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First-principles calculations of the electronic and structural properties of GaSb

© *E.-E. Castaño-González**, *N. Seña*⁺, *V. Mendoza-Estrada**,
*R. González-Hernández**, *A. Dussan*⁺, *F. Mesa*•

* Grupo de Investigación en Física Aplicada, Departamento de Física,
Universidad del Norte, Barranquilla-Colombia
⁺ Departamento de Física, Grupo de Materiales Nanoestructurados y sus Aplicaciones,
Universidad Nacional de Colombia-Colombia, Bogotá-Colombia
• Grupo NanoTech, Facultad de Ciencias Naturales y Matemáticas,
Universidad del Rosario, Bogotá-Colombia

E-mail: rhernandezj@uninorte.edu.co; fredy.mesa@urosario.edu.co

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In this paper, we carried out first-principles calculations in order to investigate the structural and electronic properties of the binary compound gallium antimonide (GaSb). This theoretical study was carried out using the Density Functional Theory within the plane-wave pseudopotential method. The effects of exchange and correlation (XC) were treated using the functional Local Density Approximation (LDA), generalized gradient approximation (GGA): Perdew-Burke-Ernzerhof (PBE), Perdew-Burke-Ernzerhof revised for solids (PBEsol), Perdew-Wang 91 (PW91), revised Perdew-Burke-Ernzerhof (rPBE), Armiento-Mattson 2005 (AM05) and meta-generalized gradient approximation (meta-GGA): Tao-Perdew-Staroverov-Scuseria (TPSS) and revised Tao-Perdew-Staroverov-Scuseria (RTPSS) and modified Becke-Johnson (MBJ). We calculated the densities of state (DOS) and band structure with different XC potentials identified and compared them with the theoretical and experimental results reported in the literature. It was discovered that functional: LDA, PBEsol, AM05 and RTPSS provide the best results to calculate the lattice parameters (a) and bulk modulus (B_0); while for the cohesive energy (E_{coh}), functional: AM05, RTPSS and PW91 are closer to the values obtained experimentally. The MBJ, Rtpss and AM05 values found for the band gap energy is slightly underestimated with those values reported experimentally.

1. Introduction

Knowledge of the physical and chemical properties of the binary compounds are relevant in the design and development of different devices that promote new technologies; among these compounds gallium antimonide (GaSb) is found, which in recent years has been investigated with growing interest facilitating the fabrication of new electronic devices of great impact [1–4]. Antimonides have attracted greater interest due to their prospective applications in rechargeable lithium batteries as anode material [5,6]. GaSb is a good candidate for the fabrication of thermophotovoltaic cells with low temperature systems [3], as well as in applications in spintronic devices when Mn atoms are introduced in the GaSb matrix [7,8], super-lattices [9], and spin efficient injectors in semiconductors, among others. In addition, due to their high electronic mobility, antimonide compounds are commonly used in the application of the fabrication of other electronic devices [10,11].

In this work, the structural and electronic properties of the compound GaSb were studied using Local Density Approximation (LDA) functional and the generalized gradient approximation (GGA), starting with the density functional theory (DFT). A correlation between the values obtained using DFT calculations, and the experimental values reported for the gap value and its implications in applications in opto-electronic devices was presented. The band structure and densities of state (DOS) revealed a gap characteristic in the GaSb semiconductor as fundamental indicator within the optical properties of the material.

2. Computational Method

For the structural study and electronic analysis of the GaSb compound, the functional density theory as it is implemented in the computational code VASP (Vienna ab initio simulation package) [12] was used. The effects of the electronic interchange and correlation were treated using in the Local Density Approximation (LDA) functional [13], the generalized gradient approximation (GGA) of Perdew-Burke-Emzerhof (PBE) [14], Perdew-Burke-Ernzerhof revised for solids (PBEsol) [15], Perdew-Wang 91 (PW91) [16], revised Perdew-Burke-Ernzerhof (RPBE) [17], Armiento-Mattson 2005 (AM05) [18] and the meta-Generalized Gradient Approximation (meta-GGA): Tao-Perdew-Staroverov-Scuseria (TPSS) [19], Revised Tao-Perdew-Staroverov-Scuseria (rTPSS) [21] and modified Becke-Johnson (MBJ) [22], within the DFT.

