

First-principles Study of the Structural, Electronic, Optical and Thermodynamic Properties of Binary Compound (AlB_2)

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Abstract— In the present study, first-principles Density Functional Theory (DFT) with Generalized Gradient Approximation (GGA) is exploited to investigate different properties of AlB_2 by using ultra-soft Pseudopotential technique. The study involves the calculations of the structural, mechanical, electronic, optical and thermodynamical properties of AlB_2 . All these properties are studied at ambient condition and at various temperatures and pressures. It is found that the volume decreases with increasing pressure. Our calculated elastic constants agree with the previous theoretical data expect for C_{12} and AlB_2 is found to be brittle. Calculated electronic band structures are doubly degenerate along Γ -A direction. The total DOS curves of this compound shares similar free-electron-like metallic features. The B $2p$ states dominate the conductivity of AlB_2 . The reflectivity spectrum shows that the material is a good reflector within the energy range, 8.15-20.65 eV and the materials should have no band gap. The static refractive index of AlB_2 is found to have the values ~ 6.76. Debye temperature increase with pressure. The temperature dependence of α is very weak at higher temperatures and higher pressures.

Keyword— First-principles, ab initio, Structural properties, Elastic properties, Electronic band structure, Optical properties, Thermodynamic properties.

1 INTRODUCTION

The recent discovery of superconductivity in MgB_2 at 39 K has reinforced the scientific importance of AlB_2 -type borides [1]. Despite the great interest in the understanding of the origin of all these characteristics and the potential use of borides for high-performance applications, many of their physical properties have been little studied. Among these, their mechanical properties, mainly its higher hardness and the related behavior under different pressures are subjects which deserve more intensive investigation. A number of theoretical and experimental [2, 3] studies exist in literature that deal with structural, elastic and electronic properties of AlB_2 compound. Specifically, Shein and Ivanovskii [4] have reported the structural and elastic properties using the full-potential linearized augmented plane-wave (FP-LAPW) method with the generalized gradient approximation (GGA) for AlB_2 . The structural properties have been studied for this compound by Oguchi [5]. The phonon properties have been investigated by Bohmen et al. [6].

In this study, we have investigated the phonon dispersion relations and thermodynamical properties of this compound in detail and interpret the salient results. To our knowledge, phonon projected density of states and thermodynamical properties, which are the important bulk properties for solids, have neither been obtained theoretically, nor experimentally for AlB_2 compound. We are interested because of the strongly varying data of simple phase AlB_2 theoretically and experimentally, including lattice dynamics properties [7, 8, 9, 10, 11, 12, 13, 14] electronic and optical properties [15, 16] high tem-

perature and high pressure properties [17, 18]. In this work, the structural and the thermodynamic properties of AlB_2 have been investigated by using a first-principles plane wave method with a relativistic analytic pseudopotential of Hartwigsen, Goedecker and Hutter (HGH) scheme [19] within density functional theory (DFT) [20, 21]. Therefore, we have aimed to provide some additional information to the existing data on the physical properties of this compound using the ab initio total energy calculations.

2 METHOD OF CALCULATION

In the present paper, all calculations have been carried out using ab initio method implemented in CASTEP code [22] using norm-conserving pseudopotentials [23] and a plane-wave expansion of the wave functions. The generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) has been incorporated for the simulation.

The Kohn-Sham energy function was rst-Pack scheme K-point sampling was used for integration over the first Brillouin zone. Directly minimized via the Conjugate - gradient method. The convergence criteria for structure optimization and energy calculation were set for this compound, to ultrafine quality with a kinetic energy cutoff of 650 eV and the k-point meshes of $13 \times 13 \times 10$.

3 RESULTS AND DISCUSSION

3.1 STRUCTURAL PROPERTIES

We first perform the geometry optimization as a function of

normal stress by minimizing the total energy. The procedure leads to a successful geometry optimization of the structures. After geometry optimization, the lattice parameters of the AlB_2 under study are obtained at different pressures. From fig. 1 we observed that, the volume decreases with increasing pressure. The variation of volume within the range 0 to 50 GPa is 17.60%. Also observed that, the normalized volume has been reduced by 17.95%.

