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Brucite ($Mg(OH)_2$) under small perturbation: A combined first principles and synchrotron X-ray diffraction study

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ABSTRACT

In this work, we discuss the discrepancy observed in previous experimental and theoretical studies in determining hydrogen's position in brucite ($Mg(OH)_2$) at ambient conditions with the aid of temperature dependent synchrotron x-ray powder diffraction (XRPD) and first-principles calculation based on density functional theory. To date, the literature reports two competing descriptions of brucite's ground state structural configuration based on *P*-3*m*1 and *P*-3 symmetry without a conclusive choice for the best solution. Our study confirms that $Mg(OH)_2$ exists in *P*-3*m*1 structure at 0 GPa and 0 K from its lattice dynamical and mechanical stability. Transition from *P*-3*m*1 to *P*-3 symmetry occurs under small structural perturbation causing a volume compression. We show with the aid of temperature dependent XRPD that perturbations causing a small volume compression can lead to a transition in brucite from hydrogen ordered (*P*-3*m*1 symmetry) to hydrogen disordered (*P*-3 symmetry) structure. DFT calculations with different exchange-correlation potentials show that the contradicting results among previous static calculations can be resolved by the use of a van der Waals density functional. Further, we report temperature dependent thermal expansion of brucite in the temperature range 110–400 K.

1. Introduction

Brucite ($Mg(OH)_2$) is an important geological mineral being a potential source of water in earth's mantle. Due to its structural simplicity and presence of hydroxyl group along its (0001) cleavage surface, it serves as a model material to study both the chemical behaviour of complex layered hydrous minerals as well as the behaviour of water on a surface having hydroxyl group [1]. Brucite has also been studied to understand the hydrogen bonding and compression behaviour of layered dense hydrous magnesium silicates (DHMS) since $Mg(OH)_2$ is present as a component unit in DMHS which are potential carriers of water in the earth's mantle [2]. Neglecting the hydrogen atom, brucite is isostructural with the family of metal hydroxides $M(OH)_2$, M = Mg, Co, Ni, Mn, Fe and Cd which consists of layer sharing octahedra with overall trigonal structure (space group symmetry *P*-3*m*1). The octahedra are distorted since the shared edges are shorter than the unshared edges due to metal-metal repulsion. Within the interlayer, the hydroxyl group is directed along the layer-stacking direction and is attached to three metal atoms. Each hydroxyl group is further surrounded by three downward pointing hydroxyl group of adjacent layers. At ambient conditions, the non-bonded H–H distances reported in the literature for these compounds are approximately 2.2 Å in $Ca(OH)_2$, 2.199 Å in $Co(OH)_2$, 2.198 Å in $MgOH_2$ and 1.92 Å in $Ni(OH)_2$ which are shorter than Pauli's van der Waals separation (2.4 Å) [3]. Under pressure, the interlayer spacing and hence the non-bonded H–H distance decreases, which increases the H–H repulsion. At a critical bond distance, the H–H repulsion destabilizes the initial structure and the structure will no longer remain in an ordered structure with *P*-3*m*1 symmetry. Hence a transition from ordered to the disordered structure under pressure is most likely to occur in all these compounds.

The crystal structure of $Mg(OH)_2$ with protons at 2*d* Wyckoff position $(1/3, 2/3, z)$ was first proposed by Zigan et al. [4]. Subsequent high pressure study showed that the proton no longer remains at 2*d* sites and are displaced from the three-fold axis, corresponding to a three-site split-atom model, where each H atom $(1/3, 2/3, z)$ is split into three positions $6i(x,\bar{x}, z)$ with an equal occupation [5]. The three site model for hydrogen disordered brucite was initially proposed by Parise et al. [6] from neutron diffraction study in the pressure range 0.4 GPa–9.3 GPa. Two models having 1/3 occupancy of three equivalent 6*i* Wyckoff position with XGT arrangement $(x,2x, z)$; $x > 1/3$ [6–9] and XLT arrangement $(x,2x, z)$; $x < 1/3$ [10] were proposed for disordered phase of $Mg(OH)_2$. The XGT and XLT model reduces the symmetry to *P*-3 with

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A combined synchrotron diffraction and first-principles investigation on structural properties of $Co(OH)_2$ under pressure up to 7 GPa

