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Lattice dynamics and equilibrium properties of boron phosphide: a first-principles study

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Abstract

The zinc-blende boron compound BP is one of the promising III–V semiconductors. The density functional linear response approach is used to explore the lattice dynamics and equilibrium properties of it. The complete phonon dispersions and corresponding phonon density of states (DOS) are computed. Simultaneously, we also make a systematic research on the thermodynamical quantities, bulk modulus, shear modulus, elastic constants, dielectric constant, piezoelectric constant, internal strain, and electron band eigenvalues of it. Our results are in reasonably good agreement with numerous experimental and theoretical investigations where available, and provide predictions where they are not.

(Some figures in this article are in colour only in the electronic version.)

1. Introduction

BP is one of the promising III–V semiconductors in the zinc-blende structure. This material exhibits excellent physical and chemical properties that make it attractive for device applications, including a wide band gap, a high melting point, high mechanical strength, etc. Technological interest in it has been stimulated in recent years by its potential use in optoelectronic and microelectronic devices working under extreme conditions.

Since it is very difficult to prepare sufficiently large single crystals of BP, which is mainly due to its high melting point (>3000 °C) and high decomposition pressure ($\sim 10^5$ atm at 2500 °C), less experimental information about its electronic and vibrational characteristics was available until recently. Up-to-date experimental achievements were reported only with a focus on its optical [1, 2], vibrational [3, 4], elastic [5, 6], and thermal [7] properties. It is therefore not surprising that the electronic and structural properties of BP have been recalculated several times, and it is noticeable that, in the available theoretical investigations,

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some useful ground-state properties of BP such as elastic constants, bulk modulus, and band structure have been obtained with accuracy [8–18].

Besides electronic and structural properties, lattice dynamics of BP are of much concern. The phonon dispersion spectra are attractive for their relevance to some important bulk properties of pure materials. Although numerous experimental and theoretical investigations have been made, it is remarkable that information about lattice dynamics and relative equilibrium properties of BP is rather scarce. To the best of our knowledge, experimental data are lacking for phonon dispersion curves, phonon DOS, piezoelectric constant and internal strain parameter of BP. The theoretical works concerned with the lattice dynamical calculation for BP are also very limited in the public literature. Previous studies were either based on semi-empirical models [14], whose model parameters were fitted from experiments as well as *ab initio* calculations, or only provided phonon frequencies at critical points in the Brillouin zone (BZ) [12, 13]. As for semi-empirical models, if only the input parameters were sufficient and well-examined, they generally run faster than the *ab initio* scheme and provide reliable calculated results. But they cannot be used to explore the new materials if the experimental data or parameters available are inadequate. Recently, full phonon dispersion curves and DOS were calculated by Pletl [19] with the first-principles pseudopotentials method. He also computed the dielectric constant and effective charges of BP, but so far other lattice dynamical properties have not been taken into consideration.

Consequently, the purpose of this work is to apply the *ab initio* pseudopotential plane wave method and the linear response approach, to provide a systematic study on lattice dynamics for BP and obtain the corresponding equilibrium properties of BP at the same time. The paper is organized as follows. In section 2, we briefly describe the computational details. In section 3, we present the results of our calculations. The conclusion is contained in section 4.

2. Method of calculation

With the development of the density functional linear response approach [20], it is now possible to acquire accurate phonon dispersion relations on a fine grid of wavevectors covering the entire BZ and, from this, several important thermodynamical quantities (such as specific heat, entropy, internal energy, etc) of the system can be conveniently evaluated. In this approach, various response functions can be calculated with respect to different perturbations. In this work, three types of perturbations are taken into account: atomic displacements ($u_m, m = 1, \dots, 3N$), static homogeneous electric field ($\epsilon_\alpha, \alpha = x, y, z$) and strain ($\eta_j, j = 1, \dots, 6$, in Voigt notation). The physical properties connected with second derivatives of total energy with respect to atomic displacements and electric field perturbations are phonon dynamical matrices, dielectric tensor and Born effective charges, while the additional strain perturbation, mixed with atomic displacements and electric field, leads to elasticity, internal strain and piezoelectricity. The theoretical frameworks for the computation of linear response functions to these perturbations can be found in [21].