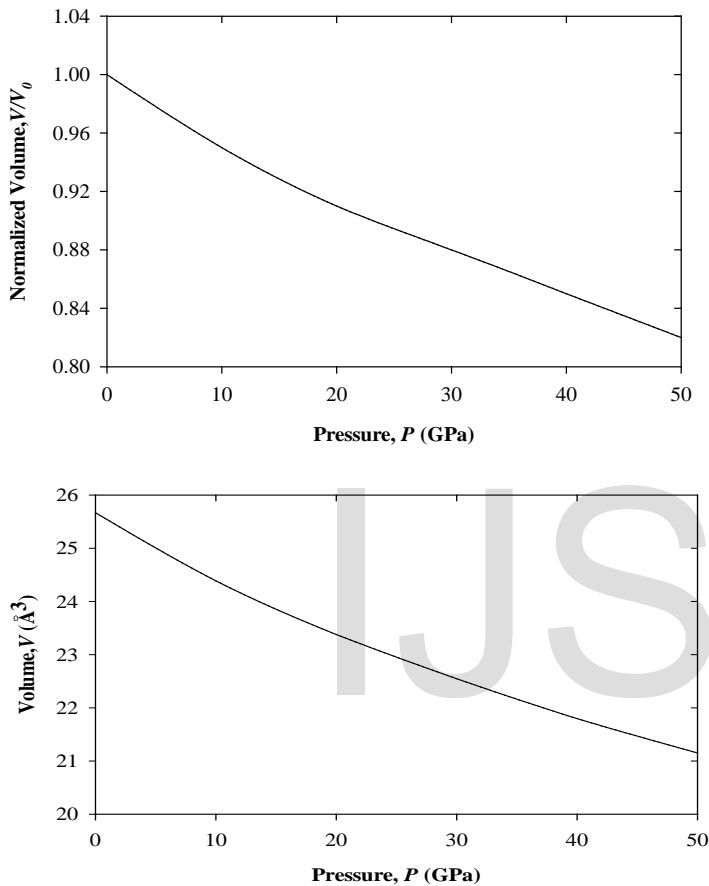


Fig. 1. Pressure dependence of unit cell volume and normalized volume for AlB_2

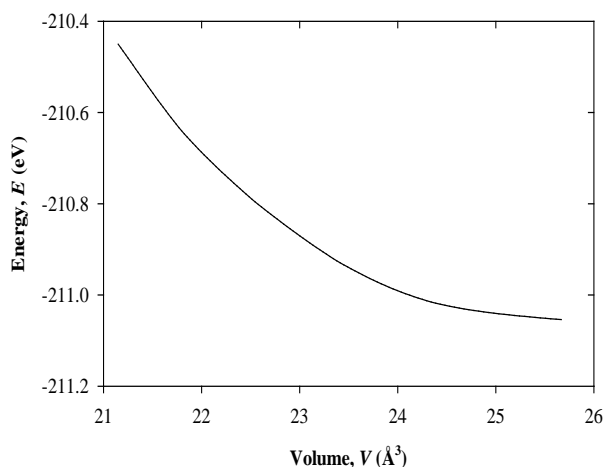


Fig. 2 Calculated values of energy E , as a function of volume for AlB_2 .

