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Polymorphism of boron phosphide: Theoretical investigation and experimental assessment

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Abstract

Stable crystal structures of wurtzite (*w*-BP) and recently discovered rhombohedral (*rh*-BP) polymorphic modifications of boron phosphide were obtained based on crystal chemistry rationale and unconstrained geometry optimization calculations within the density functional theory (DFT), and compared with known cubic polymorph (*c*-BP). Both *w*-BP and *rh*-BP are mechanically (elastic constants) and dynamically (phonons) stable and exhibit thermodynamic and mechanical properties very close to those of *c*-BP. The electronic band structures of all BP polymorphs depict semi-conducting behavior with band gap magnitudes close to 2 eV.

Keywords: *boron phosphide; polymorphism; DFT; crystal structures; mechanical properties; phonons; electronic band structures*

Introduction

Boron phosphide BP is refractory wide bandgap A^{III}B^V semiconductor [1] characterized by a unique combination of mechanical [2,3], thermal and electrical properties [4-6], high thermoelectric power [7] and outstanding chemical and high-temperature stability that makes it a promising material for a wide range of engineering applications [8].

Cubic sphalerite (*F*-43m) BP (*c*-BP) [9] is the thermodynamically stable phase of boron phosphide at ambient conditions, and it has been found to be stable at pressures up to 110 GPa [10]. Hexagonal wurtzite (*P*6₃*mc*) BP polymorph (*w*-BP) has also been reported [11], however, data on

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structure, stability region and properties of this phase are lacking in the literature. Very recently, the third polymorph, rhombohedral BP (*rh*-BP), has been discovered by transmission electron microscopy [12].

In the present work structure and properties of cubic, rhombohedral and wurtzite BP polymorphs were studied using crystal chemistry rationale and unconstrained geometry optimization calculations within the density functional theory (DFT). Good agreement with available experimental data on thermodynamic and mechanical properties of *c*-BP is observed.

Computational framework

The search for the ground state structures and energies as well as energy dependent quantities within DFT was carried out using plane-wave Vienna Ab initio Simulation Package (VASP) code [13,14] with the projector augmented wave (PAW) method [14,15] for the atomic potentials. The exchange-correlation XC effects within DFT were considered using the generalized gradient approximation (GGA) [16]. For the methodology details, the reader is referred to our previous papers [17,18]. Regarding the choice of the XC functional, the relevant studies focusing on black phosphorous [19] and phosphorene [20], both presenting layered stacking, showed the impact of using more sophisticated XC functional such as the hybrid GGA-HSE06 [21]. However, calculations using such functional didn't change the outcome of the present investigation.

For each BP polymorph, the mechanical properties were calculated (i) from the set of elastic constants C_{ij} , and (ii) using three contemporary theoretical models of hardness [22-24]. To verify the dynamic stability of BP phases, the phonon bands were calculated. The approach consists of computing the phonon modes through finite displacements of the atoms off their equilibrium positions to subsequently obtain the forces from the summation over the different configurations. The phonon dispersion curves along the main lines of the respective Brillouin zone (BZ) were obtained using first-principles phonon calculation code "Phonopy" [25], and thermodynamic properties (Helmholtz free energy, heat capacity and entropy) were calculated as functions of temperature within the harmonic approximation. Finally, the electronic band structures showing small gap insulating behavior were assessed.

Results and Discussion

Energy and crystal structures

Starting from crystal structures of *c*-BP (ICSD No. 29050) and *w*-BP (ICSD No. 615155), the calculations were carried out for the ground state configurations. In the case of *rh*-BP, the structural data of rhombohedral ZnS [26] were used.

Energy is the prevailing criterion for a first assessment of the crystal structures. From the total electronic energies (E_{tot}) the cohesive energies were obtained by deducting the atomic contributions.

The resulting atom cohesive energies of three BP polymorphs were then compared. The results provided in Table 1 show close atom average cohesive energies with a slightly more stable rhombohedral form. This validates the choice of *rh*-ZnS as the starting model for the structural refinement of *rh*-BP.

The resulting structures of three BP polymorphs shown in Figs. 1(a-c) exhibit tetrahedral stacking like that of diamond and dense polymorphs of BN. Note that the structure of rhombohedral BP can be considered as three-dimensional (3D) form of a 2D analogue with 3 B-P layers shown in Fig. 1d. The similar 2D structure was considered earlier for the study of *rh*-B₂N₂, a new rhombohedral polymorph of boron nitride [17]. However, the two-dimensional *rh*-BP is less cohesive than the 3D *rh*-BP as shown in the last line of Table 1.

The crystal data provided in Table 2 present the converged calculated new atomic positions after full unconstrained geometry optimization with successive calculations at increasing precision of **k**-mesh in the three respective Brillouin zones. A unique interatomic B–P distance of 1.97 Å was identified for all three polymorphs. The calculated lattice parameter of *c*-BP ($a = 4.541$ Å) was in good agreement with the experimental value 4.543 Å [10]. As for the calculated lattice parameters of *w*-BP ($a = 3.195$ Å, $c = 5.297$ Å), they are in good agreement with $a = 3.20$ Å and $c = 5.31$ Å values reported in [27].