As the electronic and structural properties of BP have already been addressed within the density functional theory in the local density approximation or generalized gradient approximation (GGA), we have employed a similar technique to investigate the lattice dynamics and equilibrium characteristics of it in order to supply the missing information on phonon, thermodynamics, elasticity, dielectricity, piezoelectricity and internal strain properties. Using density functional theory, we first calculate the total energy, energy band structure and ground-state wavefunctions of BP. Then, we perform linear response calculations. Second derivatives of the total energy with respect to a given perturbation as mentioned above are computed. Depending on the nature of this perturbation, a number of equilibrium properties

can be calculated. Finally, all the physical properties are extracted from the output of the post-processing programme. It is worth underlining that these quantities are evaluated within the linear response approach rather than the finite-difference method.

In the present work, Hamann scheme [22] norm-conserving pseudopotentials are used, together with plane wave basis set, and the well-established Perdew–Burke–Ernzerhof [23] exchange–correlation functional is adopted. The calculations have been performed with a cut-off energy of 12 Hartree in the plane wave expansions, which is sufficient to fully converge all properties of relevance. The k -space summation is performed using a set of 28 special points, which correspond to a (6,6,6) mesh in the Monkhorst–Pack notation, and the calculations have been carried out at the experimental lattice structure ($a_0 = 4.538 \text{ \AA}$). The results presented below have been obtained by using the ABINIT code [24], and the pseudopotentials have been generated using the FHI98PP code [25]. More technical details of the present work will be summarized in our next review paper.

3. Results and discussion

3.1. Phonon dispersions and density of states (DOS)

The calculated phonon dispersion curves along the high-symmetry lines ($L \rightarrow \Gamma \rightarrow X \rightarrow K \rightarrow \Gamma$) of irreducible BZ, together with the relative phonon DOS, are illustrated in figure 1. In the absence of neutron scattering data, we cannot confirm them. But, as a matter of fact, figure 1 is very similar to Pletl's [19] *ab initio* calculated results. The phonon frequencies at high-symmetry points are summarized in table 1. For comparison, a few experimental data and some numerical results are also listed. Our data are in good agreement with the available experimental values [4] as well as with the calculated values (error $<7\%$) of Alves *et al* [12] and Talwar *et al* [14]. It is suggested that our results are reliable and the method we used to complete this work is effective and accurate. As mentioned before, Alves *et al* [12] applied a valence overlap shell model (VOSM) with parameters to elastic constants and first-principles frozen-phonon calculations, while a semi-empirical rigid-ion model (RIM) was used by Talwar *et al* [14]. Since these semi-empirical models are both seriously restricted by the reliability of parameters, they are no longer in common use.

3.2. Thermodynamical properties

Knowledge of the entire phonon dispersion spectra and DOS make it possible to evaluate several critical thermodynamical quantities and the relative stability of the system among different crystal structures. Using the phonon frequencies and DOS reported in this paper, the temperature-dependent vibrational contribution to the Helmholtz free energy $F(T)$ and entropy $S(T)$ are computed through

$$\begin{aligned}
 F(T) &= E_{tot} + \frac{1}{2} \int g(\omega) \hbar \omega \, d\omega + k_B T \int g(\omega) \ln \left[1 - \exp \left(-\frac{\hbar \omega}{k_B T} \right) \right] d\omega, \\
 S(T) &= k_B \left\{ \int \frac{(g(\omega) \hbar \omega / k_B T)}{\exp(\hbar \omega / k_B T) - 1} d\omega - \int g(\omega) \ln \left[1 - \exp \left(-\frac{\hbar \omega}{k_B T} \right) \right] d\omega \right\},
 \end{aligned} \tag{1}$$

where $g(\omega)$ is phonon DOS and E_{tot} is the total energy. Based on $F(T)$ and $S(T)$, any other thermodynamical property can be accessed easily. In this work, thermodynamical quantities with temperature, including the internal energy $U(T)$, Helmholtz free energy

