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Dynamical behaviour in the boron III–V group: a first-principles study

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Abstract

We report first-principles calculations of the structural, electronic and dynamical properties of the zinc-blende materials BP, BAs and BSb. The ground-state and electronic properties, i.e., the lattice constant, the bulk moduli and band structure, are calculated using a plane-wave pseudopotential method within the density functional theory. A linear-response approach to the density functional theory is used to derive the high-frequency dielectric constants, the Born effective charges, and the phonon frequencies. Our results are in good agreement with numerous experimental and theoretical data where available, and provide predictions where they are not.

1. Introduction

Despite their technological promise, boron compounds have attracted little research interest in recent years. Although they are members of the III–V semiconductor family, the group B–V BP, BAs and BSb have a remarkable properties which set them apart from other III–V materials. These compounds exhibit both physical and chemical properties that differ significantly from the general trends of the III–V family. One reason is related to their extreme properties, such low ionicity [1–3], short bond lengths [4], hardness [4], high melting points [5] and wide band gap [6]. These outstanding properties are mainly related to the strong disparity in atomic size between boron and other atoms of column V.

Although considerable progress has been made in theoretical description of the structural and electronic properties of boron compounds, many of their dynamical properties are still not well established. The knowledge of the phonon spectrum is necessary and plays a significant role in determining various materials properties such as phase transition, thermodynamic stability, transport and thermal properties.

In this paper we investigate the dynamical properties of boron–V 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

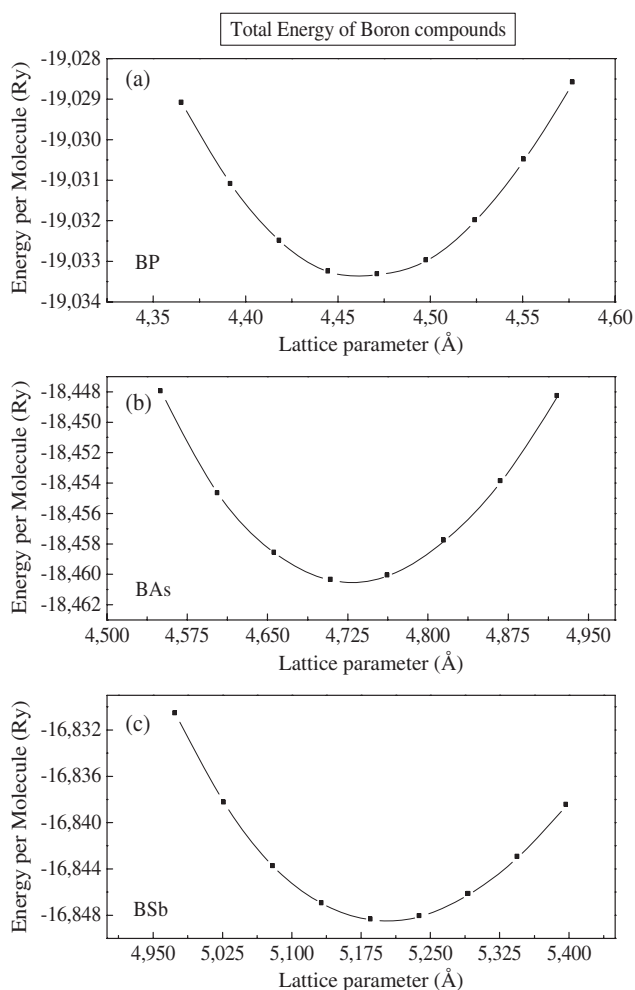


Figure 1. Total energy versus volume for the zinc-blende compounds BP (a), BAs (b), and BSb (c).

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 apply the density functional theory within the local density approximation [7] in a plane-wave basis. We have used ultrasoft Vanderbilt pseudopotentials [8], as implemented in the PWscf code [9]. The many-body electron–electron interaction is described by the Ceperley–Alder functional [10] as parameterized by Perdew and Zunger [11]. The Brillouin zone integrations are performed by sums over ten special points of the Chadi–Cohen type [12].