Comparison of simulated X-ray diffraction patterns of all BP polymorphs (Fig. 2) reveals that rhombohedral BP is difficult to distinguish from cubic BP by powder X-ray diffraction.

Charge density projections

Further illustration of electronic / crystal structure relationship focusing on the tetrahedral stacking can be provided by the charge density projections. Figs. 3(a-c) show for the three polymorphs the charge density yellow volume within the BP_3 and PB_3 tetrahedra, skewed toward P as expected from the higher electronegativity of P ($\chi = 2.19$) versus B ($\chi = 2.03$). Due to high electronegativity of N ($\chi = 3.04$) in the case of polar covalent B–N bonding [17], the character of B–P bond is expected to be more covalent. For the sake of comparison, Fig. 3d presents the sp^2 -like planar charge density in 2D *rh*-BP (Fig. 1d).

Mechanical properties

(i) *Elastic constants*

The elastic constants C_{ij} needed to derive the mechanical properties were determined by performing finite distortions of the lattice and deriving C_{ij} from the strain-stress relationship. Then fully the bulk B and shear G moduli are obtained by averaging the single-crystal elastic constants using, here, Voigt's method [28] based on a uniform strain. The calculated sets of elastic constants are given in Table 3. All values are positive, which is the first indication of mechanical stability. Further proofs

were obtained from C_{ij} combinations obeying rules related to mechanical stability. The equations providing the bulk B_V and shear G_V moduli are as follows.

- For the cubic system:

$$B_{Voigt}^{cub.} = 1/3 \{C_{11} + 2C_{12}\}$$

$$G_{Voigt}^{cub.} = 1/5 \{C_{11} - C_{12} + 3C_{44}\}$$

- For the hexagonal (trigonal) system:

$$B_{Voigt}^{hex.} = 1/9 \{2(C_{11} + C_{12}) + 4C_{13} + C_{33}\}$$

$$G_{Voigt}^{hex.} = 1/30 \{C_{11} + C_{12} + 2C_{33} - 4C_{13} + 12C_{44} + 6(C_{11} - C_{12})\}$$

The results presented in Table 3 show that all three BP polymorphs exhibit the same bulk moduli while their shear moduli differ markedly, indicating different brittleness within the series with a clear tendency of decreasing brittleness from *c*-BP to *rh*-BP.

(ii) Hardness

Vickers hardness (H_V) was predicted using three contemporary theoretical models of hardness [22-24]. The thermodynamic model [22] is based on thermodynamic properties and crystal structure, Lyakhov-Oganov approach [23] considers topology of the crystal structure, strength of covalent bonding, degree of ionicity and directionality, while Mazhnik-Oganov [24] model is based on elastic properties. The fracture toughness (K_{Ic}) was evaluated using Mazhnik-Oganov model.

Hardness and bulk moduli (B_0) calculated in the framework of the thermodynamic model are presented in Table 4. Table 5 summarizes hardness calculated using three theoretical models and other mechanical properties i.e. shear moduli (G), Young's moduli (E), the Poisson's ratios (ν) and fracture toughness (K_{Ic}).

Regardless of the model used, all three BP polymorphs have very close hardness values. As for the absolute H_V values, the thermodynamic model seems to be the most reliable, because it shows the best agreement with experimental data for *c*-BP [2]. All three polymorphs have virtually equal bulk moduli, while their shear and Young's moduli differ noticeably, decreasing in the *c*-BP – *w*-BP – *rh*-BP row (see Table 5). Fracture toughness of all three polymorphs is the same and almost half that of single-crystal cubic BN [29].

Dynamical stabilities from the phonons

Further stability criteria can be obtained from the phonon dispersion relations in the Brillouin zone, i.e. the phonon band structures. Following the method presented in the 'Computational framework'

section, the obtained phonon band structures for three BP polymorphs are shown in Fig. 4. In each panel the bands run along the main lines of the cubic BZ (Fig. 4a) and hexagonal BZ (Figs. 4b and 4c).

Along the vertical direction the frequency is given in units of Terahertz (THz). Since no negative energy magnitudes are observed, the three BP structures can be considered as dynamically stable. There are 3N-3 optical modes at high energy and 3 acoustic modes. As mentioned in Table 3, the novel rhombohedral phase *rh*-BP is expressed in hexagonal coordinates, and BZ directions are the same as in *w*-BP (Fig. 4b).

The acoustic modes start from zero energy ($\omega = 0$) at the Γ point, center of the Brillouin Zone, up to a few Terahertz. They correspond to the lattice rigid translation modes of the crystal (two transverse and one longitudinal). But the number of explicit bands is subjected to the lattice symmetry, i.e., the higher the symmetry, the more dispersion curves showing degeneracy are found for a given frequency, and therefore an apparent reduction in the number of dispersion curves is observed. In all three panels the energy range is the same for the three phases, i.e. from 0 to 25 THz, stressing furthermore their similitude but with a much lower magnitude than for diamond by Raman spectroscopy: $\omega \sim 40$ THz [30].