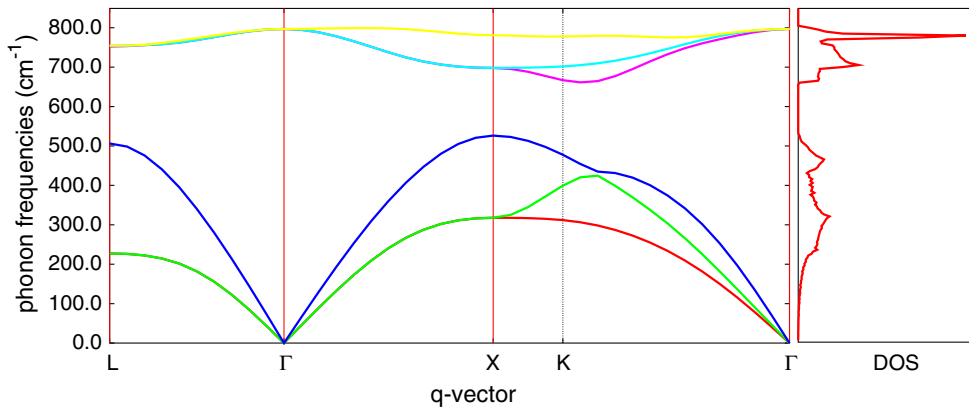


Figure 1. Theoretical phonon dispersion curves of zinc-blende BP along high-symmetry directions (left panel) and the corresponding phonon DOS (right panel).

Table 1. Summary of the most important phonon frequencies at high symmetry points of BZ calculated in this work. Theoretical values obtained by other studies and relative experimental data are also listed in this table.

Phonon mode	Present study (cm ⁻¹)	Experimental (cm ⁻¹)	Theoretical (cm ⁻¹)
LO(Γ)	797	828.9 ^a	830 ^b
TO(Γ)	797	799.0 ^a	800 ^b , 808 ^c
LO(X)	781		803 ^b , 800 ^c
LA(X)	526		502 ^b , 527 ^c
TO(X)	698		707 ^b , 701 ^c
TA(X)	318		294 ^b , 306 ^c
LO(L)	755		727 ^b , 764 ^c
LA(L)	506		529 ^b , 506 ^c
TO(L)	752		747 ^b
TA(L)	227		243 ^b

^a From [4].

^b From [14].

^c From [12].

$F(T)$, entropy $S(T)$ and constant-pressure specific heat $C_p(T)$ of the system are treated properly. The results are plotted in figure 2. From this figure, with the help of interpolation technique, we get $S(T) = 10.41, 19.99, 29.62, 38.24 \text{ J mol}^{-1} \text{ K}^{-1}$ when T is equal to 200, 298.15, 400 and 500 K, respectively, to be compared with the experimental values [26] of 10.10, 19.69, 29.8, 38.5 $\text{J mol}^{-1} \text{ K}^{-1}$. We also evaluate $C_p(T) = 5.98, 18.9, 29.39, 36.1, 40.3 \text{ J mol}^{-1} \text{ K}^{-1}$ at 100, 200, 298.15, 400 and 500 K, respectively, whereas the experimental values [26] are 5.77, 18.77, 29.72, 39, 45 $\text{J mol}^{-1} \text{ K}^{-1}$. On the one hand, we found that in the public literature, the thermodynamical properties of BP have not been calculated within the frameworks of first-principles or semi-empirical models. On the other, it is obvious that our data agree quite well with experimental values, especially in the low-temperature region. We believe that they are reliable and can help us gain a valuable insight into the thermodynamical stability of BP at high temperatures. Further investigation of this aspect should be conducted.