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Abstract – An H–H repulsion induced structural anomaly in $Co(OH)_2$ at pressure around 2.5 GPa is reported using systematic synchrotron X-ray powder diffraction and density functional theory (DFT) based first-principles calculations. The diffraction pattern evidences anomalous pressure dependence of Bragg peaks (003) and (013) compared to others indicating a much stronger change in the hydrogen sublattice with pressure. Analysis of the lattice parameters reveals a subtle but clear change in the trend of the out-of-plane to in-plane lattice constants' ratio above 2.5 GPa. Two independent pressure runs using two different pressure transmitting media yielded similar results, thus proving the observations to be independent of the minor variations in the quasi-hydrostatic conditions during the pressure run. DFT calculations were performed on an extended unit cell of $Co(OH)_2$ which enables the description of hydrogen in either ordered or disordered state. Calculations showed that only the hydrogen disordered structure is energetically favourable at high pressures. We attribute the anomalous behaviour of the (003) and (013) Bragg peaks above 2.5 GPa to the charge delocalization along hydrogen sublattice coming due to the hydrogen ordered-disordered transition, in agreement with DFT results showing the H disordered state to be energetically more favourable at higher pressure. A second-order Brich-Murnaghan equation of state (EoS) can well describe the low- and high-pressure regime separately with a 20% higher bulk modulus of the latter, further supporting the subtle transition around 2.5 GPa. Present results also complement the previous Raman spectroscopic study on $Co(OH)_2$ which reported anomalous behaviour in the $A_{1g}(2)$ mode around 2.5 GPa.

High-pressure studies of hydrous minerals have been a subject of intense research as these compounds play a major role in carrying water into earth's interior and may provide answers for many geological phenomena. Among the hydrous minerals, the simplest prototypes are the $M(OH)_2$ hydroxides, where M is a divalent cation such as Co, Ni, Cd, Fe, Mg, or Ca, which have brucite-type structures with trigonal space group $P\text{-}3m1$. Each M atom is coordinated with six oxygen atoms forming edge-sharing MO_6 octahedra with the Mg atom at the $1a$ (0, 0, 0) Wyckoff position, while the O and H atoms at the $2d$ (1/3, 2/3, z) site. Each oxygen atom is bonded with hydrogen resulting in the distribution of hydrogen atoms between the layers of MO_6 octahedra. Each upward-pointing O-H group is equidistant from three downward-pointing O-H groups and vice versa. This simple framework gives rise to the peculiar O-H–O and H–H interaction which will vary significantly as the interlayer separation changes and interlayer separation can be readily modified via high pressure. Although these $M(OH)_2$ compounds have identical lattice symmetry at ambient conditions, their

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Article

Pressure Induced Hydrogen Order–Disorder Transition in β-Ni(OH)$_2$

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Sharad Babu Pillai, Boby Joseph,* Deepak Upadhyay, Carlo Marini, and Prafulla K Jha

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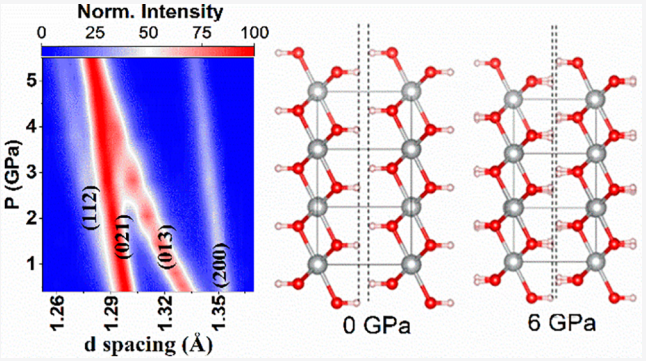
ABSTRACT: Here we address the challenging problem of pressure induced hydrogen sublattice disordering in layered hydroxides using synchrotron X-ray powder diffraction (XRPD) and first-principles calculations based on density functional theory (DFT) using β-Ni(OH)$_2$ as a model system. XRPD data demonstrate anomalous behaviors in some Bragg peaks. The shift in (003) and (013) peaks with pressure is large as compared to that of other Bragg peaks and these two peaks are not discernible above 5 GPa, similar to the characteristic observed in β-Co(OH)$_2$. The underlying changes within the structure were probed using DFT calculations on a $\sqrt{3} \times \sqrt{3} \times 1$ supercell of β-Ni(OH)$_2$. Structural relaxation yields a hydrogen disordered structure as the ground state for β-Ni(OH)$_2$ at pressures above 5 GPa. The disordered model also describes well the high pressure XRPD data. The hydrogen sublattice largely affects the electronic density of the (003) and (013) lattice planes thus permitting the development of a one-to-one correspondence of the anomalous behavior of these Bragg peaks with the hydrogen sublattice disordering. Further evidence of a possible structural rearrangement was obtained by the pressure dependence of the unit-cell volume (P vs V) as well as the ratio of the out-of-plane to in-plane lattice parameter (c/a). With the availability of a large number of data points with smaller pressure steps, the above two quantities are shown to behave differently below and above 2.5 GPa. The P vs V data are well described by a second order Birch–Murnaghan equation-of-state, whereas for c/a, a clear change in trend is observed for data above 2.5 GPa. The pressure response of β-Ni(OH)$_2$ is similar to that of Co(OH)$_2$ reported in our recent high pressure study, and therefore pressure induced hydrogen order–disorder transition may be a general characteristic of layered hydroxides.