Due to relatively large ‘hardness’ of the pseudopotential of boron, we use plane-wave basis sets up to a kinetic-energy cutoff of 50 Ryd. These basis sets are complete enough to guarantee a convergence of the calculated phonon frequencies to better than 5 cm^{-1} for all the materials studied.

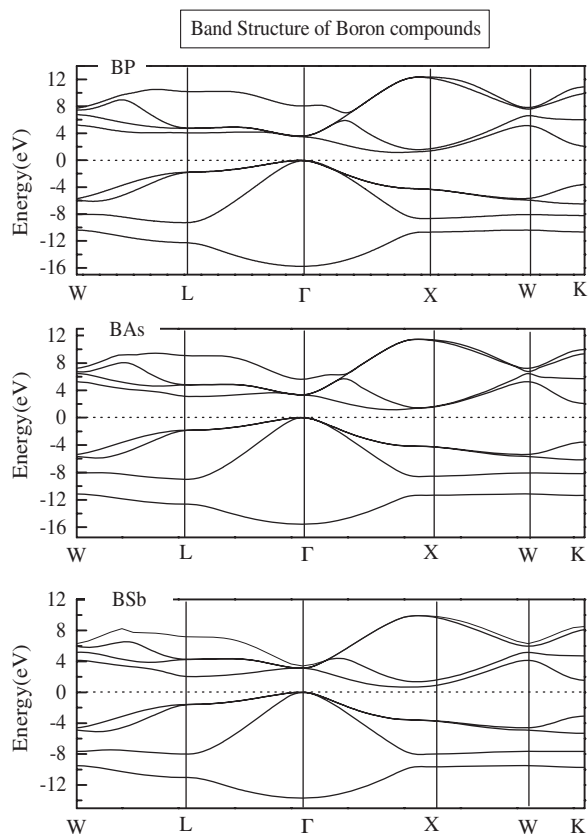


Figure 2. Band structure of the zinc-blende compounds BP, BAs, and BSb.

Table 1. The lattice parameter a , bulk modulus B , and first derivative of bulk modulus B' of the zinc-blende compounds BP, BAs and BSb.

		a (Å)	B (GPa)	B'
BP	Present cal.	4.464	176	4
	Cal. ^a	4.558	166	
	Cal. ^b	4.546	170	3
	Expt. ^c	4.538	173	
BAs	Present cal.	4.726	147	3
	Cal. ^a	4.777	145	
	Cal. ^b	4.784	137	3
	Expt. ^d	4.777		
BSb	Present cal.	5.201	109	4
	Cal. ^b	5.252	103	3
	Cal. ^e	5.120	115	5

^a Reference [2], ^b Reference [16], ^c References [17, 18], ^d Reference [17], ^e Reference [19].

The lattice-dynamical properties are calculated using the density functional perturbation theory (DFPT) [13]. In particular, eight dynamical matrices were calculated for an $4 \times 4 \times 4$ \mathbf{k} -points mesh of Monkhorst and Pack [14]. These matrices were then Fourier interpolated to obtain the phonon dispersion curves.