3.2 ELASTIC PROPERTIES

The elastic constants of solids provide link between mechanical and dynamical behavior of crystals and give important information concerning the nature of the forces operating in solids. The elastic constants, bulk modulus B , shear modulus G , Young's modulus E , and poisson's ratio ν , have been calculated in our present research work. Though the strains are imposing on the lattice, the elastic constants can be obtained at zero pressure. A hexagonal crystal has six elastic stiffness constants, C_{11} , C_{12} , C_{13} , C_{33} , C_{44} , and C_{66} [24], five of them are independent since $C_{66} = (C_{11} - C_{12})/2$. For AlB_2 , our calculated elastic constants C_{11} , C_{13} , C_{33} and C_{44} are in agreement with available theoretical data [24]. But in this case, there is some dissimilarity in the value of C_{12} with available theoretical data [24]. The elastic constants C_{11} or C_{13} measure the a or c direction resistance to linear compression, respectively. The present C_{11} is higher than C_{13} . The mechanically stable phases or macroscopic stability are dependent on the positive definiteness of stiffness matrix [25]. For hexagonal lattices, calculation must be carry out for the conditions known as the Born criteria: $C_{11} > 0$, $C_{11} - C_{12} > 0$, $C_{44} > 0$, $(C_{11} + C_{12}) C_{33} - 2C_{13}^2 > 0$. Our elastic constants calculations, shown in Table 1, completely satisfy the above conditions, indicating that the hexagonal AlB_2 is mechanically stable.

According to Hill's observation, the value of bulk modulus (in GPa) $B = B_H = (B_V + B_R)/2$ (Hill's bulk modulus), where B_V and B_R is the Voigt's and the Reuss's bulk modulus respectively. The value of shear modulus (in GPa) $G = G_H = (G_V + G_R)/2$ (Hill's shear modulus), where G_V and G_R is the Voigt's and the Reuss's shear modulus respectively. Using Voigt and Reuss formulas: $Y = 9BG/(3B+G)$ and $\nu = (3B-Y)/6B$ [14], the polycrystalline Young's modulus Y (GPa) and the Poisson's ratio ν are then obtained.

The elastic anisotropy of crystals is calculated in different ways and defined by the ratio $A = 2C_{44} / (C_{11} - C_{12})$ [26]. The factor $A = 1$ represents complete isotropy, while values smaller or greater than this measure the degree of anisotropy. Therefore, AlB_2 show anisotropic behavior (Table 2). The parameter $K_c/K_a = (C_{11} + C_{12} - 2C_{13}) / (C_{33} - C_{13})$ which expresses the ratio between linear compressibility coefficients of hexagonal crystals [27]. The value of K_c/K_a is 2.64 for AlB_2 , represents that the compressibility for the given compound along c- axis is greater than along a- axis (Table 2). According to Pugh's criteria [28], a material behaves in a ductile manner, if $G/B < 0.5$, otherwise it should be brittle. For AlB_2 , $G/B = 0.57$. Therefore, we conclude that AlB_2 show brittle behavior.

AlB ₂	0.05	0.57	2.64	[This]
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Table 1: Calculated elastic constants, C_{ij} (in GPa) for AlB₂ at zero pressure.

Compound	Elastic constants, C_{ij} (GPa)					Ref.
	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	
AlB ₂	526.55	112.01	49.35	253.53	11.01	[This]
	530.00	82.40	67.90	272.30	32.70	[2]

Table 2: Bulk modulus (B , in GPa), Shear modulus (G , in GPa), Young's modulus (Y , in GPa), Poisson's ratio ν , Anisotropic factor (A), Linear compressibility ratio k_c/k_a and ratio G/B for AlB₂, at zero pressure.

Compound	B (GPa)	G (GPa)	Y (GPa)	ν
AlB ₂	192.00	110.11	277.32	0.26

Compound	A	G/B	K_c/K_a	Ref.
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3.3 ELECTRONIC PROPERTIES

3.3.1 ELECTRONIC BAND STRUCTURE AND DENSITY OF STATES (DOS)

The calculations of the electronic band structure help one to understand the shape of the Fermi surface. The material properties can be understood if one can identify the character of dominant bands near the Fermi level, their energy etc. In this way knowledge of the electronic band structure provides predictive insight and understanding of certain very important properties of solids. The energy band structure of AlB₂ at zero pressure is illustrated in Fig.3. From these figures at least two electronic bands cross the Fermi level, indicating that the compound exhibits metallic properties. The calculated electronic band structures are doubly degenerate along Γ -A direction. In the present case, nearly flat bands are observed just below E_F in the Γ -A direction.