INTRODUCTION

High pressure studies on layer hydroxides serve as primary reference for understanding the behavior of complex hydrous minerals abundant in the earth's mantle and provide valuable information underlying various geophysical phenomena. Apart from geophysical implications, their unique structural configuration involving stacked layers incorporating hydroxyl groups gained much attention among researchers as it enables exploring various structural phenomena by manipulating the interlayer separation. The simplest prototype of layered hydroxides widely investigated belongs to the M(OH)$_2$ family [M = Mg, Ca, Co, Ni, etc], which are often referred to as brucite-type hydroxides. Even though they are structurally simple, their structures at ambient and high pressure conditions have been debated for long, questioning the preferred hydrogen sites and its effect on pressure response of the lattice. This ambiguity arose due to competing H–H repulsion and attractive hydrogen bonding in these materials. The widely accepted crystal structure of these M(OH)$_2$ is a CdI$_2$ structure in the P-3m1 space group with a metal atom at the 1a (0, 0, 0) Wyckoff position, while O and H atoms are at the 2d (1/3, 2/3, z) site. Under pressure, the interlayer separation of layers decreases and hydrogen atoms from opposite layers comes close to each other, thereby increasing the contribution of H–H repulsion to nonbonded atomic interactions. Since the distance cannot be reduced arbitrarily, at a critical interlayer separation, H–H repulsion destabilizes the initial structure.[1] Though this phenomenon sounds trivial, the structural changes driven by H–H repulsion exhibits large diversity among M(OH)$_2$ compounds.

High pressure spectroscopic[2−7] and crystallographic[4,5,8−10] studies of M(OH)$_2$ compounds showed that they exhibit complex structural phenomena such as structural frustration, sublattice (H-layer) amorphization,[11] and pressure-induced amorphization.[2,3,12] Ca(OH)$_2$ has been shown to undergo

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First principles study of hydrogen bond symmetrization in δ-AlOOH

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The high pressure behaviour of the hydrous mineral δ-AlOOH has been investigated by many experimental and theoretical studies, but the discrepancy in predicting the value of hydrogen symmetrization pressure was not resolved. Here, we investigated the high pressure behaviour of δ-AlOOH using first principles calculations and found that with proper optimization using pressure routine control, local density approximation (LDA) predicts the hydrogen symmetrization pressure as 15 GPa which is in good agreement with the experimentally predicted value which resolves the existing discrepancy and hence proving the validity of LDA in predicting the hydrogen symmetrization pressure. We further studied the compressibility behaviour of δ-AlOOH at low pressures and confirmed the $P2_1nm$ to Pnnm transition of δ-AlOOH shown by the experimental work [Kuribayashi *et al.*, Phys. Chem. Miner. **41**, 303–312 (2014)]. We have also analysed the dependence of elastic constants, elastic moduli, sound velocities, and Raman spectrum of δ-AlOOH with pressure and found that a subtle change in the position of the hydrogen atom at hydrogen symmetrization pressure results into drastic changes in elastic and vibrational properties. Further, this study has been used to discuss the seismic anomalies observed in the upper mantle beneath the Deccan Volcanic Province in India and the Java subduction zone in the eastern flank of the Indian Ocean. *Published by AIP Publishing.* https://doi.org/10.1063/1.5019586

I. INTRODUCTION

The hydrous mineral δ-AlOOH which is stable between 40 to 138 GPa and 1270 to 1750 K has gained much interest in the community of geophysicists and geochemists due to its occurrence in the mantle condition, being a source of water transportation to the deep mantle and a potential water reservoir in cold conducting slabs.[2–9] Furthermore, δ-AlOOH, a polymorph of diaspore (α-AlOOH) and boehmite (γ-AlOOH), is also important for incorporating a significant amount of Mg and Si into the structure.[10] The recently found stable solid solution of AlOOH-$MgSiO_2(OH)_2$ under lower mantle conditions and turning increasingly aluminous with increasing pressure-temperature conditions[7,8,11–13] suggests the existence of the aluminium end member at the base of the mantle. δ-AlOOH without H atoms at ambient conditions exists in the orthorhombic phase with space group $P2_1nm$ very close to the $CaCl_2$ type of SiO_2.[10,14,15]