Calculations were done using optimized values of a k-point mesh of $8 \times 8 \times 8$, centered in the Γ-point of the Irreducible Brillouin Zone (IBZ) and a cutoff energy of the plane waves was expanded until 800 eV. For the pseudopotential of gallium (Ga) and antimonite (Sb), valence electrons in the states of: Ga (s^2p^1) Sb (s^2p^3) were considered. The position of the system of study was $(0, 0, 0)$ for the Ga atom and $(0.25, 0.25, 0.25)$ for the Sb atom, as shown in Fig. 1. For the density calculation of the states, a k-point screen of $16 \times 16 \times 16$, and the energy bands of high symmetry paths: L−Γ−X−U, K−Γ in the first zone of Brillouin.

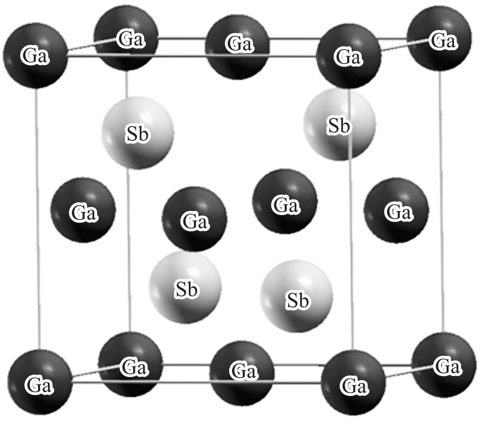

Figure 1. Crystalline structure of the compound GaSb.

3. Results and discussion

The GaSb crystal structure crystal structure was obtained and is presented in Fig. 1.

The crystal structure of GaSb is a GaAs-type (zinc-blende) structure, characterized by the Ga atom position in the corners of the cell and in the center of each one of the faces; while the position of the Sb atoms are given by the symmetric positions considered by $(0.25, 0.25, 0.25)$. Lattice parameters, bulk modulus, and its derivations in respect to the GaSb pressure were calculated for the different functionals, adjusting the data with the total energy *vs.* volume of the unit-cell of the Murnaghan equation of state [23]:

$$E(V) = E_0 + \frac{B_0 V}{B_0'}\left[\left(\frac{V_0}{V}\right)^{B_0'}\frac{1}{B_0' - 1} + 1\right] - \frac{B_0 V_0}{B_0' - 1}, \quad (1)$$

where B_0 is the bulk modulus (fundamental property, since it determines the hardness of the cubic crystals and plays an important role in the establishment of the stability criteria). B_0'-its first derivative, V_0 is the volume of equilibrium, and E_0 is the energy of equilibrium of the structure. The cohesion energy of GaSb was determined using equation (2):

$$E_{\mathrm{coh}} = \frac{E_{\mathrm{bulk}} - N_{\mathrm{Ga}}E_{\mathrm{Ga}} - N_{\mathrm{Sb}}E_{\mathrm{Sb}}}{N_{\mathrm{GaSb}}}, \quad (2)$$

where E_{Ga} and E_{Sb} are the total energies of the isolated gallium and antimonide atoms (supercell of 15 Å) respectively. N_{Ga}, N_{Sb} and N_{GaSb} are the numbers of atoms of gallium and antimonide within the unit cell and finally E_{bulk} is the total energy of the GaSb crystal.

The results obtained of the energy of cohesion (E_{coh}) *vs.* volume for the interchange and correlation functionals studied; LDA, PBE, PBEsol, PW91, AM05, rPBE, TPSS and RTPSS, are presented in Fig. 2.