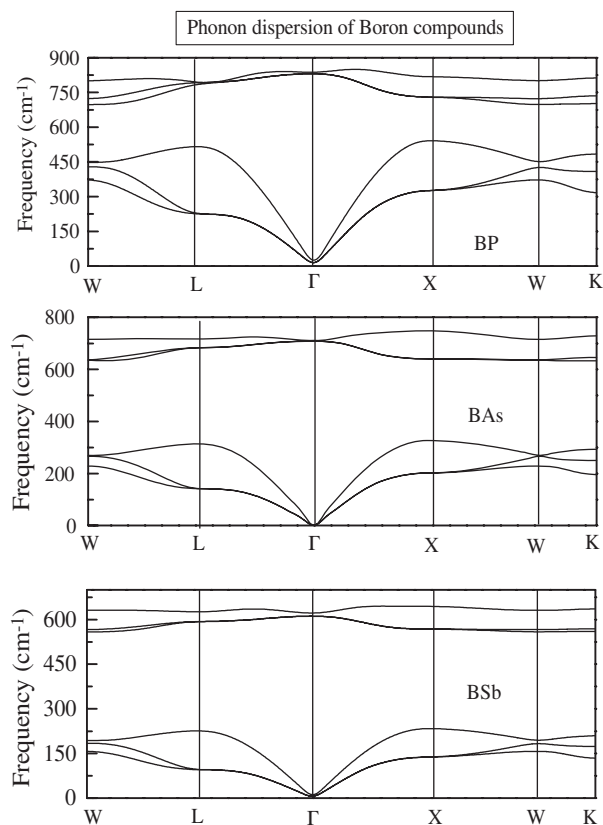


Figure 3. Calculated phonon dispersion for BP, BAs, and BSb.

Table 2. Macroscopic dielectric constant ϵ_{∞} , and Born effective charge Z of the zinc-blende compounds BP, BAs and BSb.

	BP	BAs	BSb
ϵ_{∞}			
Present cal.	9.37	9.65	11.30
Expt. ^a	9.6		
Cal.	9.27 ^b	9.8 ^c	
Z			
Present cal.	-0.75	-0.57	-1.30
Expt. ^d (absolute value)	1.34		

^a Reference [17], ^b Reference [21], ^c Reference [22], ^d Reference [20].

3. Results

3.1. Ground state and electronic properties

The calculated ground-state energies plotted as a function of lattice parameter for the zinc-blende phase for BP, BAs and BSb are shown in figure 1. In table 1, we give the calculated structural properties as obtained from a fit of the total energy as a function of volume to the Murnaghan equation of state [15]. The other calculations (band structure, phonon, etc)

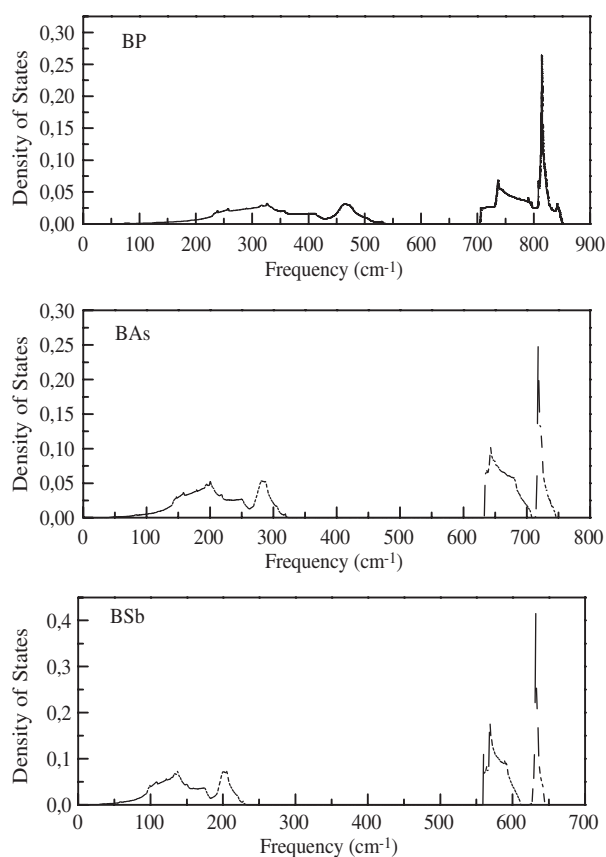


Figure 4. Calculated density of states of phonon dispersion for BP, BAs, and BSb.

are performed with the calculated lattice parameters. We obtained good agreement with the theoretical and experimental data. The boron compounds have smaller lattice constants and large bulk modulus than the other III–V compounds.

Our calculated electronic band structures for BP, BAs, and BSb along the various symmetry lines are given in figure 2. There is an overall topological resemblance of the present band structures and those calculated by Wentzcovitch *et al* [2], Zaoui *et al* [16], and Ferhat *et al* [19].