Thermodynamic properties

Thermodynamic properties of BP polymorphs were calculated from the phonon frequencies using the statistical thermodynamic expressions on a high precision sampling mesh in the Brillouin zone. The properties of all three polymorphs were very similar over a wide temperature range. Fig. 5 shows the temperature changes of heat capacity at constant volume C_V , entropy S and Helmholtz free energy $F = U - TS$, where U is the internal energy, S is the entropy and T is the absolute temperature.

For the heat capacity of cubic BP, an excellent agreement of calculated C_V values with experimental data [31-33] is observed in the 5-700 K range. The deviation of experimental points from the calculated curve above 700 K is evidently due to the limitations of the method used (AC calorimetry [31]) at high temperatures.

Electronic structures

The electronic band structures were obtained using full potential augmented spherical wave (ASW) method [34,35], and the GGA for the XC effects [16]. In the minimal ASW basis set, the outermost shells chosen to represent the valence states and the matrix elements were constructed using partial waves up to $l_{max} = 2$. Self-consistency was achieved when charge transfers and energy changes between two successive cycles were $\Delta Q < 10^{-8}$ and $\Delta E < 10^{-6}$ eV, respectively. The integrations within the respective Brillouin zones (cubic, hexagonal and rhombohedral) were done with

successive calculations and progressive augmentation of **k**-mesh precision. For the sake of comparison we considered boron nitride that also has 3 three-dimensional polymorphs [18]. As a matter of fact, such comparison is justified by the chemical characteristics of the constituting elements regarding electronegativity according to Pauling χ [36]: $\chi(\text{B}) = 2.04$, $\chi(\text{P}) = 2.19$ and $\chi(\text{N}) = 3.04$. Then $\Delta\chi(\text{BN}) = 1$ is six times higher than $\Delta\chi(\text{BP}) = 0.15$, letting expect a larger covalent character in BP *versus* BN as shown below.

Such behavior should be illustrated quantitatively from inspection of the respective electronic band structures. In Fig. 6 the bands show resemblance of shape, but large differences can be observed regarding the broader valence band (VB) in BN (~20 eV) *versus* BP (~12 eV), and the band gap separating VB from empty CB. The energy gaps of all three BN polymorphs are about 4 eV whereas these values for i.e. ~2 eV that is in perfect agreement with literature data for cubic BP ($E_g = 2.02$ eV [37]) . Finally, the band gap of the hypothetical 2D *rh*-BP (Fig. 1d, Table 2d) was found to be significantly smaller than that of graphite-like BN.

Conclusions

Following recent discovery of rhombohedral form of boron phosphide, investigations within quantum theoretical framework of the density functional theory allowed the conclusion of a viable structure for rhombohedral BP which is as cohesive as known cubic and wurtzite BP polymorphs. Further quantitative criteria of mechanical and dynamical stability for *rh*-BP were obtained from the elastic properties and phonon dispersions. All three BP polymorphs exhibit very close thermodynamic and mechanical properties, and their electronic band structures obtained with full potential all electrons calculations point to band gaps close to 2 eV, indicating the larger covalence with respect to BN polymorphs.

Author Contributions

Vladimir L. Solozhenko: Conceptualization. X-ray diffraction. Hardness evaluation.

Samir F. Matar: Methodology. Computation. Visualization. Software. Resources.

Both authors contributed equally to investigation, data curation, formal analysis, validation and writing at all stages.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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Table 1 Total and atom averaged energies of different BP phases considered in the present work

	Space group	Z	E _{tot} (eV)	E _{coh./atom} (eV)
<i>c</i> -BP	<i>F</i> -43 <i>m</i>	4	-51.59	-1.161
<i>w</i> -BP	<i>P</i> 6 ₃ <i>m</i> <i>c</i>	2	-25.77	-1.158
<i>rh</i> -BP	<i>R</i> 3 <i>m</i>	1	-12.91	-1.170
2D <i>rh</i> -BP	<i>R</i> 3 <i>m</i>	1	-12.15	-0.80

Atomic energies in eV: B (-5.33); P (-5.24)

Table 2 Calculated structure parameters of BP polymorphs.

a) *c*-BP, space group $F\bar{4}3m$ (No. 216). $a = 4.541$ (4.543 [10]) Å

Atom	Wyckoff	x	y	z
B	$4a$	0	0	0
P	$4c$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$

$d(\text{B-P}) = 1.965$ (1.97) Å.

b) *w*-BP, space group $P6_3mc$ (No. 186). $a_{\text{hex}} = 3.195$ (3.20 [27]) Å; $c_{\text{hex}} = 5.297$ (5.31 [27]) Å

Atom	Wyckoff	x	y	z
B	$2b$	$\frac{1}{3}$	$\frac{2}{3}$	0.0
P	$2b$	$\frac{1}{3}$	$\frac{2}{3}$	0.375

$d(\text{B-P}) = 1.96$ Å.