There exist many experimental[2–4,9,10,15] and theoretical[6,16–18] studies mainly based on first principles calculations focussing on hydrogen bond symmetrization in δ-AlOOH. However, there is a large difference in these experimental and theoretical results including hydrogen symmetrization pressure. The hydrogen bond symmetrization is a structural change of the hydrogen atom to the middle point of two neighbouring oxygen atoms associated with the deformation of the potential surface existing between two oxygen atoms from double minimum to single minimum under pressure.[19] The hydrogen bond symmetrization helps in stabilizing the hydrous mineral such as δ-AlOOH and phase D ($MgSi_2O_6H_2$) under pressure.[20] Using first principles calculations, Tsuchiya *et al.*[16] reported that δ-AlOOH with the symmetric hydrogen bond is stable at 28 GPa. In another study, it was found that δ-AlOOH undergoes structural transformation from space group $P2_1nm$ to Pnnm with O-H bond symmetrization at the same pressure.[6] Further, the diagonal elastic constants C_{11} and C_{22} and the shear elastic constants C_{44}, C_{55} and C_{66} increase anomalously and normally, respectively, at 28 GPa.[6] The compressibility of δ-AlOOH close to 30 GPa reported by Tsuchiya *et al.*[16] is quite far from the earlier studies reported in Refs. 14 and 17. While Panero and Stixrude[17] identified the symmetric hydrogen bond at 0 GPa, Vanpeteghem *et al.*[14] did not observe any phase transition up to 22.5 GPa from their high pressure synchrotron powder X-ray diffraction experiments. Using Raman and Nuclear Magnetic Resonance (NMR) spectra, Xue and Kanzaki[21] ruled out the formation of hydrogen bond symmetrization in δ-AlOOH at ambient conditions. However, they emphasized an important role of this strong bonding in the stability of δ-AlOOH under high pressure conditions. Li *et al.*[18] however fixed an upper limit of 50 GPa for the said hydrogen bond symmetrization using theoretical calculations. Further, Sano-Furukawa *et al.*[22] reported the characteristic changes in XRD profiles of δ-AlOOH and δ-AlOOD up to 20 GPa and found alteration in their compressional properties. However, *in situ* high pressure X-ray diffraction of δ-AlOOH[22] and neutron diffraction study of δ-AlOOD[23] suggested a subtle change in the compressibility below ∼10 GPa due to hydrogen bond symmetrization. A single crystal synchrotron X-ray diffraction study by Kuribayashi *et al.*[1] predicted a pressure induced structural phase transition of

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Catalytic activity and underlying atomic rearrangement in monolayer CoOOH towards HER and OER

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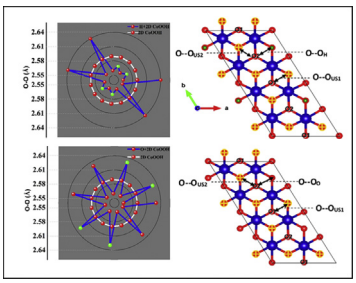
HIGHLIGHTS

- Activity of 2D CoOOH investigated for HER and OER via DFT calculations.
- Interplanar O–O separation on adsorption of H/O on pristine 2D CoOOH.
- Adsorption of H and O atom turns 2D CoOOH into metallic.
- 2D CoOOH is a potential candidate for better HER activity as compared to OER.

GRAPHICAL ABSTRACT



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ABSTRACT

For efficient hydrogen and oxygen production, design and synthesis of cost-effective, stable and active materials are inevitable. In this work, the catalytic activity of 2D CoOOH towards hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) has been investigated using first principles calculations based on density functional theory. The adatom induced structural rearrangement have been investigated from structural parameters as well as charge redistribution in 2D CoOOH. The preferred site for hydrogen and oxygen adsorption were found to be the top site of oxygen atom of 2D CoOOH. The catalytic activity of HER and OER towards 2D CoOOH was studied by calculating the Gibbs free energy. Our study revealed that the 2D CoOOH serve better as a catalyst for HER than OER with adsorption energy of −0.45 and −3.68 eV respectively suggesting its efficient use for hydrogen production. We further investigated the changes in electronic properties of 2D CoOOH on adsorption of hydrogen and oxygen atom.