The density of states (DOS) of a system describes the number of states per interval of energy at each energy level that are available to be occupied. A DOS of zero means that no states can be occupied at that energy level. The total and partial electronic density of states (DOS) of AlB₂ is presented in Fig.4 at zero pressure. It can be seen from this figure that the major contributions around the Fermi energy are mainly from the B $2p$ states and also suggest that the B $2p$ states dominate the conductivity of AlB₂. Al atom has a small contribution to the total DOS. The total DOS curves of this compound share similar free-electron-like metallic features. The features of the DOS curves of AlB₂ look similar as expected due to their isoelectronic and isostructural nature. We find that for AlB₂, $N(E_F) = 0.41$. On the other hand, according to McMillan formula for T_c [29], J. Kortus and other workers showed that the most probable MgB₂ based medium T_c superconductor is a consequence of a high density of states, $N(E_F)$ at the Fermi level.

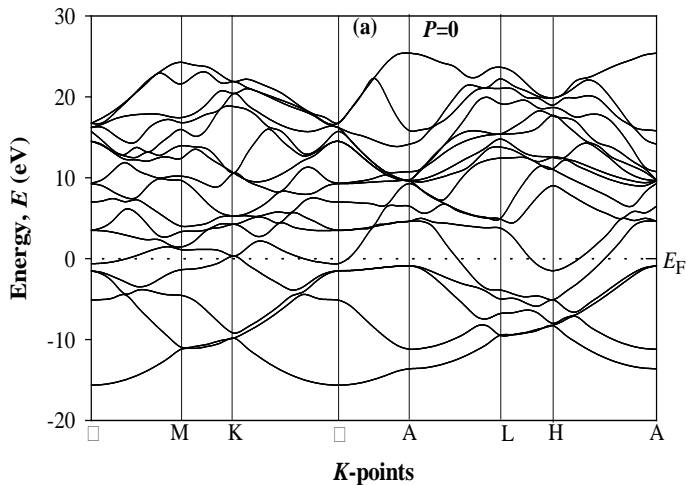


Fig. 3 Electronic band structure of AlB₂

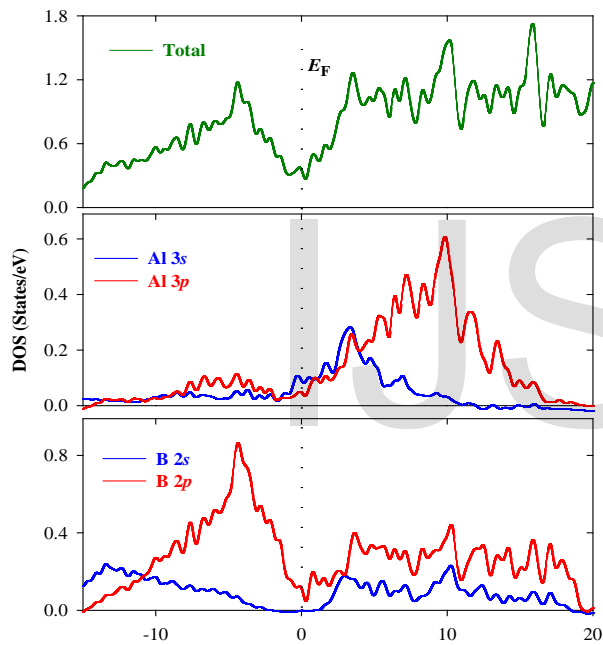
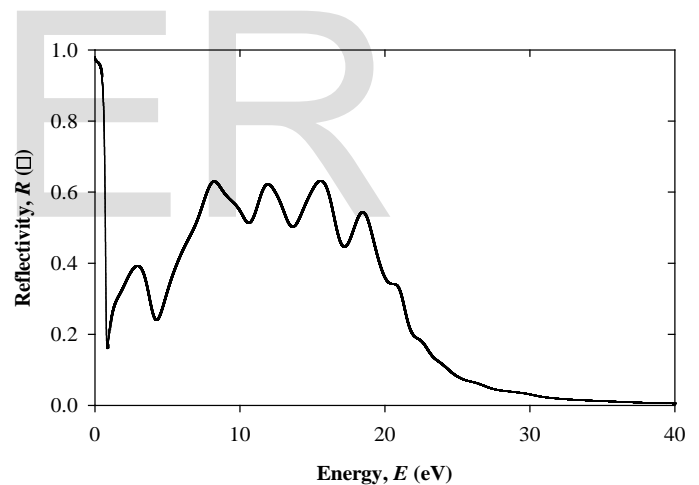
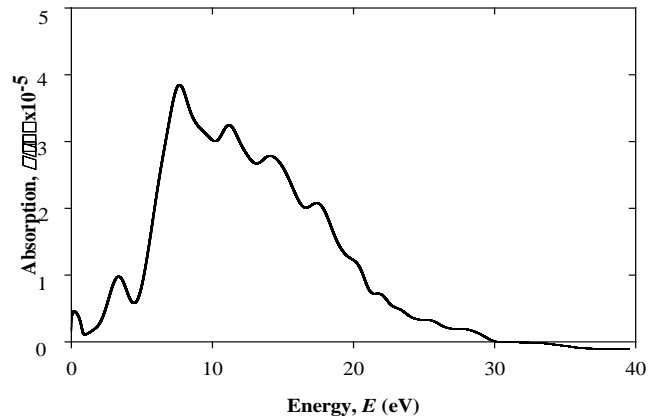


