

Journal id: TPHL_A_430586

Corresponding author: A. Zaoui

Title: First-principles study of the ground state stability of III–V bismuth compounds

NO QUERIES

First-principles study of the ground state stability of III–V bismuth compounds

A. Zouai^{a*}, D. Madouri^{bc} and M. Ferhat^c

^a*L. M. L. (UMR 8107), Polytech'Lille, Université des Sciences et de la Technologie de Lille, Cité Scientifique, Avenue Paul Langevin, 59655 Villeneuve D'ascq Cedex, France;* ^b*Faculté des Sciences, Université d'Oran Es Senia, Oran, Algeria;* ^c*Département de Physique, LEPM, Université des Sciences et de la Technologie d'Oran, Algeria*

(Received 29 June 2009; final version received 1 September 2009)

In this letter, full potential linearized augmented plane wave method has been used to shed light on the role of relativistic effects on the stability of the zinc-blend (ZB) and PbO phases of III–V bismuth compounds: BBi, AlBi, GaBi, and InBi. In particular, for the heavier III–V bismuth (InBi), ZB phase is found to be the most stable in the case of non-relativistic calculation. However, the stable phase becomes PbO when relativistic effect is considered. Relativistic effects reduce the structural parameters (lattice parameters and bulk modulus) of III–V bismuth compounds. These effects become important when the atomic number increases. For the non-relativistic approximation, all studied compounds are found to be stable in the ZB structure, however, the relativistic correction induces strong reduction of the total energy difference ($\Delta E_{\text{ZB-PbO}}$). Moreover, the total energy difference between the relativistic and non-relativistic approximations is important for all compounds. The most affected by the relativistic effects is InBi. The origins of these relativistic effects are explained in terms of stabilization (destabilization) of s, and $p_{1/2}$ ($p_{3/2}$ and d) orbital energies.

Keywords: *ab initio*; compound semiconductors; band calculations

III–V semiconductor compounds are characterized by their tendency to crystallize in zinc-blend (ZB) and wurtzite (W) structures. Theoretical and experimental works have revealed that ZB and the W phases are the most common crystal structures of III–V compounds [1–5]. However, remarkable difference was recently noticed between the physical properties of conventional III–V and the heavier bismuth III–V compounds. These latter are semi-metallic [6]; whereas the remaining III–V compounds are semiconductors. Moreover, the ZB phase is found to be the most stable for BBi [7], AlBi [6,8], and GaBi [6–8], while the heavier III–Bi (TlBi and InBi) compounds stabilize in the tetragonal PbO structure [1,8,9]. This is usually ascribed to relativistic effect [10]. The relativistic s(p)-orbital contraction(expansion) of Bi atom has long been associated with the 'inert pair effect' in coordination chemistry,

*Corresponding author. Email: azaoui@polytech-lille.fr

Table 1. Atomic s, p, and d orbital energy levels (in eV) in non-relativistic (NRL) and relativistic (RL) approximations for III and V elements.

	E_s -NRL	E_s -RL	E_p -NRL	E_p -RL	E_p^* -NRL	E_p^* -RL	E_d -NRL	E_d -RL
B	9.90	9.90			4.02	4.01		
Al	8.02	8.04			3.02	3.02		
Ga	8.98	9.17			2.91	2.91	19.72	18.85
In	7.89	8.33			2.86	2.89	19.75	18.09
N	18.84	19.87	8.30	8.28	8.30	8.31		
P	14.73	14.80	6.30	6.25	6.30	6.31		
As	14.769	15.20	5.96	5.82	5.96	6.11	41.44	40.05
Sb	12.51	13.65	5.53	5.28	5.53	5.89	35.07	32.80
Bi	11.58	14.00	4.99	3.96	4.99	5.79	30.73	24.88

whereby the tight bound $6s^2$ electron becomes chemically inert in compounds containing Tl, Pb, and Bi, which consequently have effective chemical valence of 1, 2, and 3, respectively. This is rather than 3, 4, and 5 implied by their outer electron configurations s^2p^1 , s^2p^2 , and s^2p^3 . In the present article, we study the structural stability of III–V bismuth compounds from quantitative first-principles calculations based on relativistic/non-relativistic approaches.

To this end, we employed the full potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN2k code [11]. The exchange and correlation effects were treated using the generalized gradient approximation (GGA) [12]. We expand the basis function up to $R_{MT} K_{MAX} = 8$ (R_{MT} is the plane wave radii, K_{MAX} is the maximum 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 approximation is used for valence electrons. Accurate Brillouin zone integrations are performed using the standard special k points technique of Monkhorst and Park (MP) [13]. For the ZB and tetragonal phases, we have used $8 \times 8 \times 8$ MP meshes. The corresponding integrations points over the irreducible Brillouin Zone are: 43 k -points for the ZB phase, and 75 k -points for the tetragonal (PbO) phase. The number of k -points turns out to be sufficient for the accuracy of the calculated total energy (1 mRy/unit cell).