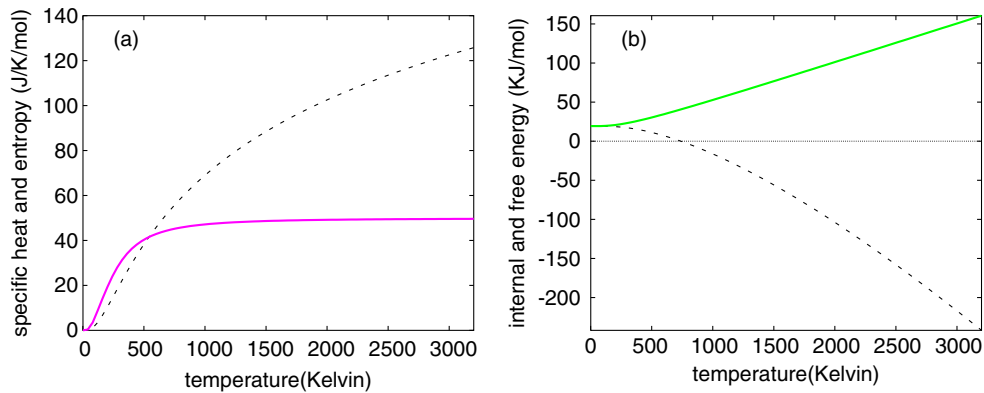


Figure 2. Calculated thermodynamical quantities with temperature of zinc-blende BP. (a) Constant-pressure specific heat (solid curve) and entropy (dashed curve) are plotted versus temperature. (b) Internal energy (solid curve) and Helmholtz free energy (dashed curve) are plotted versus temperature.

3.3. Bulk modulus, shear modulus and elastic constants

In the linear response approach, elastic tensor C_{jk} can be calculated from the second derivative of total energy with respect to small strain perturbation through

$$C_{jk} = \Omega_0^{-1} \frac{d^2 H_c}{d\eta_j d\eta_k}, \quad (2)$$

where Ω_0 denotes the volume of unit cell and H_c denotes energy per unit cell. For an isotropic cubic crystal, the bulk modulus and shear modulus are evaluated by

$$B = \frac{1}{3}(C_{11} + 2C_{12}), \quad (3)$$

$$G = \frac{1}{2}(C_{11} - C_{12}). \quad (4)$$

The calculated bulk modulus (B), shear modulus (G) and elastic constants C_{11} , C_{12} and C_{44} of BP in the zinc-blende structure at experimental volume are given in table 2. It is clearly seen that our results of C_{11} , C_{44} and G are overestimated but C_{12} and B are underestimated compared with experimental data [5, 6]. With respect to the experiments in [5], the bulk modulus is underestimated by $\sim 5\%$. In section 2, we specified that our calculations have been carried out at the experimental lattice constant. It is apparent that our results make a difference compared with the experiments, which is perhaps derived from the pseudopotentials we used. The theoretical bulk modulus, shear modulus and elastic constants of BP at the theoretical equilibrium lattice volume that is not equal to the experimental value have been obtained by researchers several times [13, 15–17], but using different pseudopotentials or basis sets. As expected, the differences between all these calculated results are quite small. Recently, Hassan *et al* [18] applied the full potential linearized augmented plane wave (FP-LAPW) method to reproduce the elasticity of BP successfully. For comparison, their results are also listed in table 2.

3.4. Dielectric and piezoelectric properties

In addition to elastic tensor, dielectric tensor, piezoelectric tensor and internal strain tensor connect to the second derivatives of total energy. For example, piezoelectric tensor ($e_{j\alpha}$) can

Table 2. Calculated elastic constants, bulk modulus B , and shear modulus G of BP in the zincblende structure at experimental volume compared with experiments and other theoretical works. It is noticeable that other theoretical works were done at a different calculated equilibrium lattice volume.

	Present study	Experimental	Theoretical
C_{11} (Mbar)	3.56	3.15 ^a	3.59 ^b , 3.29 ^c
C_{12} (Mbar)	0.68	1.00 ^a	0.81 ^b , 0.98 ^c
C_{44} (Mbar)	2.05	1.60 ^a	2.02 ^b , 1.54 ^c
B (Mbar)	1.64	1.73 ^a , 2.67 ^d	1.72 ^b , 1.70 ^c
G (Mbar)	1.44	1.08 ^a	1.39 ^b , 1.16 ^c

^a From [5].

^b From [13].

^c From [18].

^d From [6].

Table 3. Calculated dielectric constant ϵ , piezoelectric constant e , displacement–response internal strain parameter Γ and force–response internal strain parameter Λ of BP along with experimental and other theoretical values where available. For the dielectric constant ϵ_{dd} ($d = x, y, z$), here d stands for the electric field direction. For piezoelectric constant e_{nd} ($n = 1, \dots, 6$; $d = x, y, z$), n is the strain direction in Voigt notation and d is the electric field direction.

	Present study	Experimental	Theoretical
$\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz}$	09.27	9.61 ^a	9.43 ^b , 7.8 ^c
$e_{4x} = e_{5y} = e_{6z}$ (C m ⁻²)	-0.11	-	-
Γ (Bohr)	00.32	-	0.31 ^d
Λ (Hartree/Bohr)	00.12	-	-

^a From [27].