All these materials are characterized by an indirect band gap along the $\Gamma \rightarrow X$ direction (close to the X point). The most prominent feature of the band structures of these compounds is the small splitting at the X point ($X_{1v} - X_{3v}$) compared with the other III–V compounds.

3.2. Dielectric and lattice dynamics properties

The interest in macroscopic dielectric constant ϵ_∞ and the Born effective charge Z is motivated by the study of the lattice dynamic of the boron compounds. In table 2, we compare the calculated dielectric constant of the boron compounds with available experimental and theoretical values. The calculated dielectric constant of BP and BAs agrees respectively with the experimental [20] and theoretical data [21, 22]. To the best of our knowledge, no experimental or theoretical values exist for BSb.

The Born effective charge Z represents the charge of the ion interacting with the macroscopic electric field. It is also referred to as the dynamic effective charge, as distinct from the static charge that results from the static transfer of an electron from the cation to

Table 3. Phonon frequencies calculated at high-symmetry points for BP (a), BAs (b) and BSb (c).

Phonon mode	Present study (cm ⁻¹)	Experimental (cm ⁻¹)	Theoretical (cm ⁻¹)
(a) BP			
LO(Γ)	837	829.9 ^a	830 ^c , 797 ^d
TO(Γ)	813	799 ^a	808 ^b , 800 ^c , 797 ^d
LO(X)	818		800 ^b , 803 ^c , 781 ^d
LA(X)	542		527 ^b , 502 ^c , 526 ^d
TO(X)	729		701 ^b , 707 ^c , 698 ^d
TA(X)	326		306 ^b , 294 ^c , 318 ^d
LO(L)	792		764 ^b , 727 ^c , 755 ^d
LA(L)	516		506 ^b , 529 ^c , 506 ^d
TO(L)	787		747 ^c , 752 ^d
TA(L)	224		243 ^c , 227 ^d
(b) BAs			
LO(Γ)	710		
TO(Γ)	708		
LO(X)	748		
LA(X)	326		
TO(X)	640		
TA(X)	201		
LO(L)	716		
LA(L)	313		
TO(L)	683		
TA(L)	141		
(c) BSb			
LO(Γ)	621		
TO(Γ)	611		
LO(X)	644		
LA(X)	233		
TO(X)	568		
TA(X)	138		
LO(L)	626		
LA(L)	226		
TO(L)	593		
TA(L)	95		

^a Reference [20], ^b Reference [23], ^c Reference [24], ^d Reference [21].

the anion. By convention, Z stands for the cation charge (the effective charge of the anion being $-Z$). The values of the calculated Born effective charge in units of electron charge of the boron compounds are listed in table 2. The calculated Z for all the boron compounds is negative, while the III–V compounds have a positive effective charge. This might be seen as an indication that the B atom plays the role of the ‘anion’ with respect to the effective charge in BP, BAs, and BSb. The calculated Born effective charge value for BP is smaller than the previously reported experimental value [20], while for BAs and BSb no data are available for comparison. Z can be determined experimentally from the energy splitting of LO(Γ) and TO(Γ) phonon modes [20]. The observed difference between the calculated and the measured Born effect charge results mainly from the difference in LO(Γ) and TO(Γ) phonon frequencies.