The non-relativistic and relativistic orbital energies for the elements of groups III and V are given in Table 1, and plotted for the group V in Figure 1. We notice the following remarks:

- (i) relativistic effects are more important for group V than group III,
- (ii) relativistic effects increased with atomic number Z , i.e. $B \rightarrow In$ and $N \rightarrow Bi$,
- (iii) s and p^* ($p_{1/2}$) orbital are stabilized and contracted, while $p(p_{3/2})$ and d orbital are destabilized and expanded, which in turn lower (increase) the s , $p^*(p, d)$ orbital energies, and
- (iv) the s orbital are strongly affected, while the p , p^* and d orbital are affected relatively to a lesser extent.

From the above considerations, it is clear that orbital energies will induce strong relativistic effects on the structural properties of III–V compounds.

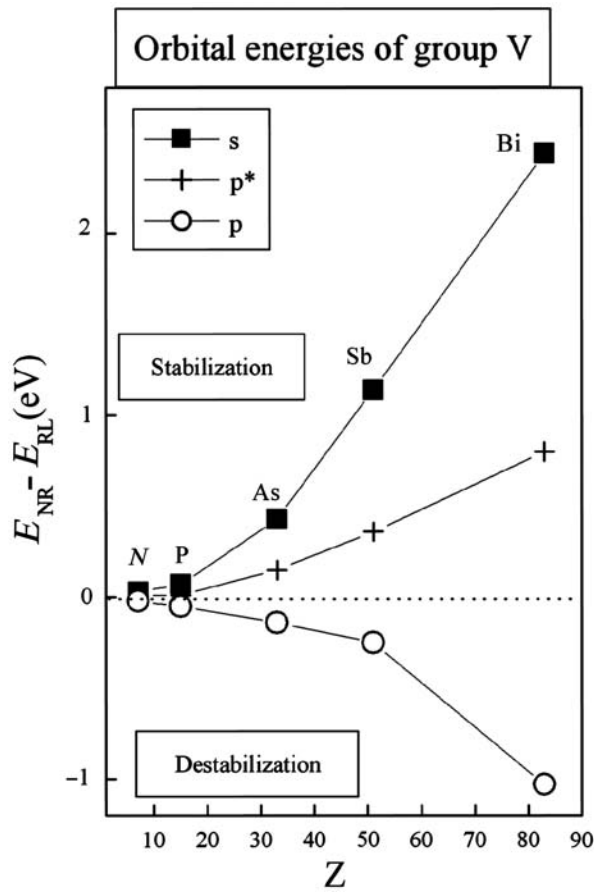


Figure 1. s, p*, and p orbital energies difference between non-relativistic and relativistic approximations ($E_{NR}-E_{RL}$) for V elements.

Table 2. Calculated structural parameters for III-Bi compounds in the ZB phase.

		Relativistic		Non-relativistic	
		A (Å)	B (GPa)	A (Å)	B (GPa)
BBi	This work	5.535	72.30	5.523	88.64
	LDA (pseudopotential)	5.39 ^a	87.7 ^a		
AlBi	This work	6.448	38	6.493	44.60
	LDA (pseudopotential)	6.266 ^a	48.2 ^a		
GaBi	This work	6.461	35.47	6.465	41.79
	LDA (pseudopotential)	6.178 ^a	46.1 ^a		
	Experimental	6.33 ^b			
InBi	This work	6.867	30.71	6.901	36.84

Notes: ^aReference [15].

^bReference [16].

Table 3. Calculated structural parameters for InBi in the tetragonal PbO phase.

		Relativistic			Non-relativistic		
		A (Å)	C (Å)	B (GPa)	A (Å)	C (Å)	B (GPa)
InBi	This work	5.016	5.035	42.00	4.974	5.011	42.00
	Experimental ^a	5.00	4.77				

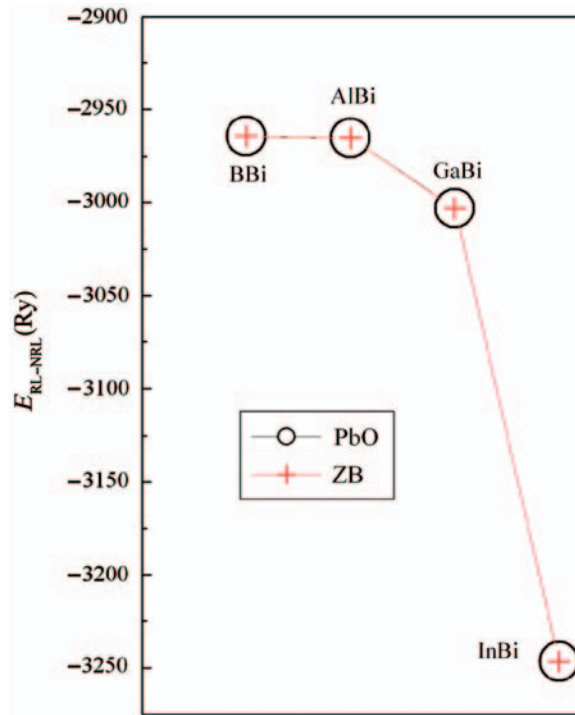
Note: ^aReference [1].