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First principles high pressure studies on group-14 element pernitrides

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ABSTRACT

The search of ultra hard materials is inevitable in high pressure device applications. Nitrides of group-14 elements have been foreseen as potential candidates in replacing existing hard materials. In a recent experiment, pyrite structures of SiN_2, GeN_2 and SnN_2 have been synthesized at high pressure and are shown to have high bulk modulus. Though their existence and bulk modulus are known, limited studies have been devoted to SiN_2, GeN_2 and SnN_2. In the present work, we have performed the first principles calculations to investigate structural, electronic, mechanical and vibrational properties at ambient as well as high pressure condition. The physical properties of SnN_2 and high pressure lattice dynamical properties of SiN_2 and GeN_2 are explored for the first time. SiN_2 has higher bulk modulus among all MN_2 (where M = Si, Sn and Ge), and increases further with increase in pressure. The increase in elastic moduli of MN_2 have been related to the shortening of M-N bond length at high pressure. Electronic properties of these pyrites suggest that the bandgap increases with pressure. We further characterize these MN_2 at high pressure using theoretically calculated Raman spectra. Frequency of N–N stretching A_g and T_g modes confirms the single bond character of nitrogen dimer in all studied MN_2 compounds.

1. Introduction

The search for excellent mechanical properties such as high hardness and strength of a material has drawn the attention of researchers towards ultrahard and superhard materials like diamond and cubic boron nitride [1]. However, due to their own limitations, new materials such as nitrides, oxides, and borides with properties comparable to those of diamonds [2–5] are being searched for better replacements. Exploration of pernitrides began after many experimental and theoretical attempts in search of nitrogen rich stoichiometries [6–16]. A series of transition metal pernitrides (MnN_2, TaN_2, NbN_2, VN_2, ZrN_2, and HfN_2) were predicted using combined first principles calculations and global structure search method. Recently, Alkhaldi and Kroll [17] considered chemical potential change of molecular nitrogen in their first principles calculations and derived pressure-temperature phase diagrams for guiding experimental synthesis as well as predicting the formation of nitrogen rich stoichiometries under high pressure and temperature. The quest for nitrogen rich materials is still considered as an important motif among material scientists due to their interesting chemical properties and possibility of being environmental friendly high density materials following which researchers have proposed various experimental and conceptual strategies for having nitrogen rich compounds [18–32], including stable nitrides with electro-positive elements at high pressure [23,32]. Several group-14 nitrides of the stoichiometry M_3N_4, where M replaces the group-14 elements, have been widely investigated for their mechanical properties both experimentally and theoretically [33–38]. The high stability and easy release of molecular N_2 makes the synthesis of nitrogen-rich stoichiometries such as C_3N_4 and $C_{11}N_4$ challenging [39]. Weihrich et al. [39] provided a hypothetical pyrite type structure for CN_2, iso-electronic to SiP_2 [40] and proposed that the formation of CN_2 does not involve the breakage of strong N–N bond of N_2 compared to the formation of other CN_x compounds. The realization of the pyrite structure allows building a three-dimensional network of C–N bonds without changing the strong N–N bonding.

Limited studies have been done on group-14 elemental pernitride stoichiometry MN_2 (M = Si, Ge, Sn) in pyrite structure [41–43]. Weihrich et al. [41] showed the pyrite SiN_2 to be an insulator with calculated optical band gap of 5.5 eV and GeN_2 to be semiconducting with band gap of 1.4 eV. Chen et al. [43] suggested the formation of SiN_2 in the pyrite structure at a pressure above

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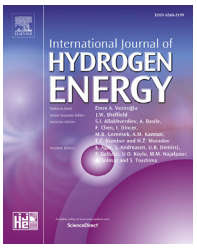

Hydrogen evolution reaction and electronic structure calculation of two dimensional bismuth and its alloys

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ABSTRACT

We present a systematic ab initio study of atomic hydrogen and oxygen adsorption on bismuthene monolayer and its alloys with arsenic and antimony through electronic structure calculations based on density functional theory within generalized gradient approximation. We systematically investigated the preferable adsorption site for hydrogen and oxygen atom on 2D Bi, BiAs and BiSb. It was found that the hydrogen atom prefers top site of bismuth atom and oxygen atom prefers to reside in the hexagonal ring of these 2D bismuth alloys. The free energy calculated from the individual adsorption energy for each monolayer subsequently guides us to predict the best suitable catalyst among the considered 2D monolayers. The 2D BiSb serves better for hydrogen evolution reaction (HER) with hydrogen adsorption energy as −1.384 eV while 2D BiAs is suitable for oxygen evolution reaction (OER) with oxygen adsorption energy as −1.092 eV. We further investigated the effects of the adsorbate atom on the electronic properties of 2D Bi, BiAs and BiSb. The adsorption of oxygen on 2D BiAs and BiSb was shown to reduce the bulk band gap by 40.56 and 67.79% respectively which will be advantageous for the observation of Quantum Spin Hall effect at ambient conditions.