Fig.4. Total and partial DOS at p =0 GPa

3.4 OPTICAL PROPERTIES

Optical properties are important in solid state Physics because the study of the optical functions of solids provides a better understanding of the electronic structure. Fig. 5 show the optical functions of AlB₂, calculated for photon energies up to 40 eV for the polarization vector in [100] direction. We have used a 0.5 eV Gaussian smearing for all calculations. The reflectivity spectrum shows that the material is a good reflector within the energy range, 8.15-20.65 eV. This compound has absorption bands in the low energy range due to its metallic nature. In the energy-loss spectrums, the first peaks are found at $\omega_{-p} = 21.02\text{eV}$, corresponding to the abrupt reduction of reflectivity,

$R(\omega)$. This indicates to a rapid reduction in the reflectance. we see that the photoconductivity starts with zero photon energy, which indicates that the materials should have no band gap. It is seen that the real part $\epsilon_1(\omega)$ of the dielectric function vanishes at about 21.03 eV. This is the energy at which the reflectivity exhibits a sharp drop and the loss function, shows a first peak for AlB₂ is 21.02 eV. The static refractive index of AlB₂ is found to have the values ~ 6.76



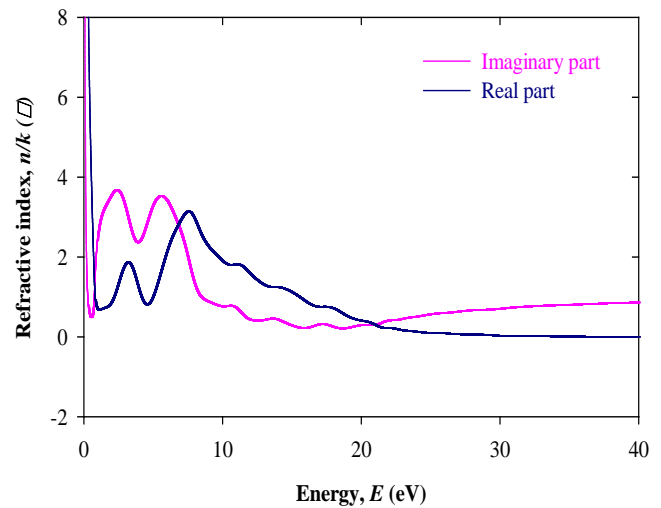
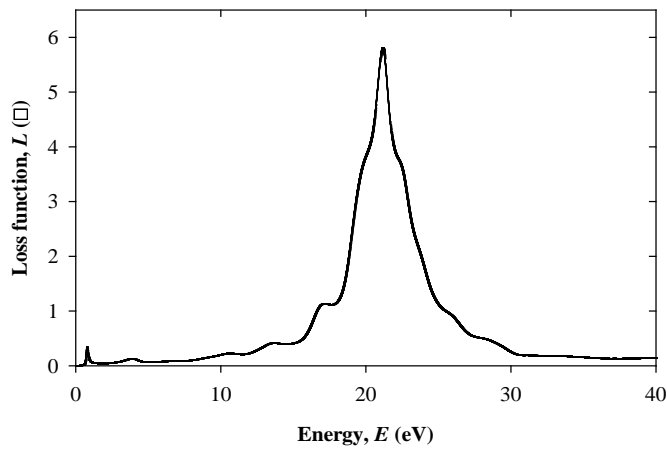
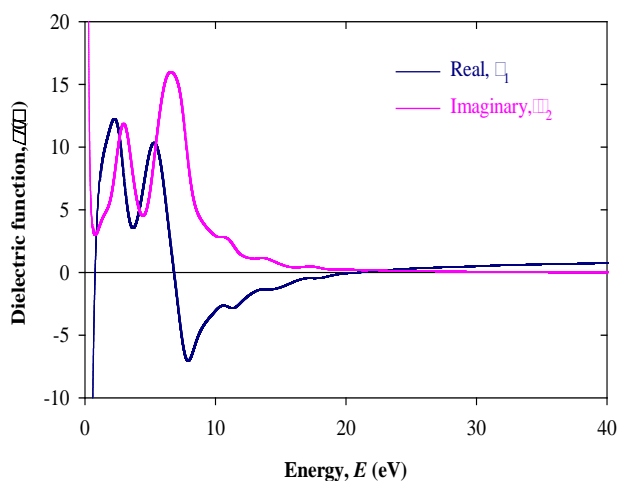
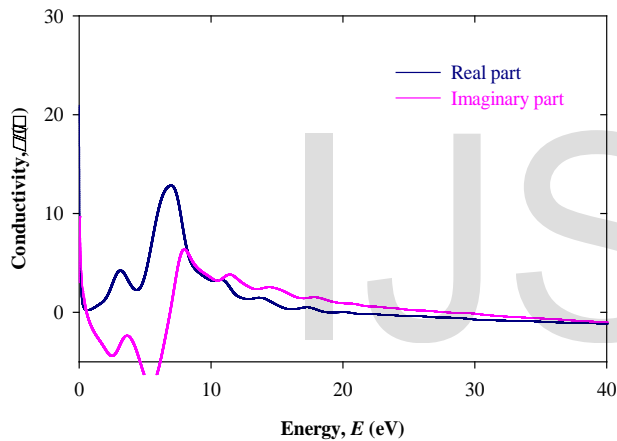


Fig. 5 (a) Reflectivity spectra, (b) Absorption coefficient, (c) Loss function, (d) Conductivity, (e) Dielectric function, (f) Refractive index of AlB₂.