Figure 2. Total energy difference between the relativistic (RL) and non-relativistic (NRL) cases for the ZB and PbO phases of BBi, AlBi, GaBi, and InBi.

70 The calculated total energies for BBi, AlBi, GaBi, and InBi in the ZB phase are fitted to the Murnaghan [14] equation of states to obtain structural parameters. The calculated structural parameters for the relativistic and non-relativistic cases are given in Table 2. The calculated lattice parameter and bulk modulus are generally in agreement with the previous calculations. For InBi, in the observed [1] tetragonal (PbO) phase (*tp4*-type (*B10*)), our calculated structural parameters for this structure
75 agree favorably with the experimental structural parameters values [1]. It is clear from Tables 2 and 3, that the relativistic effects reduce the structural parameters

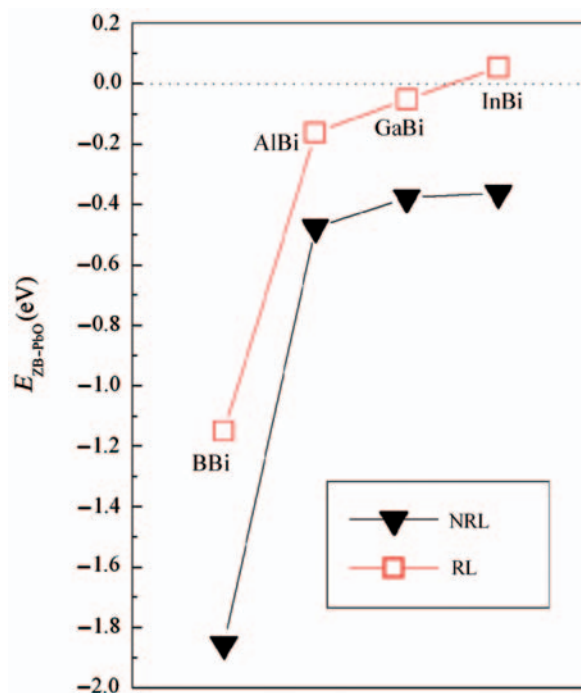


Figure 3. Total energy difference between ZB and PbO phases of III-Bi compounds in the relativistic (RL) and non-relativistic (NRL) approximations.

(lattice parameters and bulk modulus) of III-V bismuth compounds. These effects become important when the atomic number increases.

In Figure 2, we present the total energy difference between the relativistic and non-relativistic approximations for BBi, AlBi, GaBi, and InBi in the ZB and PbO phases. We notice the followings:

- (i) all compounds are stable in the relativistic case and
- (ii) the total energy difference between the relativistic and non-relativistic approximations is important for all compounds. The most affected by the relativistic effects is InBi.

In Figure 3, we present the total energy difference ($\Delta E_{\text{ZB-PbO}}$) between the ZB and PbO phases for III-Bi groups, in both relativistic and non-relativistic cases. The total energy difference increases as the anion (Bi) becomes heavier, i.e., from BBi to InBi. For the non-relativistic case all compounds are found stable in the ZB structure, however, the relativistic correction induces strong reduction of the total energy difference ($\Delta E_{\text{ZB-PbO}}$). Consequently, PbO phase is stabilized over the ZB phase more quickly for the bismuth III-V compounds. Nevertheless, BBi, AlBi, and GaBi are found stable in the ZB phase even in the relativistic case. For InBi, our total energy calculations clearly show the importance of the relativistic effects on the relative stability of the ZB and the PbO phases. Without relativist corrections