Introduction

Topological insulators (TIs) have gained great research enthusiasm in recent years due to their newly discovered quantum states and exotic properties [1,2]. Many layered thin films have been predicted to show quantum spin hall (QSH) effect, among which graphene was the first two dimensional (2D) candidate followed by silicene [3], germanene [3], stanene [4,5], plumbene [6] and arsenene [7]. However, the weak spin-orbit coupling (SOC) in these 2D materials results in an unobservable bulk gap not enough to support accessible QSH effect experimentally at room temperature (RT) [8]. Further, materials with strong SOC such as heavy metal bismuth (Bi) [9,10] and antimony (Sb), [11] their films were proposed to be Topological insulators and have been grown on various substrates [12,13]. However these topological insulators were shown to have very small finite band gap ~0.6 eV for bilayer Bi film making QSH observation challenging at room temperature. Other series of monolayer honeycomb structures from group IV and binary compounds comprising of group III and V were studied systematically using first principles calculation

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Vibrational and Raman Spectroscopic Study of Cubic Boron Nitride Under Pressure Using Density Functional Theory

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Pressure-dependent mechanical, vibrational and Raman spectroscopic study of the cubic boron nitride in context of recent experimental Raman spectroscopic has been performed using the *ab initio* calculations based on density functional theory. Detailed analysis of the pressure-dependent mechanical and phonon properties shows that the pressure significantly affects the elastic constants and phonon frequencies. There is a systematic variation of elastic properties with pressure while a polynomial expression is used to fit the pressure dependence of the Raman shift. The longitudinal optical–transverse optical (LO-TO) splitting reduces with pressure, and the intensity of both LO and TO peaks start diminishing after 750 GPa. The phonon dispersion curves up to 1000 GPa indicate its dynamical stability. The lower slope of frequency versus pressure for the LO and TO modes at higher pressures suggests its use for pressure calibration at higher pressures.

Key words: High pressure, *ab initio*, Raman spectroscopy, phonons, stability

INTRODUCTION

In recent years, cubic boron nitride (c-BN), a diamond-like polymorph having an amazing aspect of sp^3 hybridization, with the widest band gap of 6.3 eV among III-group nitride semiconductors, has been extensively studied. It has some outstanding properties such as hardness, chemical inertness, and high thermal conductivity.[1–15] c-BN, which is a dense allotrope of boron nitride, belongs to a face-centred cubic lattice with space group $F\bar{4}3$ m. The large interest in this compound originates from its promising potential for short-wavelength light-emitting diodes, semiconducting lasers, optical detectors and high-temperature, high-power and high-frequency devices.[16–18]

Since most of these applications require the involvement of phonons and subjecting c-BN to extreme conditions, the study of vibrational properties as a function of high pressure and temperature is required.[9] Raman spectroscopy is a direct tool to probe the changes in bonding and structure of materials through investigation of their vibrational properties at extreme conditions.[15] The Raman spectrum of c-BN exhibits two intense lines at 1054 cm^{-1} and 1305 cm^{-1} at ambient conditions due to zone-centre transverse optical (TO) and longitudinal optical (LO) modes, respectively.[15] Many studies have reported on the pressure and temperature dependences of the frequency shift of Raman modes.[9,19–24] However, the LO mode has not been clearly observed in high-pressure experiments using a diamond anvil cell above 3 GPa due to the overlap of this mode with the intense Raman line of diamond.[15] Therefore, use of the TO mode for the pressure calibration of diamond anvil cells under high-pressure and -temperature conditions was proposed.[9,23,24] First-principles computations and other theoretical methods predict that the cubic (B3) BN transforms to the rock-salt (B1) structure at pressures between 394 GPa and 1100 GPa,[2,25,26] well beyond the current limits of both experimental measurements and industrial needs. Recently, de Koker[27] used first-principles molecular dynamics to evaluate the thermodynamics of zinc blende structured and liquid boron nitride at extreme conditions

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COMMUNICATION

Unexpected persistence of cis-bridged chains in compressed AuF_3

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Raman scattering measurements indicate that cis-bridged chains are retained in AuF_3 even at a compression of 45 GPa - in contrast to meta-GGA calculations suggesting that structures with such motifs are thermodynamically unstable above 4 GPa. This metastability implies that novel gold fluorides (e.g. AuF_2) might be attainable at lower pressures than previously proposed.

