscibility of gap, and the solubility of Bi in InAs is quite limited. This is due to the structural dissimilarity between tetragonal InBi and cubic InAs. Growing such good quality of III-InBi (or InBi-V) crystal alloys would thus re-

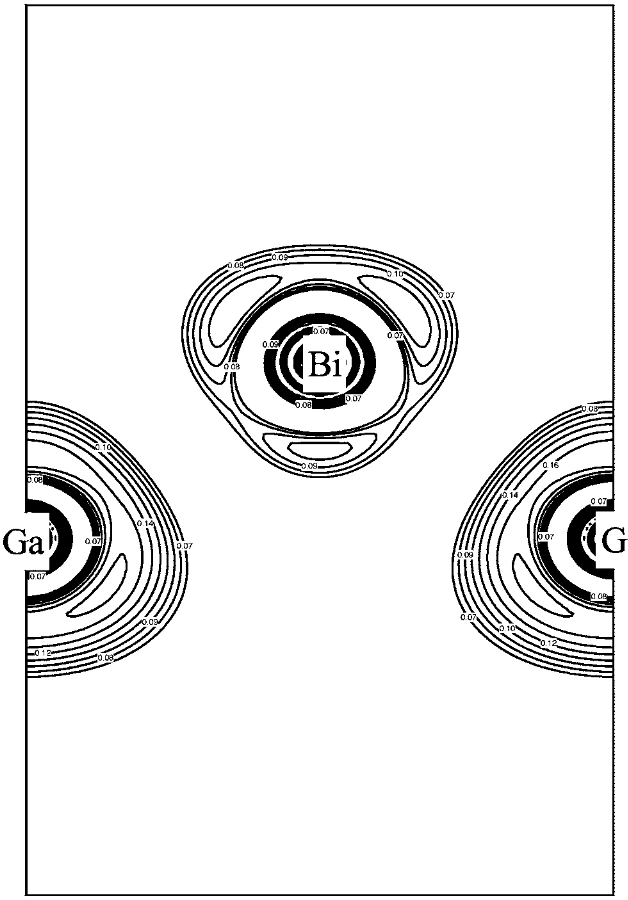

FIG. 5. Charge density plot for the Γ_{6c} state of GaBi in the (110) plane.

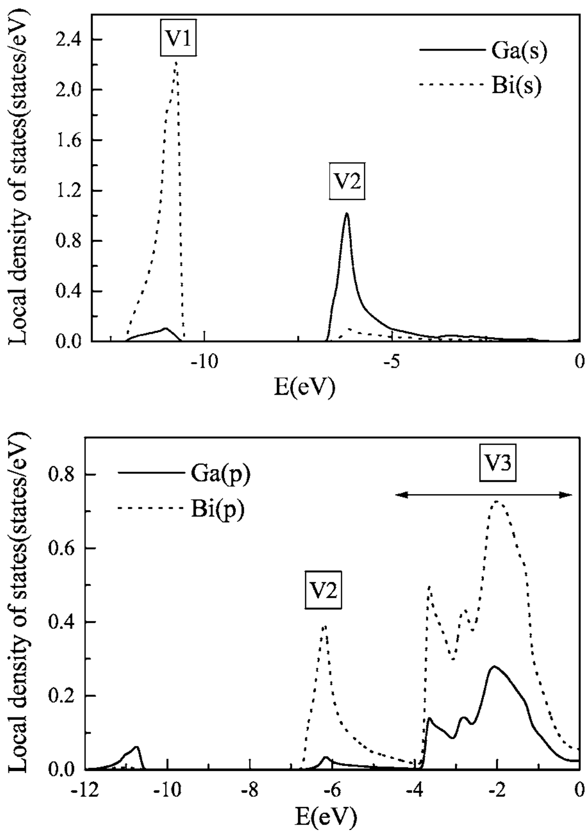

FIG. 6. The atomic-projected local density of states (DOS) of GaBi for *s* orbital (a) and *p* orbital (b).

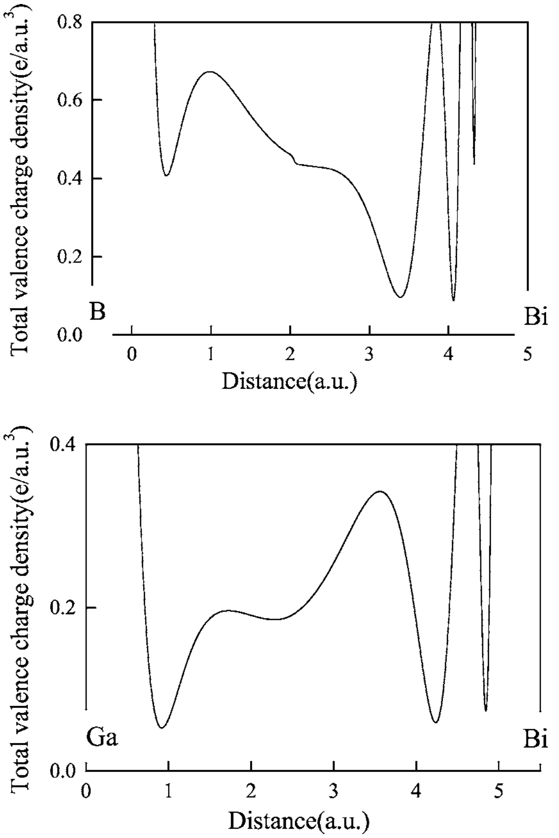

FIG. 7. Total valence charge density plot for BBi (a), and GaBi (b) in the (110) plane.