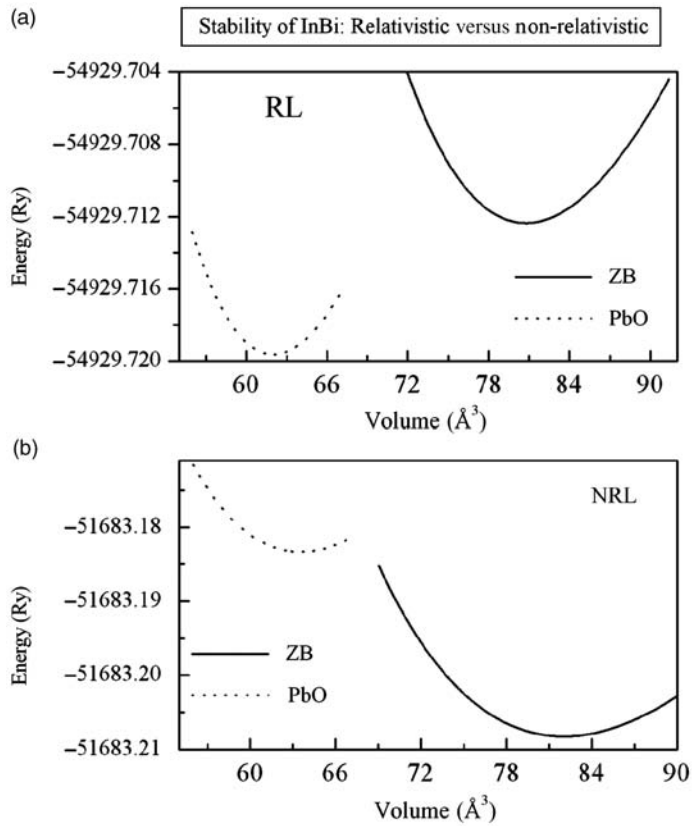


Figure 4. Total energy versus volume for InBi in the ZB and PbO phases: (a) relativistic approximation (RL); (b) non-relativistic approximation (NRL).

(Figure 4b), the ZB phase is found to be the most stable, however with the relativistic effect, the lower energy configuration is shown to be the tetragonal PbO phase (Figure 4a).

In summary, we have performed *ab initio* calculations using FP-LAPW, in order to study the relativistic effects on the structural properties of III–V bismuth compounds. According to the obtained results, we have noticed the following deductions:

- (i) Relativistic effects reduce the structural parameters (lattice parameters and bulk modulus) of III–V bismuth compounds. These effects become important when the atomic number increases.
- (ii) All studied compounds are stable in the relativistic case.
- (iii) The total energy difference between the relativistic and non-relativistic approximations is important for all compounds. The most affected by the relativistic effects is InBi.
- (iv) For the non-relativistic approximation, all compounds are found stable in the ZB structure; however, the relativistic correction induces strong reduction of the total energy difference ($\Delta E_{\text{ZB-PbO}}$).

- 115 (v) Our total energy calculations clearly show the importance of the relativistic effects on the relative stability of the ZB and PbO phases. For InBi without relativistic effect, the ZB phase is found to be the most stable. However with the relativistic effect, the most stable phase is PbO.

The origins of these relativistic effects are explained in terms of stabilization (destabilization) of s and $p_{1/2}$ ($p_{3/2}$ and d) orbital energies.

References

- 120 [1] P. Villars and L. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, American Society for Metals, Metals Park, OH, 1985.
[2] S.B. Zhang and M.L. Cohen, *Phys. Rev. B* 35 (1987) p.7604.
[3] A. Muñoz and K. Kunc, *Phys. Rev. B* 44 (1991) p.10372.
[4] Chin-Yu Yeh, Z.W. Lu, Z. Froyen and A. Zunger, *Phys. Rev. B* 46 (1992) p.10086.
125 [5] S.Q. Wang and H.Q. Ye, *Phys. Stat. Sol. (b)* 1 (2003) p.45.
[6] M. Ferhat and A. Zaoui, *Phys. Rev. B* 73 (2006) p.1151070.
[7] D. Madouri and M. Ferhat, *Phys. Status Solidi (b)* 242 (2005) p.2856.
[8] M. Ferhat and A. Zaoui, *Appl. Phys. Lett.* 88 (2006) p.161902.
[9] N. Saidi-Houat, A. Zaoui and M. Ferhat, *J. Phys. Condens. Matter* 19 (2007) p.106221.
130 [10] J.C. Phillips, *Bonds and Bands in Semiconductors*, Academic, New York, 1973.
[11] P. Blaha, K. Schwarz and J. Luitz, *WIEN2k*, Vienna, University of Technology 1997 [improved and updated Unix version of the original copyrighted wien code, witch was published by P. Blaha, K. Schwarz, P. Sorantin, and S.B. Trickey, *Comput. Phys. Commun.* 59 (1990) p.399].
135 [12] J.P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) p.3865.
[13] H.J. Monkhorst and J.D. Park, *Phys. Rev. B* 13 (1976) p.5188.
[14] F.D. Murnaghan, *Proc. Natl. Acad. Sci. USA* 30 (1944) p.5390.
[15] S.Q. Wang and H.Q. Ye, *Phys. Phys. Rev. B* 66 (2002) p.235111.
140 [16] S. Tixier, M. Adamcyk, T. Tiedje, S. Francoeur, A. Mascarenhas, P. Wei and F. Sciettekatte, *Appl. Phys. Lett.* 82 (2003) p.2245.