In Fig. 2, a shift of the minimum value of E_{coh} through the different functionals with a value of around 5.00 eV for the functional rPBE going through 6.50 eV (functional PBEsol) and reaching a minimum when the LDA functional (with a value of 7.45 eV) can be observed. The corresponding values to the relative error percentage for each one of the structural parameters, a, B_0, and E_{coh} are reported in Table. The value determined using LDA shows a higher energetic stability, which is characteristic of this type of approximation. The variations found for the prediction of the band-gap energy (E_{gap}) of the diverse functionals is owed to the approximations that were done in the DFT, at the end of the energy of exchange-correlation, underestimate this value. This is a known error of DFT in semiconducting compounds type II–IV and III–V, in which there is a systematic tendency for the prediction of the band-gap energy in respect to the experimental value [20].

The obtained values for the different exchange-correlation functionals are reported in Table. The experimental and theoretical results obtained by other GaSb authors in the literature, are also reported for each one of the cases. In Table, the values of the structural parameters (a, B_0) and the energy of cohesion (E_{coh}) can be observed, obtained using eight different functionals: LDA, PBE, PBEsol, PW91, rPBE, AM05, TPSS and RTPSS. The reported values are in accordance with the experimental [25] and theoretical [24] data reported by other authors. The general tendency when approximating the electronic density using only dependent terms of the local density (LDA) of underestimating the value of the lattice parameters (an error of 0.024%) with respect to the experimental values, resulting in an overestimation of the bulk modulus of 49.40 GPa (error of 14.07%) and the energy of cohesion (error of 19.46%). In contrast to LDA, functionals that employ the local density and its local spatial variations for the description of the exchange-correlation potential (GGA approximation) correct the underestimation (overestimation) of the lattice parameters (bulk modulus and energy of cohesion). However, a considerable over-evaluation of the GaSb structural

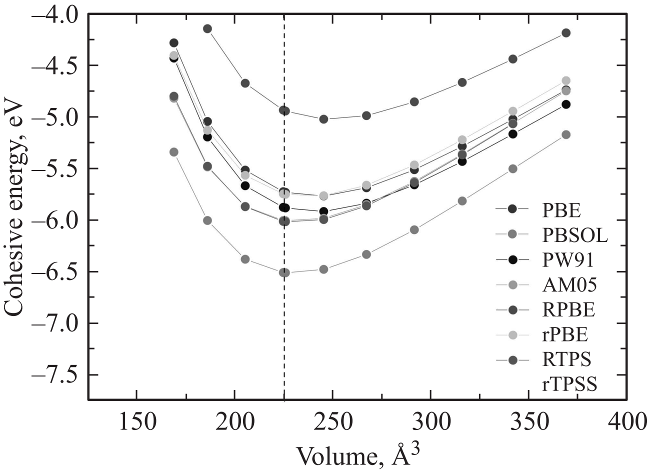

Figure 2. Energy of cohesion as function of the volume of GaSb calculated with different functionals. An intermittent vertical line indicates the experimental equilibrium volume.

Structural parameters A, volume V_0 with one GaSb molecule, volume module B_0 and its derivative B_0', energy of cohesion E_{coh}, bandgap energy E_{gap}, energy of Ga-4s states (up and down) and phonon frequencies at Γ-point for the GaSb, calculated with different functionals