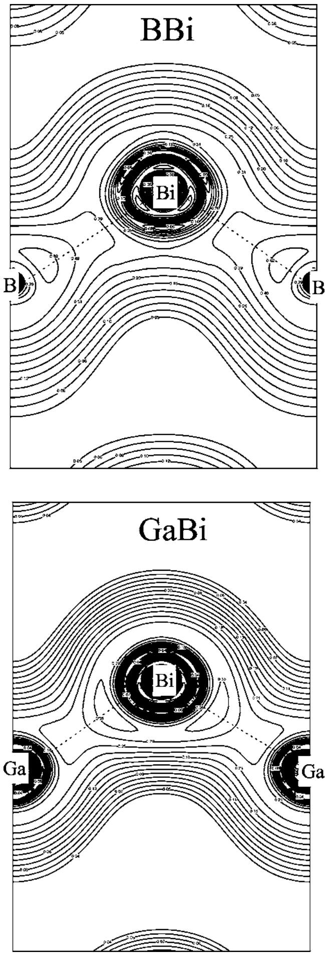

FIG. 8. Total valence charge density plot for BBi (a), and GaBi (b) along the bond.

quire to use a tetragonal substrate to favor the emergence of a tetragonal phase rather than a cubic structure.

The calculated relativistic band structures, including spin-orbit coupling, for BBi, AlBi, GaBi, and InBi are displayed in Fig. 3. All compounds show negative band gap of −0.085 eV, −1.81 eV, −2.91 eV, and −4.75 eV for BBi, AlBi, GaBi, and InBi, respectively. However, it is well known that the energy band gaps are not given accurately from the GGA calculation because it does not truly represent quasiparticle excitation energies. If we compare our −2.91 eV for GaBi and the LDA corrected band gap[2] of −1.45 eV, we can expect that real band gap of BBi and AlBi to be moderately positive, while in GaBi and InBi it remains still semimetallic.

The unusual characteristic of the band structure in III-Bi compounds is related to their inverted bands. From Fig. 4 we may see that the Γ_{6c} state is below the Γ_{8v} state and the antibonding Γ_{6c} band (Fig. 5), which is empty and concave upwards in typically III-V semiconductors (e.g., GaAs), becomes occupied and concave downwards. This is merely a consequence of the relativistic contraction of the 6*s* electrons of Bi atoms. The calculated 6*s* level without relativistic effect is −11.02 eV, and is −13.57 eV with relativistic effect, which lower considerably the 6*s* level of Bi. Hence the relativistic effects reduce consequently the band gap of the bismuth compounds.

Figure 6 shows the calculated atom-projected *s* and *p* band density of states of GaBi, for others III-Bi. The main features are the same as for GaBi, and the discussion here is valid also for those compounds. The lowest valence band (*V*1) is a bonding Bi 6*s* band, the antibonding band *V*2 is derived mainly from the Bi 3*p* and *X* (*X*=B, Al, Ga, In) *s* orbitals, while the highest band *V*3 is a bonding Bi *p* and *X* *p* orbitals. In the case of BBi we observe a strong *p*-*p* mixing in the *V*3 band. We notice that in the other III-Bi compounds, *V*3 is derived mostly from the anion *X* *p* orbital, which is typical for III-V semiconductors.

To complete the entire basic background for the III-Bi compounds, let us investigate their bonding character. We show in Figs. 7 and 8 the valence charge density distributions, without including *d* band, in the plane $(1\ -1\ 0)$ and along the $\langle 111 \rangle$ direction of BBi and GaBi as prototypes. The first remark to notice is the inverted charge transfer between the anion and the cation in BBi. The cation is playing the opposite role by attracting the maximum of charges. This situation follows the same trends observed in other boron compounds such as BP, BAs, and BSb.[21–25] This unusual behavior appears to be originate from the small core size of *p* electrons in B. Boron has a deep and localized pseudopotential compared to the atoms of elements from other rows. The charge moves toward the bond center giving rise to a strong localization around the cation. This means a negative ionicity of the bond according to the charge transfer behavior which characterize in a natural way the bond/ionicity and its characteristics. Therefore, the criterion to define the ionicity parameter is obviously different to the well-known semiconductors and consequently will not obey any of the previous scales such as the one of Phillips.[26] Some models[26–28] linked to charge transfer may be more appropriate for such materials. However it seems that the only algorithm model that agrees with the above analysis is the one of Zaoui *et al.*[28] based on a simple formulation of ionicity taking into account the charge transfer profile. For all the other models the ionicity is expected to remain positive and therefore they could not express the real behavior. The valence charge density of GaBi shows an obvious delocalization of charges toward the bond center in spite of the slight transfer noticed around the anion side, which reflects a strong covalent bond for this compound. This tendency is expected to be similar for AlBi and InBi.

IV. CONCLUSION

This study reports a detailed investigation on the electronic structure, ground state properties and bonding nature of III-Bi compounds using first principles FLAPW methods. The most relevant conclusions are summarized as follows:

(i) The zinc-blende structure is found to be the most stable for BBi, AlBi, and GaBi, while InBi prefers the tetragonal PbO structure. The latest phase is stabilized over the zinc-blende phase as the cation became heavier.

(ii) The calculated band structure with an estimated corrected band gap shows an inverted band gap for these compounds where we notice the important role of 6*s* orbital.

(iii) The charge density distribution exhibits an opposite role between the anion and the cation for the case of BBi. The maximum of charge is pronounced and localized around the boron side. For GaBi, the tendency follows the other semiconductors family, which can be guessed to be the same for AlBi and InBi. We notice a delocatization of charge with a slight transfer from Ga to Bi reflecting a small ionic contribution.

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