c) 3D *rh*-BP, space group $R\bar{3}m$ (No. 160). $a_{\text{rh}} = 3.215$ Å; $\alpha = 59.99^\circ$.
Parameters in hexagonal setting are $a_{\text{hex}} = 3.217$ Å; $c_{\text{hex}} = 7.866$ (i.e. $h\text{-B}_3\text{P}_3$)

Atom	Wyckoff	x	y	z
B	$3a$	0.0	0.0	0.012
P	$3a$	0.0	0.0	0.263

$d(\text{B-P}) = 1.97$ Å.

d) 2D *rh*-BP, space group $R\bar{3}m$ (No. 160). $a_{\text{rh}} = 4.611$ Å; $\alpha = 40.74^\circ$.
Parameters in hexagonal setting are $a_{\text{hex}} = 3.210$ Å; $c_{\text{hex}} = 12.665$ (i.e., $h\text{-B}_3\text{P}_3$)

Atom	Wyckoff	x	y	z
B	$3a$	0.0	0.0	0.0
P	$3a$	0.0	0.0	0.668

$d(\text{B-P}) = 1.85$

Table 3 Elastic constants C_{ij} and Voigt values of bulk (B_V) and shear (G_V) moduli of BP polymorphs (all values are in GPa).

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{55}	B_V	G_V
<i>c</i> -BP	342	75			186		164	202
<i>w</i> -BP	406	58	23	455	174	135	164	180
<i>rh</i> -BP	392	57	39	410	168	150	163	171

Table 4 Vickers hardness (H_V) and bulk moduli (B_0) of boron phosphide polymorphs calculated in the framework of the thermodynamic model of hardness [22]

	Space group	a (Å)	b (Å)	c (Å)	ρ (g/cm ³)	H_V (GPa)	B_0 (GPa)
<i>c</i> -BP	$F-43m$	4.5410	4.5410	4.5410	2.964	30	183
<i>w</i> -BP	$P6_3mc$	3.1946	3.1946	5.2970	2.964	29	183
<i>rh</i> -BP	$R3m$	3.2174*	3.2174*	7.8660*	2.952	29	182

* hexagonal setting

Table 5 Mechanical properties of boron phosphide polymorphs: Vickers hardness (H_V), bulk modulus (B), shear modulus (G), Young's modulus (E), Poisson's ratio (ν) and fracture toughness (K_{Ic})

	H_V			B		G_V	$E^{\S}$	$\nu^{\S}$	$K_{Ic}^{\ddagger}$
	T^*	$LO^{\dagger}$	$MO^{\ddagger}$	B_0^*	B_V				
	GPa								
<i>c</i> -BP	30 ^{**}	25	38	183 ^{††}	164	202	430	0.063	1.6
<i>w</i> -BP	29	25	34	183	164	180	395	0.098	1.6
<i>rh</i> -BP	29	25	32	182	163	171	380	0.111	1.5

* Thermodynamic model [22]

† Lyakhov-Oganov model [23]

‡ Mazhnik-Oganov model [24]

§ E and ν values calculated using isotropic approximation

** Experimental value $H_V = 34(2)$ GPa [2]

†† Experimental value $B_0 = 174(2)$ GPa [3]