	A, Å Err, %	V_0, Å^3 Err, %	B_0, Gpa Err, %	B_0'	E_{coh}, eV Err, %	E_{gap}, eV Err, %	$E_{4s\text{-up}}$, $E_{4s\text{-dn}}$, eV	Frequencies at Γ, cm^{-1}
LDA	6.080 0.024	224.750 0.098	49.40 14.07	4.45	7.45 19.46	0.398 103.51	−9.238 −8.804	223.332
PBE	6.260 2.840	245.310 8.288	41.30 36.44	4.02	5.72 4.89	0.208 289.42	−9.184 −8.503	229.640
PBEsol	6.090 0.131	225.860 0.390	46.20 21.96	5.11	6.50 7.69	0.428 89.25	−9.195 −8.499	226.411
PW91	6.259 2.820	245.196 8.246	41.60 35.45	4.01	5.87 2.21	0.217 273.27	−9.227 −8.576	229.647
AM05	6.091 0.147	225.977 0.442	44.30 27.20	5.29	6.00 0.00	0.482 68.04	−9.146 −8.452	227.124
RPBE	6.260 2.84	245.314 8.290	38.60 45.98	4.60	4.93 21.70	0.236 243.22	−9.129 −8.392	232.604
TPSS	6.259 2.827	245.196 8.246	42.80 31.65	3.66	5.74 4.52	0.352 130.11	−9.294 −8.411	229.229
RTPSS	6.090 0.131	225.866 0.393	44.80 25.78	5.33	6.01 0.16	0.513 57.89	−9.299 −8.436	228.828
MBJ						1.015 20.19		

Theoretical values reported

	A, Å	V_0, Å^3	B_0, Gpa	B_0'	E_{coh}, eV	E_{gap}, eV	$E_{4s\text{-up}}$, $E_{4s\text{-dn}}$, eV	Frequencies at Γ, cm^{-1}
PP-LDA [21]	5.981	213.954	57	4.66		12.14	−9.153, −8.804 [28]	
FP-LDA [21]	6.053	221.774	54	4.26		1.85		
FP-GGA [21]	6.219	240.525	45	4.02		1.88		
HF [21]	6.212	239.714	63			3.53		
LMTO [21]					0.47	4.05		
PP-PW [21]					0.54	1.64		

Experimental values reported

A, Å	V_0, Å^3	B_0', Gpa	E_{coh}, eV	E_{gap}, eV	Frequencies at Γ, cm^{-1}
6.082 [22]	224.977 [22]	56.35 [22]	6.00 [24]	0.81 [25]	222.7–230 (ΓTO) [26,27] 232.6–237 (ΓLO) [26,27]

parameters is presented itself. When analyzing the obtained results using the different functionals, it was possible to observe that the LDA and PBEsol allowed the calculation of the lattice parameters and the bulk modulus in a more precise way. While for the attainment of the energy of cohesion, the use of the PBEsol and RTPSS functionals was more efficient, because these values are closer to the experimentally and theoretically ones reported in the literature (see Table) [24].

The calculations obtained for the energy of cohesion in this investigation evidenced the percentages of error in some significant cases, which were 19.46% (LDA), 4.89% (PBE), 7.69% (PBEsol), 2.21% (PW91), 0.00% (AM05), 21.70% (rPBE), 4.52% (TPSS), 0.16% (RTPSS), with respect to the experimental results. According to the variation of the rigidity of the material with the pressure, the calculated values for the derivative of the bulk modulus B_0' agree with the ones theoretically reported in the literature [24]. However, it was not possible to make a comparison with any experimental value, because there has been not reported value up to this point. The dispersion of the B_0' results was relatively minimal, and in average, it was closed to 4.52,