3.5 THERMODYNAMIC PROPERTIES

To investigate the thermodynamic properties of AlB₂, we employ the quasi-harmonic Debye model. We computed the thermodynamic parameters including the normalized volume, bulk modulus, thermal expansion coefficient, specific heats, and Debye temperature etc. at several temperatures and pressures. The detailed description of quasi-harmonic Debye model can be found in the literatures [30, 31]. The bulk modulus increases linearly with increasing pressure and it drops by 40.44% from 0 to 50 GPa. In the low-temperature limit, the specific heat exhibits the Debye T^3 power-law behavior and both approach the classical asymptotic limit of $C_V = 3nNk_B = 74.81$ J/mol-K for this compound. We know that the Debye temperature is related to the maximum thermal vibration frequency of a solid. Due to this relationship, the variation of Debye temperature with pressure and temperature also reveals the changeable vibration frequency of the particles in AlB₂. In the present work, the Debye temperature Θ_D , increases by 28.34% when the pressure is increased. It is also observed that as the pressure increases, the increase of α with temperature becomes smaller, especially at higher temperatures. At a given temperature, α decreases strongly with increasing pressure, the thermal expansion coefficient α at 1200 K is just a little larger than at 1000 K, which means that the temperature dependence of α is very weak at higher temperatures and higher pressures.