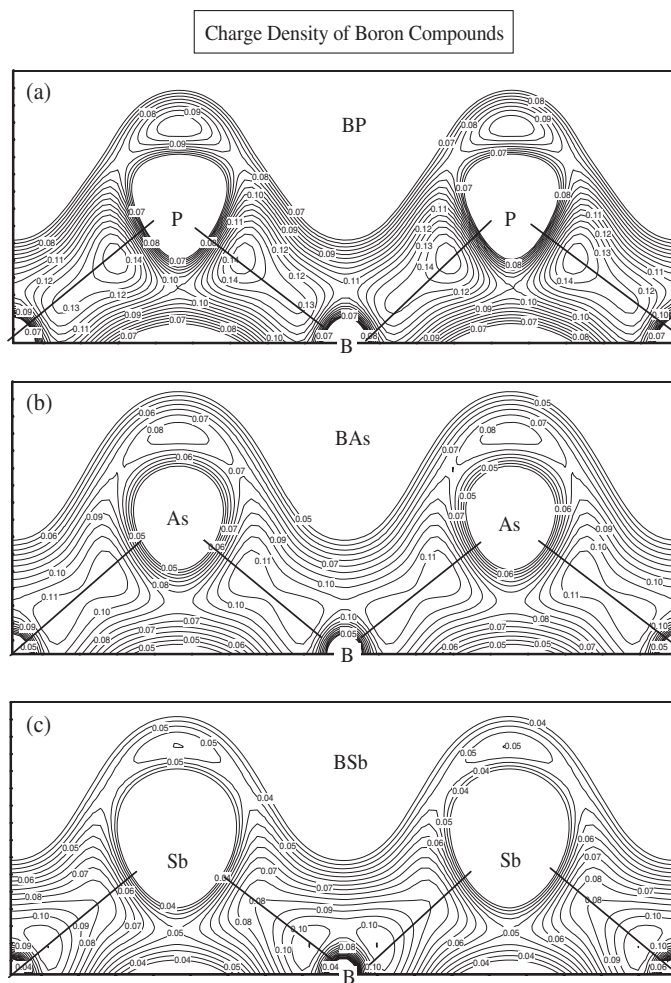


Figure 5. Total valence charge density plot of BP (a), BAs (b), and BSb (c) in the (110) plane.

3.3. Vibrational properties

The calculated phonon dispersion curves and phonon density of states are presented respectively in figures 3 and 4 for BP, BAs and BSb. The phonon frequencies resulting for the high symmetry points in the zinc-blende Brillouin zone are listed in table 3. Our calculated results are compared with available theoretical and experimental data.

For BP, a direct comparison with Raman scattering spectroscopy [20] is only possible for the zone-centre (i.e., at the Γ point); the TO(Γ) and LO(Γ) modes agree well with the experimental data. We underestimate the zone-centre LO–TO splitting by 5 cm^{-1} . The relative overestimation of the theoretical values nearly corresponds to the value that we have estimated because of the underestimation of the lattice constant within the LDA. Our data agree with the semi-empirical models [23, 24], and DFTP calculations [21].

The agreement between our computations and experimental and theoretical data for BP gives confidence in our results for BAs and BSb, where neither experimental nor theoretical data are available. The present parameter-free calculations stand, therefore, as reliable predictions for the full phonon dispersion curves of BAs and BSb.

The most prominent features of the phonon dispersion of BP, BAs and BSb are as follows.

- (i) For the BSb \rightarrow BAs \rightarrow BP sequence where the boron (B) atom is common, the zone-centre optical phonon mode increases with the decrease of the cation mass.
- (ii) For BP, there is a relatively small gap between the acoustical and optical phonon branches. The gap is opened with increasing anion masses (e.g., BP \rightarrow BAs \rightarrow BSb).
- (iii) As compared to other III–V compounds where the TO and LO phonons show pronounced dispersive behaviour, in BP, BAs, and BSb, the dispersion of the TO and LO phonons modes is weakly dispersive.
- (iv) The LO–TO splitting at the zone-centre is 24.1, 2 and 10 cm^{-1} for BP, BAs, and BSb respectively. This splitting is very weak compared with other III–V semiconductors, which reflects the strong bonding of these compounds (see figure 5).

4. Summary

In summary, we have applied a density functional perturbation theory to study the lattice dynamics of the boron–group V compounds BP, BAs, and BSb in the zinc-blende structure. Our calculated phonon modes are in good agreement with available experimental and theoretical works for BP, BAs and BSb. The present calculations provide new lattice dynamics results for these compounds, since at the present time neither experimental nor theoretical results are available.

We have highlighted the main differences in the phonon spectra of these materials compared with those of other III–V compounds. In particular we found an unusual weak LO–TO splitting at the zone-centre.

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