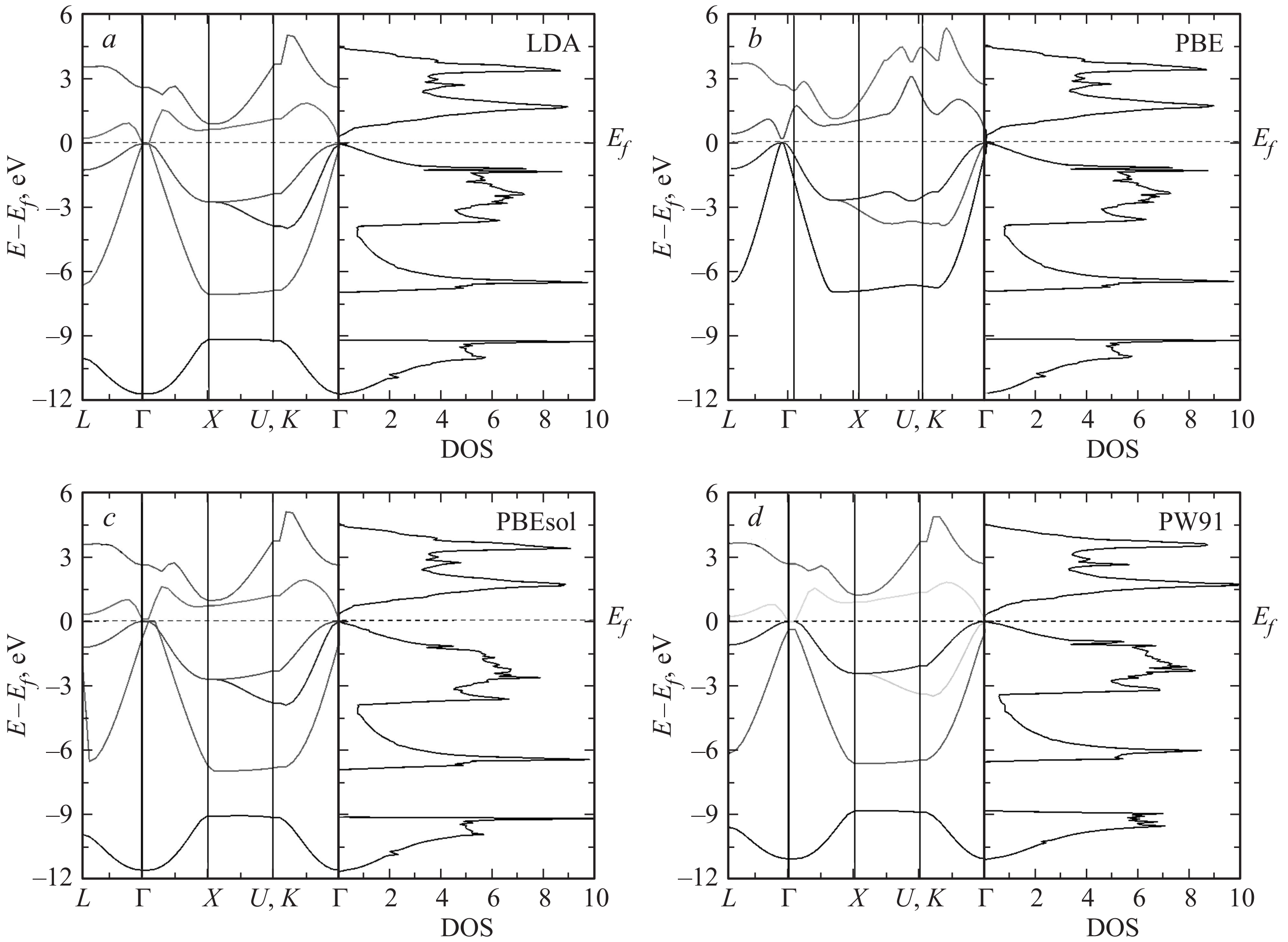

Figure 3. Band structures and density of states of GaSb, obtained using the (*a*) LDA, (*b*) PBE, (*c*) PBEsol, (*d*) PW91, (*e*) AM05, (*f*) RPBE, and (*g*) RTPSS functionals. An intermittent horizontal line indicates the Fermi level.

which is a typical value for III–V semiconductors. In Table, we also show the atomic energy levels (up and down) for the 4*s*-states of Gallium atom (4*s*-Ga). We noted that the 4*s*-Ga energy levels are very close together and they are in good agreement with LDA results: 9.153 and 8.804 eV [28].

In respect to the electronic properties, Fig. 3 shows the electronic band structure and total density of states (DOS) for the GaSb, where the values of the parameters of the calculated lattices were used with every functional (LDA, PBE, PBEsol, PW91, AM05, rPBE, TPSS and RTPSS). It can be observed that the band structure and the density of states are qualitatively similar in the energetic position of the electronic states.

