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Lattice dynamics study of bismuth III–V compounds

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Abstract

We present first-principles calculations of the structural and lattice-dynamical properties for cubic bismuth III–V compounds: BBi, AlBi and GaBi. The ground-state properties, i.e., the lattice constant and the bulk modulus, are calculated using a plane wave pseudopotential method within density functional theory. A linear-response approach to density functional theory is used to derive the phonon frequencies. The effect of pressure on the dynamical charges and the longitudinal optical–transverse optical splitting is also examined.

1. Introduction

Among the III–V semiconductors the bismuth: BBi, AlBi, GaBi, and InBi as well as their alloys have attracted both scientific and technological interest in recent years. It is expected that most of the III–Bi compounds should have a small or even negative gap [1–5]. Thus adding bismuth to III–V semiconductors is of great importance for numerous optical and electronic applications including lasers, solar cells, transistors, and devices based on spintronics. Recent theoretical and experimental works have been devoted to GaAsBi, for which the unusually large band gap reduction [1, 3, 6–8], and giant spin orbit bowing [7], with Bi alloying is a key factor in realizing these applications. These outstanding properties are mainly related to the strong disparity in atomic size between Bi and As, and to the large relativistic effects induced in bismuth. Although considerable progress has been made in theoretical description of the structural and electronic background of bismuth compounds, many of their dynamical properties are still not well established. Recent theoretical studies have addressed similar properties on boron further III–V and II–VI compounds [9–16]. Understanding the dynamical properties of these systems is important for characterization purposes. This requires in turn an accurate knowledge of the bulk phonon dispersion of pure materials. In this paper we investigate the dynamical properties of III-bismuth compounds by employing the plane wave pseudopotential method, density functional theory, and a linear-response technique. The rest of the paper is organized as follows. In section 2, we briefly describe the computational method used in the present work. Results will be presented in section 3. A summary of the work will be given in section 4.

2. Method

We have applied density functional theory within the local density approximation [17] in a plane wave basis, with ultrasoft Vanderbilt pseudopotentials [18], as implemented in the PWscf code [19]. The many-body electron–electron interaction is described by the Ceperley–Alder functional [20] as parameterized by Perdew and Zunger [21]. The Brillouin zone integrations were performed by summation over 10 special points of the Chadi–Cohen type [22]. The lattice-dynamical properties are calculated using density functional perturbation theory (DFPT) [23]. In particular, eight dynamical matrices were calculated for $4 \times 4 \times 4$ k-points mesh of Monkhorst and Pack [24]. These matrices were then Fourier interpolated to obtain the phonon dispersion curves.

3. Results

The total energy of the zinc-blende phase of III-Bi compounds has been calculated for different volumes of the lattice parameter and fitted to the Murnaghan equation of state [25] in order to obtain the equilibrium lattice constant a, and the bulk modulus B. The calculated static properties are given in table 1, where, good agreement is noticed with available theoretical results.

The calculated phonon dispersion curves and total phonon density of states are presented in figures 1–3 for BBi, AlBi,

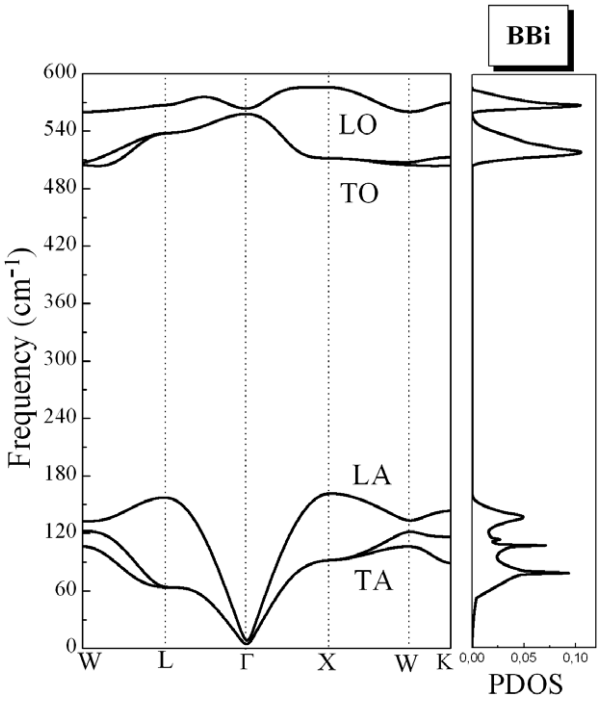

Figure 1. Calculated phonon dispersion and phonon density of states (PDOS) of BBi.