Due to its chemical inertness gold forms connections mainly with highly reactive elements. In fluorine-rich compounds gold usually adopts the +3 oxidation state,[1] although compounds with gold(I),[2] gold(II),[3,4] and gold(V)[5,6] are also known. Only two binary gold fluorides are stable in the solid state: AuF_3 [7] and AuF_5.[5] Both AuF and AuF_2 can only be stabilized as isolated molecules in a collision-free environment.[8,9] Organometallic compounds containing gold both in the +1 and +3 oxidation state are important catalysts in a range of reactions,[10] and AuF_3 is a promising precursor for the synthesis of extremely Lewis acidic catalysts.[11,12]

Theoretical studies hint at the increased reactivity of fluorine at high pressure (p > 1 GPa).[13–20] This creates an opportunity for the stabilization of novel gold fluorides, as indicated by some early studies.[21–23] Indeed, recent calculations suggest that at large compression AuF_2, AuF_4, and even AuF_6 become thermodynamically stable.[19,20] However, these predictions still await experimental verification. In no fact high-pressure experimental data has been reported even for the most stable gold fluoride, AuF_3.

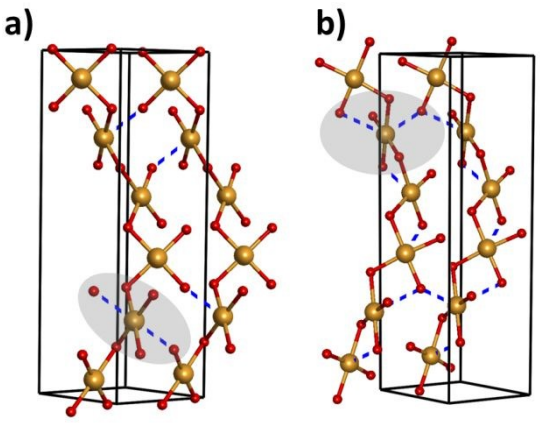

Fig. 1 The ambient-pressure $P6_122$ structure of AuF_3 (a) together with the high-pressure $P6_1$ polymorph (b). Gold/red balls mark Au/F atoms. Grey lobes mark differences in secondary Au···F contacts (depicted with dashed blue lines)

In an attempt to understand how large compression affects the properties of AuF_3, we performed a study combining both experimental (Raman spectroscopy) and theoretical (Density Functional Theory, DFT) methods‡. At ambient condition AuF_3 adopts a hexagonal structure (space group $P6_122$, $Z = 6$)[24] comprised of cis-bridged helical AuF_3 chains built from planar AuF_4 squares (Fig. 1a). Apart from two pairs of Au-F bonds (bridging: R_b = 2.00 Å, terminal: R_t = 1.88 Å) there are two equivalent inter-chain Au···F contacts (R_{inter} = 2.76 Å). The square planar coordination of Au^{3+} (d^8 electron count) leads to diamagnetic properties of AuF_3; the orange colour of this compound indicates presence of an electronic band gap between 2.5 and 2.9 eV.

The non-centrosymmetric $P6_122$ structure exhibits 28 Raman-active modes ($5A_1 + 12E_2 + 11E_1$). By comparing the ambient-pressure Raman spectrum with frequencies and intensities of Raman bands simulated with DFT (ESI†, Table S1

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† Electronic Supplementary Information (ESI) available: experimental and calculation details, comparison between theory and calculations at ambient pressure, simulated Raman spectra, depiction of the *C2/c(α)* and *C2/c(β)* structures, crystal structure of the novel high-pressure polymorph of AuF_3. See DOI: 10.1039/x0xx00000x

Inorganic Chemistry

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High-Pressure Phase Transitions of Zinc Difluoride up to 55 GPa