Results indicate that the compound GaSb (see Fig. 3) is a direct compound in Γ–Γ. The band gap within the functional approximations LDA and GGA is closer to zero. The aforementioned would indicate that the material studied corresponds to a metal, which contradicts the situation regarding the semiconducting nature of GaSb. This can be attributed to a lack of thermic exactness of exchange-correlation in the approximations LDA and GGA, which do not allow the determination of the band gap energy in an exact manner in semiconductor materials. On the other hand, the meta-GGA type functionals improved the theoretic results in comparison with the calculated values. With this, the semiconductor behavior of this compound could be observed. Two electronic bands were able to be distinguished as well, the first one below the Fermi level (valence band) and the second one above the Fermi level (Conduction band). The energy bands were calculated along the paths: Λ–Γ–X–Γ, K–Γ in the First Brillouin zone. In all cases, the Fermi level corresponds to the zero in graphic band structure and density of states (DOS).

In the band structure, it can be observed that the band structure is direct; meaning that the valence band maximum (VBM), and conduction band minimum (CBM) are located at the same *k*-point (Γ-point) with energy of: 0.398, 0.208, 0.428, 0.217, 0.482, 0.236, 0.352, 0.513 and 1.015 eV, for the functionals: LDA, PBE, PBEsol, PW91, AM05, rPBE, TPSS, RTPSS and MBJ, respectively. These values are summarized in Table, along with their respective percentages of error for each of the functionals. It was clearly observed that the functionals MBJ and RTPSS showed the lowest percentages of error when being compared to the experimental values reported in the literature [26]. In addition, we note the tendency that the approximations LDA