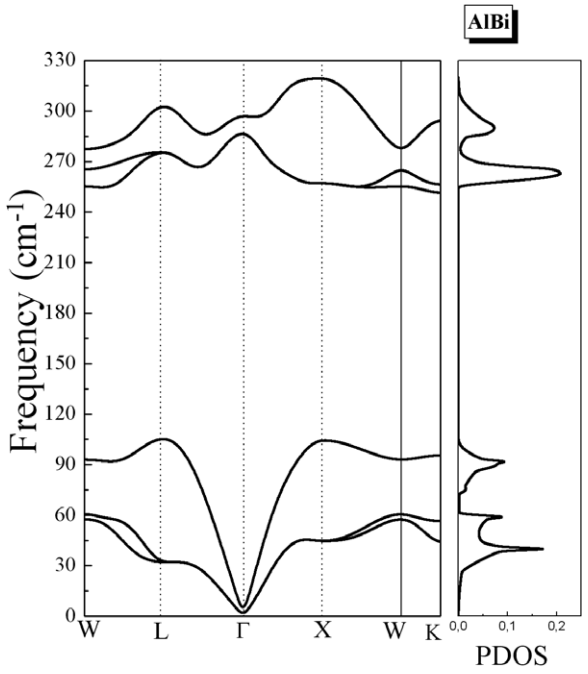

Figure 2. Calculated phonon dispersion and phonon density of states (PDOS) of AlBi.

Table 1. The lattice parameter a, and the bulk modulus B of the zinc-blende compounds BBi, AlBi and GaBi.

		a (Å)	B (GPa)
BBi	Present cal.	5.371	87.3
	Cal.[a]	5.529	72.21
	Cal.[b]	5.39	87.7
AlBi	Present cal.	6.27	46.1
	Cal.[a]	6.46	39.1
	Cal.[b]	6.266	48.2
GaBi	Present cal.	6.186	46.9
	Cal.[a]	6.47	39.1
	Cal.[b]	6.178	46.1
	Exp.[c]	6.33	

[a] Reference [5].
[b] Reference [2].
[c] Reference [6].

and GaBi, respectively. The phonon frequencies resulting from the high symmetry points in the zinc-blende Brillouin zone are listed in table 2 and compared with available theoretical and experimental data.

For GaBi a direct comparison with Raman scattering spectroscopy [28, 29] is only possible for the zone-centre (i.e., at Γ point). The obtained TO (Γ) and LO (Γ) modes give 199 and 205 respectively, which agree well with the experimental data of 186 [28], 189 [29] for TO (Γ) modes and 214 [28], 196 [29] for LO (Γ) modes. No theoretical calculations exist so far for GaBi. The agreement between our computations and experimental data for GaBi supports our results for BBi and AlBi, where no experimental data are available. Good agreement is noticed for the phonon frequency of BBi compared with recent *ab initio* calculations [22, 23].

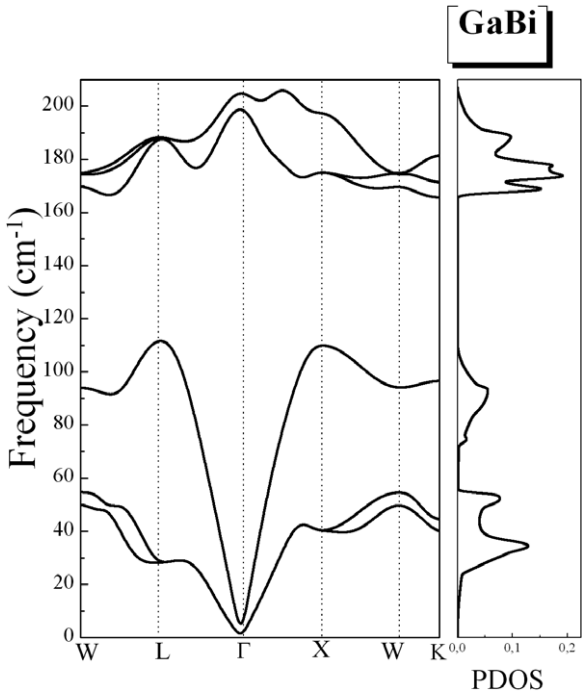

Figure 3. Calculated phonon dispersion and phonon density of states (PDOS) of GaBi.

The most prominent features of the phonon dispersion of BBi, AlBi, and GaBi are:

(a) The transverse optical (TO) phonon modes of III-bismuth show flatness along the high symmetry direction, and a very sharp peak in the phonon DOS.
(b) Compared to AlBi and GaBi, the longitudinal optical (LO) phonon modes of BBi show small dispersion along the

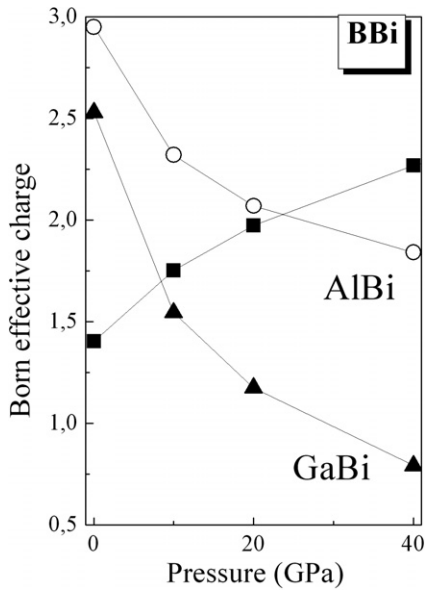

Figure 4. Born effective charge versus hydrostatic pressure of BBi, AlBi, and GaBi.