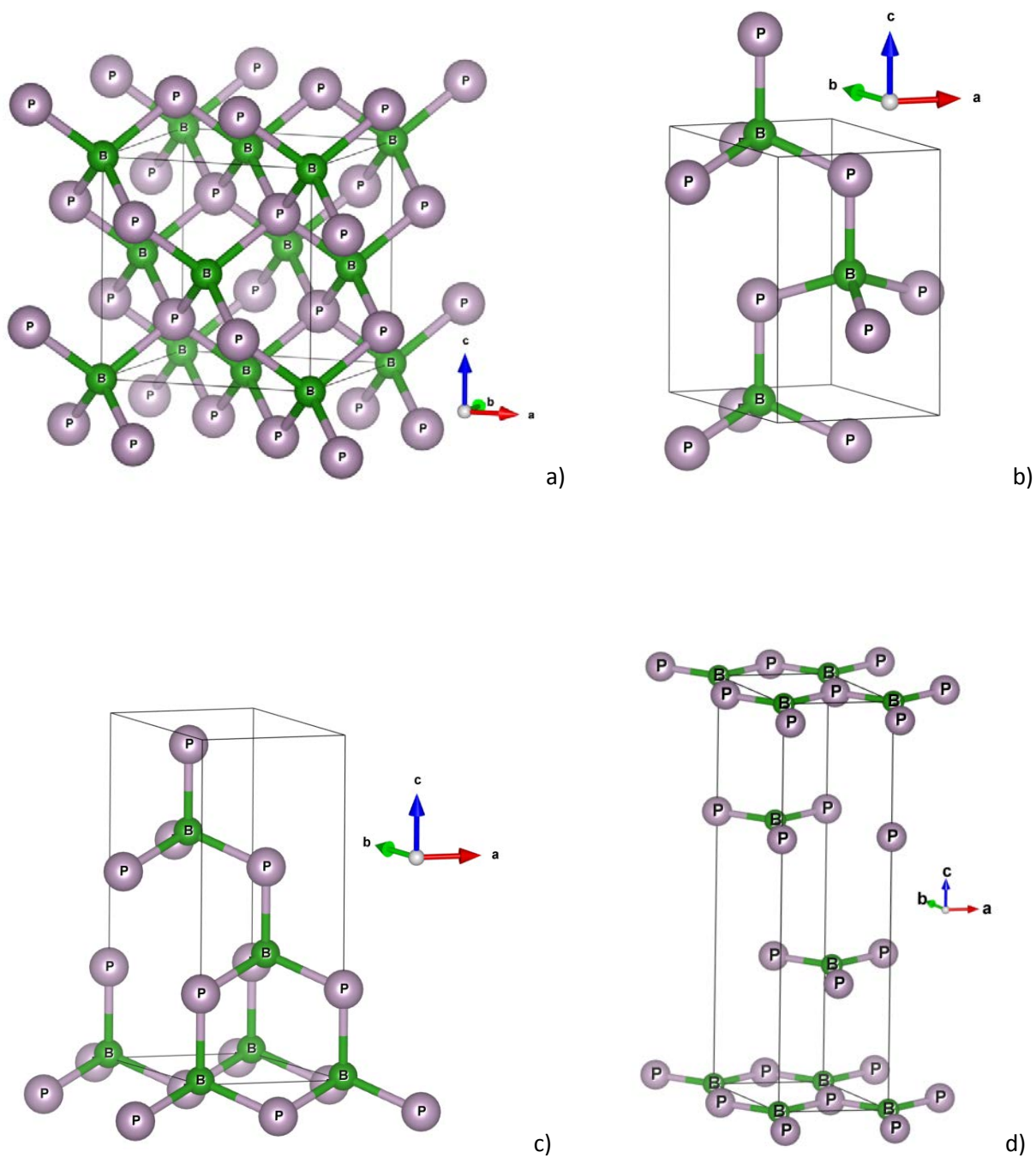


Fig. 1 Crystal structures of boron phosphide polymorphs: *c*-BP (a); *w*-BP (b); *rh*-BP (hexagonal axes) - 3D (c) and 2D (d).

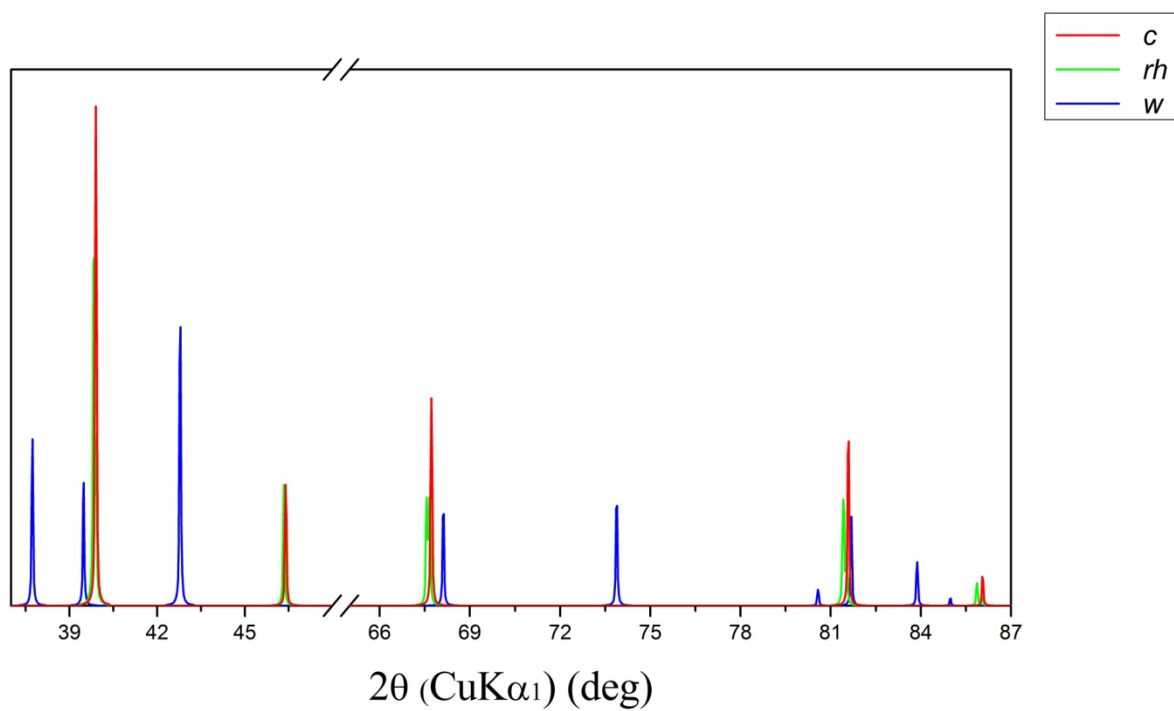


Fig. 2 Simulated X-ray diffraction patterns of three boron phosphide polymorphs.