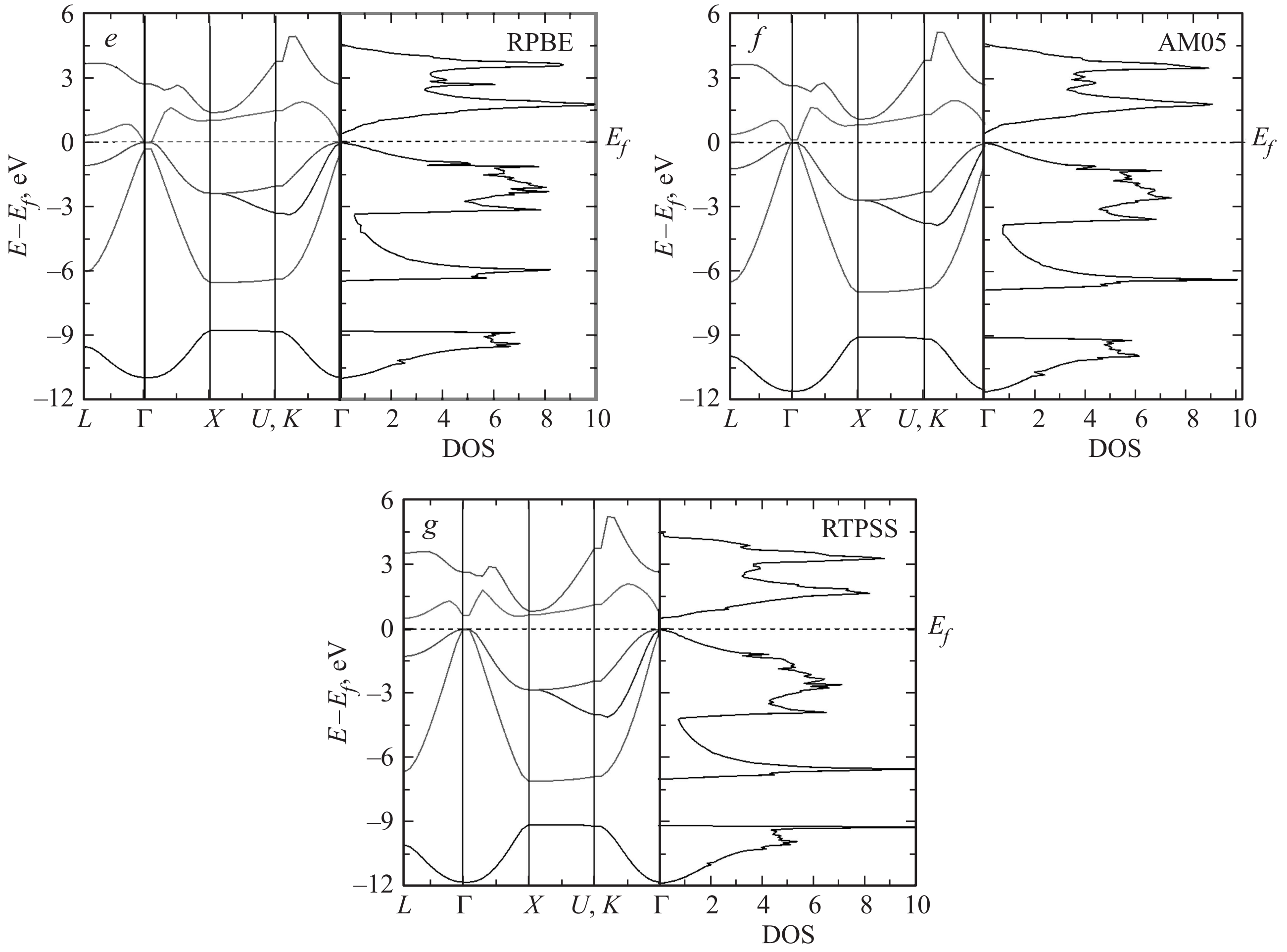

Fig. 3 (*the pattern continued*).

and GGA greatly underestimate the band gap energy of the GaSb compound, as it has been observed in other type III−V semiconductors.

In table, the values obtained for the phonons at the Γ-point are also observed, which are close to the reported values by McGlinn et al. [26] and Aoki et al. [27], by means of Raman spectroscopy. Values fluctuate in a range between 222.7 and 230 cm^{-1} for TO and 232.6 and 237 cm^{-1} for LO. However, this study does not specify what type of phonon mode belongs to the value observed. The comparison between our calculations and the experiment indicated that the computational focus used to determine the vibrational properties of the system offer optimum results with experimental values.

4. Conclusion

In this work, the structural and electronic properties of GaSb were studied by means of first-principle calculations, using LDA functionals and the generalized gradient approximation (GGA) of: PBE, PBEsol, PW91 and meta-GGA: RPBE, AM05, TPSS, RTPSS and MBJ in the DFT. The structural parameters calculated (A), (V_0), (B_0) and the energy of cohesion E_{coh} agree with the experimental results reported in the literature. Starting with the different functionals used, it was possible to establish that the LDA and PBEsol functionals provide better results for the parameter calculations of the lattice (A) and the bulk modulus (B_0), while for the energy of cohesion (E_{coh}) the functionals were obtained with closer values than those experimentally reported. The calculated values for the forbidden energy band agree with the experimentally reported values. However, the functional MBJ shows a lower percentage of error with respect to the experimentally reported values. This work may be used as future reference for theoretical and experimental studies based on GaSb.

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References

[1] C.H. Fu, Y.H. Lin, W.C. Lee, T.D. Lin, R.L. Chu, L.K. Chu, P. Chang, M.H. Chen, W.J. Hsueh, S.H. Chen, G.J. Brown, J.I. Chyi, J. Kwo, M. Hong. Microelectronic Eng., **147** (1), 330 (2015).

[2] Zhang Lixue, Sun Weiguo, Xu Yingqiang, Zhang Lei, Zhang Liang, Si Junjie. Infr. Phys. Technol., **65**, 129 (2014).