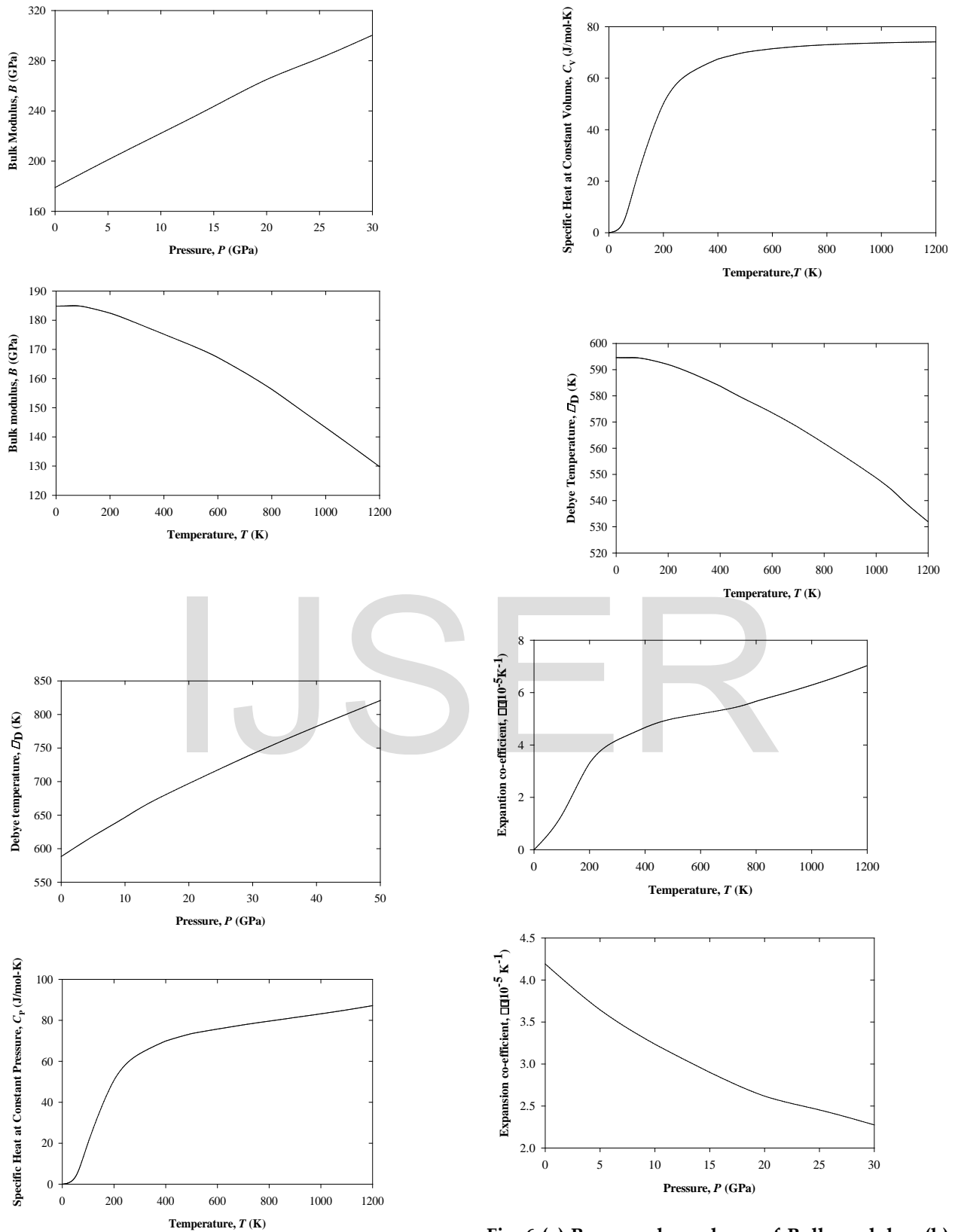


Fig. 6 (a) Pressure dependence of Bulk modulus, (b) Temperature dependence of Bulk modulus at zero pressure, (c) Temperature dependence of specific heat at constant volume at $p = 0$ GPa, (d) Temperature dependence of specific heat at constant pressure at $p = 0$ GPa, (e) Pressure depend-

ence of Debye temperature at $T = 300$ K, (f) Temperature dependence of Debye temperature at $P = 0$ GPa, (g) Pressure dependence of expansion co-efficient, (h) Temperature dependence of expansion coefficient at $p = 0$ GPa of AlB_2 .

4 CONCLUSIONS

The results we present on several ground states, the structural, elastic, electronic, optical and thermodynamic properties for AlB_2 are obtained using the first-principles calculations implemented in CASTEP code within the GGA approximation.

Our results are mostly in agreement with the available experimental and theoretical findings. Thermodynamical results at various temperatures and pressures were not considered in previous experiments and comprise the original contributions of this study. It is observed that the lattice parameters and normalized lattice parameters decrease smoothly with increasing pressure. The calculated elastic constants allow us to obtain the macroscopic mechanical parameters of AlB_2 , namely bulk modulus and shear modulus. The elastic anisotropy of crystals is calculated in different ways and defined by the ratio $A = 2C_{44} / (C_{11} - C_{12})$. The factor $A = 1$ represents complete isotropy, while values smaller or greater than this measure the degree of anisotropy. Since, here $A = 0.05$, therefore, AlB_2 show anisotropic behavior. The parameter $K_c/K_a = (C_{11} + C_{12} - 2C_{13}) / (C_{33} - C_{13})$ which expresses the ratio between linear compressibility coefficients of hexagonal crystals. The value of K_c/K_a is 2.64 for AlB_2 , represents