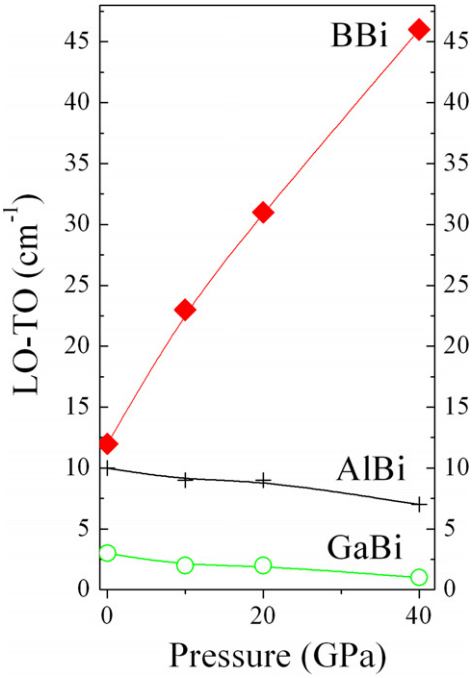

Figure 5. Pressure dependence of LO–TO splitting of BBi, AlBi, and GaBi.
(This figure is in colour only in the electronic version)

Table 2. Phonon frequencies obtained at high symmetry points for BBi, AlBi and GaBi. Experimental data are given in parentheses.

Phonon modes	BBi	AlBi	GaBi
Γ_{LO}	563, 552[a], 560[b]	297	205 (214[c], 196[d])
Γ_{TO}	558, 551[a], 550[b]	287	199 (186[c], 189[d])
X_{LO}	585, 589[a]	319	188
X_{LA}	161, 157[a]	104	112
X_{TO}	511, 495[a]	257	188
X_{TA}	91, 87[a]	44	28
L_{LO}	567, 567[a]	303	197
L_{LA}	157, 155[a]	105	110
L_{TO}	538, 531[a]	275	175
L_{TA}	63, 69[a]	32	40

[a] Reference [26].
[b] Reference [27].
[c] Reference [28].
[c] Reference [29].

high symmetry direction, which induce a sharp peak in the phonon DOS.

(c) Strong flatness of the transverse acoustic (TA) mode over a large part of the Brillouin zone, which is not typical for other III–V compounds, giving a pronounced peak in the corresponding phonon DOS.

(d) The LO and TO branches are separated in all V–Bi compounds. This feature was never seen in typical III–V materials. For the BBi → AlBi → GaBi sequence, the zone-centre of optical phonon mode decreases with the increase of the cation mass.

(e) The LO–TO splitting at the zone-centre is 5, 10, and 6 cm^{-1} for BBi, AlBi, and GaBi respectively. This splitting is very weak compared with other III–V semiconductors.

(f) For all materials we found that LA(LO) phonon modes in the zone-edge at X point, are characterized by the motion of the heavier (lighter) atoms Bi(B, Al, Ga).

The change of the Born effective charge under compression of bismuth compounds is presented in figure 4. This is also referred to as the dynamical effective charge, as distinct to the static charge, i.e., the change in electron polarization upon ionic displacement. The Born effective charge decreases with rising pressure for AlBi and GaBi; with opposite behaviour in the case of BBi, where the Born effective charge increases with decreasing volume. This result is in agreement with the recent *ab initio* calculations of BBi [27]. The decrease of the Born effective charge with decreasing volume, is found for most of the III–V and II–VI compounds except for SiC [30], AlN, and GaN [31]. The pressure behaviour of the dynamical charge indicates an electron charge transfer from bismuth to Al(Ga) atoms for AlBi(GaBi) and from boron to bismuth atoms for BBi, i.e., a reduction of the ionicity of the bond (see [32] for additional evidence), in the case of AlBi and GaBi. An increase of the ionicity is observed—however—for BBi. The unusual behaviour of BBi, is due to the anomalous valence charge density, characterized by a charge transfer towards the cation 'B' atom [4, 5].

Finally we now turn to the pressure dependence of the splitting between LO and TO phonon modes of BBi, AlBi and GaBi. Figure 5 shows the increase of the LO–TO splitting of BBi with rising pressure, which is in contrast with the behaviour of most of III–V semiconductors [33, 34]. This is a direct consequence of the net pressure effect discussed above for the boron effective charge. However for AlBi and GaBi we found that the LO–TO splitting decreases with decreasing volume, as found for other III–V semiconductors.

4. Summary

In summary, we have presented *ab initio* calculations of the ground-state and dynamical properties of bismuth III–V compounds BBi, AlBi, and GaBi in the zinc-blende structure. The results for the lattice constants and phonon frequencies are in good agreement with available theoretical and experimental data. We have highlighted the main differences in the phonon spectra of these materials compared with the other III–V compounds. In contrast to AlBi, GaBi, and other III–V semiconductors, we found that the born effective charge and LO–TO splitting of BBi increases with rising pressure.

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