[3] Ye Hong, Shu Yue, Tang Liangliang. Sol. Energy Mater. and Solar Cells, **125**, 268 (2014).

[4] Yang Guandong, Zhu Feng, DongShan. J. Cryst. Growth, **316** (1), 145 (2011).

[5] J.T. Vaughey, J. O'Hara, M.M. Thackeray. Electrochem. Solid-State Lett., **3** (1), 13 (2000).

[6] M. Morcrette, D. Larcher, J.M. Tarascon, K. Edström, J.T. Vaughey, M.M. Thackeray. Electrochimica Acta, **52**, 5339 (2007).

[7] E. Dynowska, J. Bak-Misiuk, P. Romanowski, J.Z. Domagala, J. Sadowski, T. Wojciechowski, S. Kret, B. Kurowska, A. Kwiatkowski, W. Caliebe. Rad. Phys. Chem., **80**, 1051 (2011).

[8] A. Wolska, M.T. Klepka, K. Lawniczak-Jablonska, J. Sadowski, A. Reszka, B.J. Kowalski. Rad. Phys. Chem., **80**, 1026 (2011).

[9] Sun Wei-Feng, Li Mei-Cheng, Zhao Lian-Cheng. Superlat. Microstr., **49**, 81 (2011).

[10] N. Liu, G.Y. Gao, J.B. Liu, K.L. Yao. Computational Mater. Sci., **95**, 557 (2014).

[11] N. Liu, G.Y. Gao, J.B. Liu, K.L. Yao. Physica B: Condens. Matter, **405**, 1663 (2010).

[12] D. Varshney, G. Joshi, M. Varshney, Swarna Shriya, G. Kresse, J. Hafner. Phys. Rev. B, **49**, 14251 (1994).

[13] J.P. Perdew, A. Zunger. Phys. Rev. B, **23**, 5048 (1981).

[14] J.P. Perdew, K. Burke, M. Emzerhof. Phys. Rev. Lett., **77**, 3865 (1996).

[15] J.P. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, X. Zhou, K. Burke. Phys. Rev. Lett., **100**, 136406 (2008).

[16] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais. Phys. Rev. B, **46**, 6671 (1992).

[17] B. Hammer, L.B. Hansen, J.K. Norskov. Phys. Rev. B, **59**, 7413 (1999).

[18] J. Tao, J.P. Perdew, V.N. Staroverov, G.E. Scuseria, Phys. Rev. Lett., **91**, 146401 (2005).

[19] P. Scharoch, M. Winiarski, Computer Phys. Commun., **184**, 2680 (2013).

[20] J.P. Perdew, A. Ruzsinszky, G.I. Csonka, L.A. Constantin, J.W. Sun. Erratum, **106**, 179902 (2011).

[21] F. Tran, P. Blaha. Phys. Rev. Lett. **102**, 226401 (2009).

[22] F.D. Murnaghan. Proc. National Academy Science, **30**, 244 (1944).

[23] R. Ahmed, F. Aleem, S. Javad, H. Rashid, H. Akbarzadeh. Theor. Phys., **52**, 527 (2009).

[24] N.N. Sirota, F.M. Gololobov. Dokl. Akad. Nauk SSSR, **144**, 398 (1962).

[25] A.H. Reshak. Eur. Phys. J. B, **47**, 503 (2005).

[26] T.C. McGlinn, T.N. Krabach, M.V. Klein, G. Bajor, J.E. Greene, B. Kramer, S.A. Barnett, A. Lastras, S. Gorbatkin. Phys. Rev. B, **33**, 8396 (1986).

[27] K. Aoki, E. Anastassakis, M. Cardona. Phys. Rev. B, **30**, 681 (1984).

[28] S. Kotochigova, Z.H. Levine, E.L. Shirley, M.D. Stiles, C.W. Clark. Phys. Rev. A, **55**, 191 (1997).

Редактор К.В. Емцев