that the compressibility for the given compound along c- axis is greater than along a- axis. We conclude that the band structures of AlB_2 are mainly dominated by B $2p$ states. The calculated electronic band structures of AlB_2 are doubly degenerate along Γ -A direction. When the pressure is increased from 0 to 50 GPa, it is seen that the flat band along Γ -A direction become more flat. It is observed that the major contributions around the Fermi energy are mainly from the B $2p$ states and also suggest that the B $2p$ states dominate the conductivity of AlB_2 . In the Conduction bands, the peaks of Al $3s$ are slightly broadening and the intensities are slightly decreased. It is also observed that for this compound the total DOS decreases with increasing pressure.

The negative values of $\epsilon_1(\omega)$ indicate that the compound has a Drude-like behavior. We therefore choose to add a conventional Drude contribution to the calculated results. In the low-temperature limit, the specific heat exhibits the Debye T^3 power-law behavior and both approach the classical asymptotic limit of $C_V = 3nNk_B = 74.81$ J/mol-K. The variation of Debye temperature with pressure and temperature also reveals the changeable vibration frequency of the particles in AlB_2 . In the present work, the Debye temperature Θ_D , increases by 28.34% when the pressure is increased from 0 to 50 GPa. It is noted

that at zero pressure α increases exponentially with temperature at low temperatures and gradually turns to a linear increase at high temperatures. At a given temperature, α decreases strongly with increasing pressure, the thermal expansion coefficient α at 1200 K is just a little larger than at 1000 K, which means that the temperature dependence of α is very weak at higher temperatures and higher pressures.

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