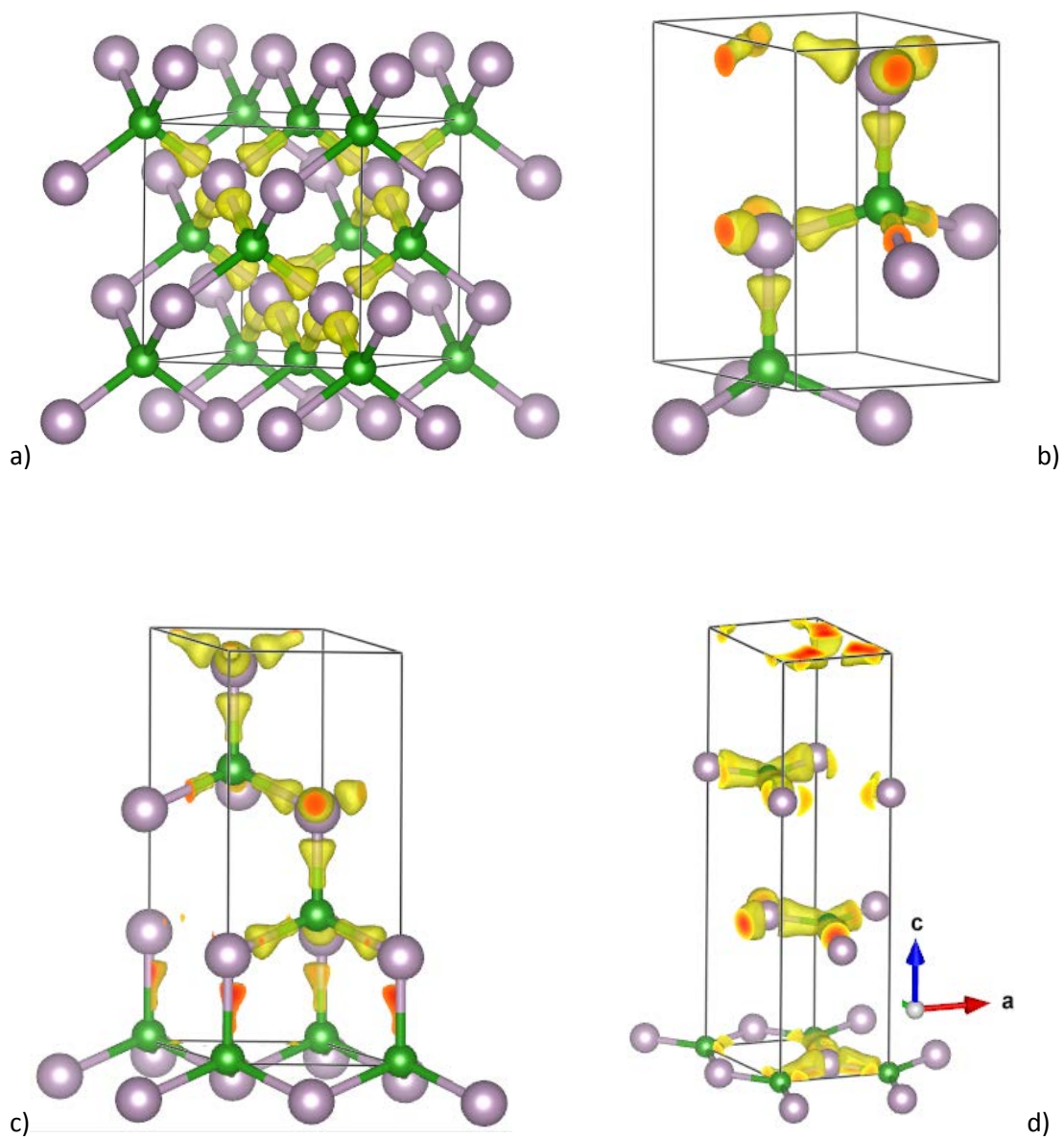


Fig. 3 Boron phosphide polymorphs: *c*-BP (a); *w*-BP (b); *rh*-BP (hexagonal axes) - 3D (c) and 2D (d). Charge density projections highlighting the tetrahedral shape of the charge skewed toward P.