^c From [29].

^b From [19].

^d From [13].

be calculated using

$$e_{j\alpha} = -|q_e|\Omega_0^{-1}a_{v\alpha}\frac{d^2H_c}{d\eta_j d\varepsilon_v}, \quad (5)$$

where $|q_e|$ is the proton charge and $a_{v\alpha}$ the matrix representation of the real space lattice vector \vec{a} . In table 3, we present the calculated values of the dielectric constant ϵ , piezoelectric constant e , displacement–response internal strain parameter Γ and force–response internal strain parameter Λ , along with the available experimental data and previous theoretical values. For the piezoelectric constant and internal strain parameters, reliable theoretical and experimental values are both required at present, so our data are predictive. Gironcoli *et al* [28] have published their first-principles linear response approach to the piezoelectricity and dielectricity of several III–V semiconductors, but boron compounds are not considered. The dielectric constant of 9.27 is a little smaller than the values of 9.61 from [27] and 9.43 from [19]. The value of the piezoelectric constant is negative (−0.11). We note that GaP also has a negative piezoelectric constant, but two III–V semiconductors (AlP and InP) have a positive one [28]. However, the piezoelectric constant being the sum of two almost cancelling contributions, it is not surprising that its sign may change for chemically similar compounds. The Γ value of 0.32 is close to the value of 0.31 found in [13]. It is smaller than the same

Table 4. Electron band eigenvalues for the lowest conduction band and the valence bandwidths for BP. Energy values are in eV. A comparison is made with the available theoretical and experimental data.

	Present study	Experimental	Theoretical
$\Gamma_{15v} \rightarrow \Gamma_{15c}$	3.42	5.0 ^a	3.45 ^d , 4.4 ^a
$\Gamma_{15v} \rightarrow \Delta_{\min}$	1.28	2.0 ^b	1.12 ^d , 1.9 ^a
$\Gamma_{1v} \rightarrow \Gamma_{15v}$	15.43	16.5 ^c	15.78 ^d , 16.8 ^a

^a From [10].^b From [1].^c From [2].^d From [16].

properties of AlP (0.618), GaP (0.533) and InP (0.652) [28]. For the Λ value of 0.12, at present we have no experimental and theoretical data to compare with our results.

3.5. Energy band structure

As a by-product of this work, we finally verify that the calculated GGA band structure agrees with that found in [9–11, 16]. The full valence bandwidth ($\Gamma_{1v} \rightarrow \Gamma_{15v}$) of 15.43 eV and the direct gap ($\Gamma_{15v} \rightarrow \Gamma_{15c}$) of 3.42 eV compare well with the values of 15.78 and 3.45 eV from [16]. We also obtain an indirect gap ($\Gamma_{15v} \rightarrow \Delta_{\min}$) of 1.28 eV at $\Delta_{\min} = (0.0, 0.417, 0.417)$, which is close to the value of 1.12 eV found in [16] but differs significantly from the observational value of about 2.0 eV [1, 2]. As is well known, the band gaps of BN, BP, BAs and BSb are seriously underestimated in the local density approximation scheme. Our GGA eigenvalue spectrum matches more with other *ab initio* calculations than with observational values (see table 4). It is suggested that the GGA scheme insignificantly improves the accuracy of band structure calculations in this work. For reproducing the most important features of the band structures of BN, BP, BAs and BSb, it is argued that the first-principles quasiparticle approximation (*GW* approximation) approach may be a better choice [10].

4. Conclusion

In this paper, we have presented a systematic density functional linear response study of the lattice dynamics and relevant equilibrium properties of BP in the zinc-blende structure. The phonon band structure and DOS in full are shown. Several critical thermodynamical quantities including $C_p(T)$, entropy, free energy and internal energy with temperature are illustrated. Elastic constants, bulk modulus, shear modulus and dielectric constant are provided. Piezoelectric constant and internal strain parameters are also predicted. Our results agree with numerous experimental and theoretical studies wherever available and supply some of the missing physical properties of BP. This may promote the application of BP in electronic and optical devices. In order to obtain the whole prospect of physical and chemical characteristics of BP and other III–V semiconductors, further first-principles calculations should be carried out in the future. Enhancements to improve the ability of predicting the accuracy of calculations are underway.

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