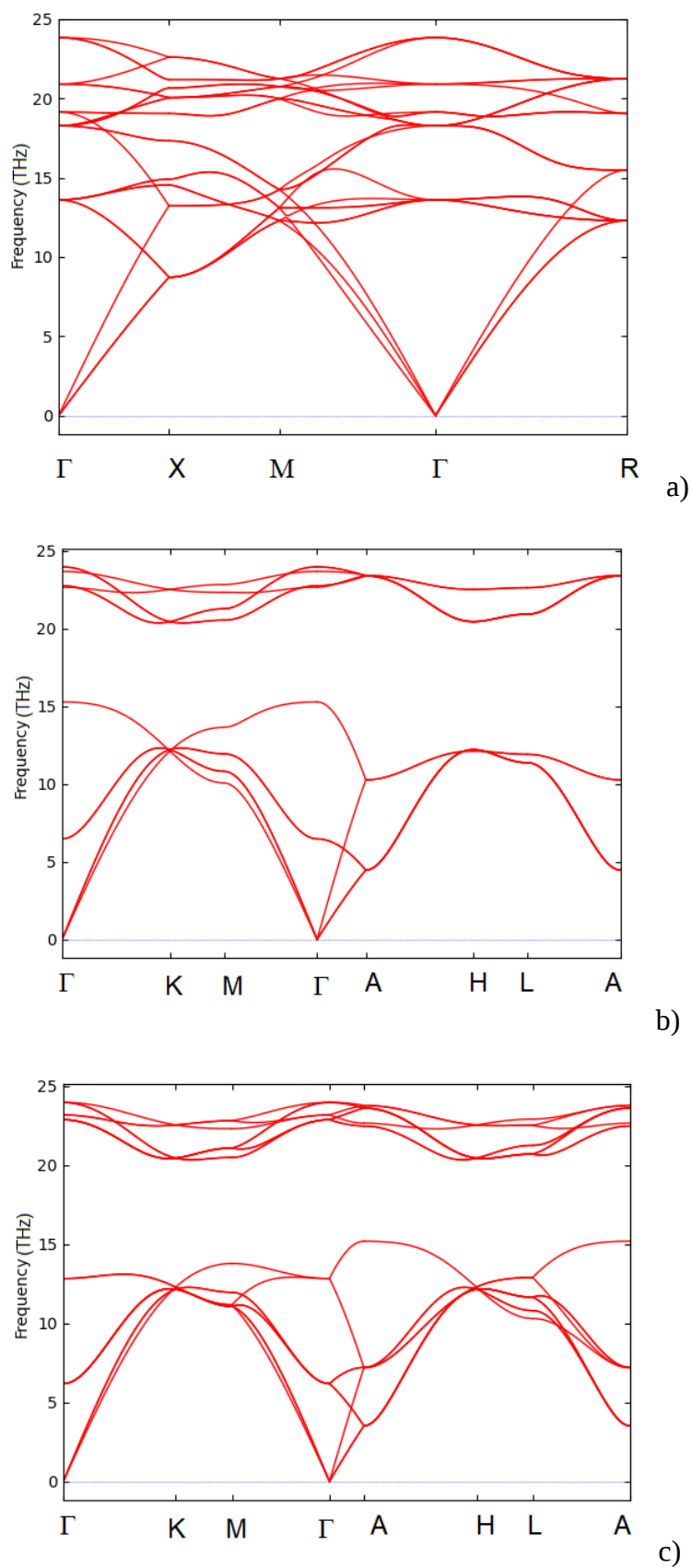


Fig. 4 Phonon band structures of boron phosphide polymorphs: a) *c*-BP; b) *w*-BP; c) *rh*-BP.

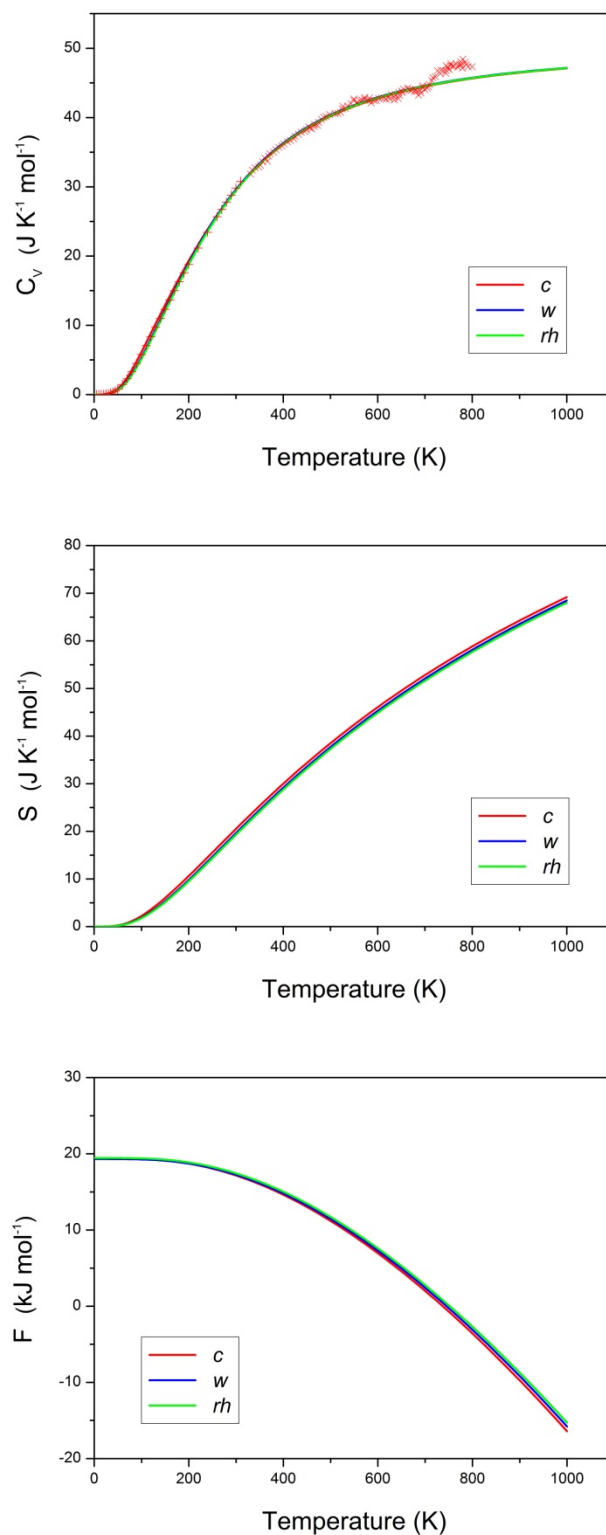


Fig. 5 Thermodynamic properties (specific heat at constant volume C_V , entropy S and Helmholtz free energy F) of three boron phosphide polymorphs as functions of temperature. Experimental C_V values for *c*-BP are shown as diagonal [31,32] and upright [33] crosses.

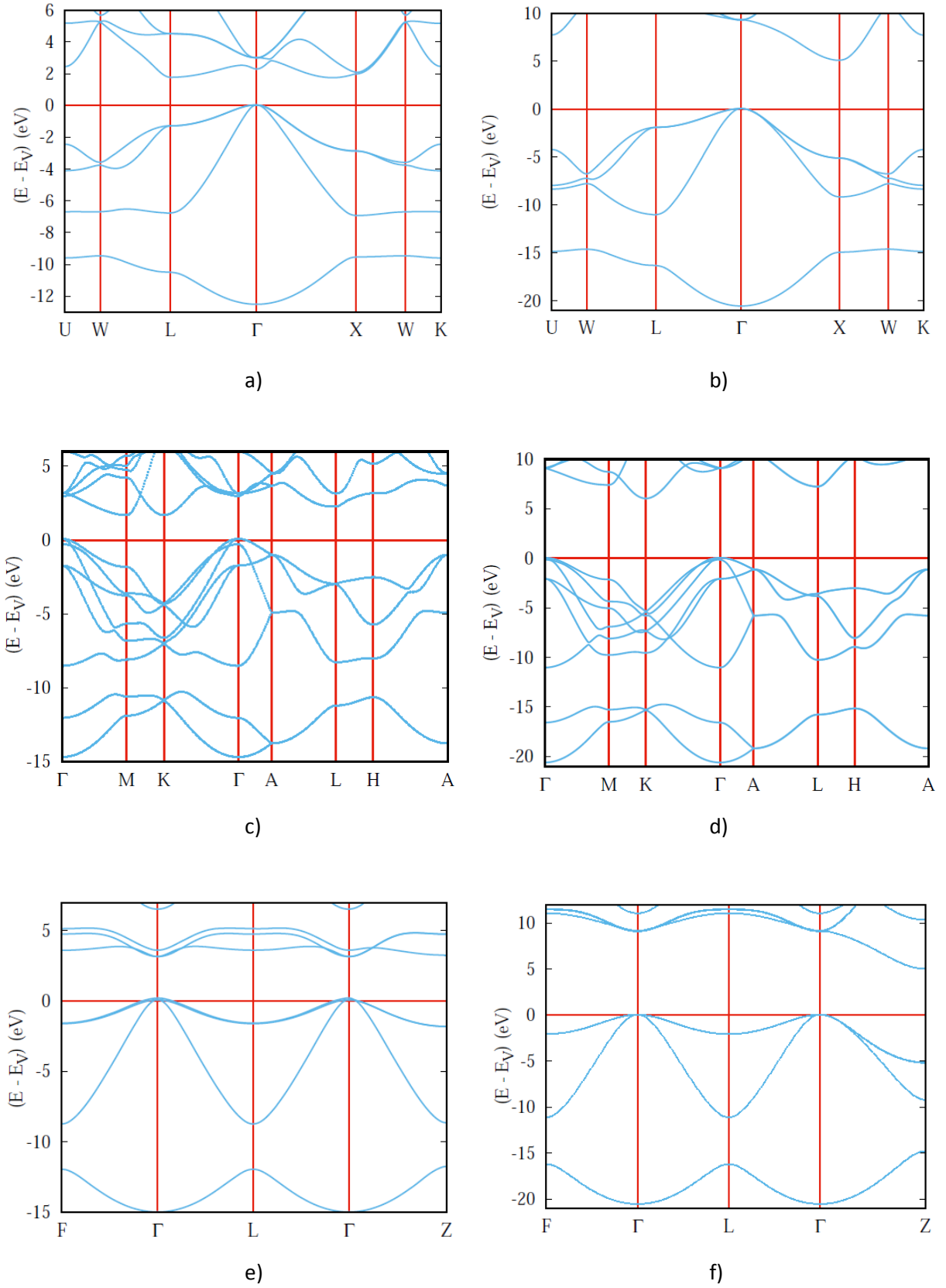


Fig. 6 Electronic band structures of BP and BN polymorphs: a) *c*-BP; b) *c*-BN; c) *w*-BP; d) *w*-BN; e) *rh*-BP; f) *rh*-BN