Dominik Kurzydłowski,* Anna Oleksiak, Sharad Babu Pillai, and Prafulla K. Jha

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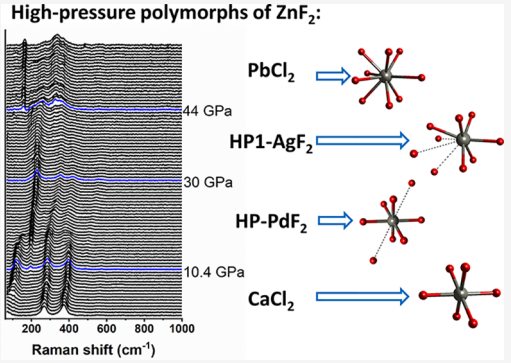
ABSTRACT: Studying the effect of high pressure (exceeding 10 kbar) on the structure of solids allows us to gain deeper insight into the mechanism governing crystal structure stability. Here, we report a study on the high-pressure behavior of zinc difluoride (ZnF_2)—an archetypical ionic compound which at ambient pressure adopts the rutile (TiO_2) structure. Previous investigations, limited to a pressure of 15 GPa, revealed that this compound undergoes two pressure-induced phase transitions, i.e., $TiO_2 \rightarrow CaCl_2$ at 4.5 GPa and $CaCl_2 \rightarrow$ HP-PdF_2 at 10 GPa. Within this joint experimental−theoretical study, we extend the room-temperature phase diagram of ZnF_2 up to 55 GPa. By means of Raman spectroscopy measurements we identify two new phase transitions, HP-$PdF_2 \rightarrow$ HP1-AgF_2 at 30 GPa and HP1-$AgF_2 \rightarrow PbCl_2$ at 44 GPa. These results are confirmed by density functional theory calculations which indicate that in the HP1-AgF_2 polymorph the coordination sphere of Zn^{2+} undergoes drastic changes upon compression. Our results point to important differences in the high-pressure behavior of ZnF_2 and MgF_2, despite the fact that both compounds contain cations of similar size. We also argue that the HP1-AgF_2 structure, previously observed only for AgF_2, might be observed at large compression in other AB_2 compounds.



INTRODUCTION

The rationalization of the crystal structures of solids is an ongoing endeavor in material sciences. Concepts such as the Goldshimdt tolerance factor,[1] Pauling rules,[2] and the bond-valence index[3] are important tools for understanding and predicting crystal geometry. Metal difluorides (MF_2) are an excellent group of compounds for testing these and other concepts.[4,5] One reason for this is the large variation of the M^{2+} cationic radius which increases from 0.45 Å for Be^{2+} to 1.35 Å for Ba^{2+} (Shannon's effective ionic radius for 6-fold coordination, $R_{M^{2+}}$).[6] Another important feature of MF_2 systems lies in the range of electronic configurations adopted by M^{2+} cations, i.e., for group 2 metals they exhibit a closed-shell and for group 12 and 14 a filled subshell (*d* for group 12, *s* and *d* for group 14), while transition-metal cations have an open *d* shell.

In recent years particular attention was drawn to phase transitions of MF_2 compounds induced by pressures exceeding 1 GPa (=10 kbar). Numerous experimental and theoretical investigations were conducted in order to establish the phase sequence for these compounds.[7−25] The motivation for these studies was the fact that the behavior of difluorides at these conditions can serve as an analogue of the high-pressure transformations of dioxides, in particular, of SiO_2.[7,8] Moreover, high-pressure studies on MF_2 systems revealed a surprisingly wide range of structures adopted by these compounds. At ambient conditions difluorides exhibit structures belonging either to the rutile (TiO_2) or fluorite (CaF_2) family, with the exception of BeF_2 and SnF_2.[26,27] In contrast, at high pressure the potential energy surface of MF_2 systems is characterized by a number of local minima of similar enthalpy, often separated by large energy barriers.[18]

For transition-metal difluorides, it was found that the high-pressure phase transition sequence differs considerably between ions of similar size but with different *d* electron count, as witnessed by comparing MnF_2 (d^5 system)[8,19] and CoF_2 (d^7 electron count).[20] Moreover, for d^9 cations (Cu^{2+}, Ag^{2+}), the high-pressure polymorphism is strongly influenced by structural distortion arising from an uneven occupation of the e_g orbitals (often erroneously referred to as the Jahn−Teller effect),[28,29] as well as strong spin−spin magnetic interactions.[24] In this context the phase transitions of zinc difluoride are of interest, as the Zn^{2+} cation can be viewed as a nonmagnetic ($3d^{10}$ electronic configuration) counterpart of Mn^{2+}, Co^{2+}, and Cu^{2+}. Given the nearly identical size of Zn^{2+} and Mg^{2+} ($R_{Zn^{2+}}$ = 0.74 Å, $R_{Mg^{2+}}$ = 0.72 Å) one could expect that the phase transition of ZnF_2 would be similar to those exhibited by MgF_2.[18] However, experimental data for the former compound is only available to a moderate pressure of 15 GPa,[9,10,25] while theoretical predictions were restricted to pressures not exceeding 12 GPa and performed taking into account only a limited number of possible structure types.[11,12]

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Chapter 29
Strain-Induced Changes in Vibrational Properties of Arsenene and Antimonene

Sharad Babu Pillai, Himadri R. Soni and Prafulla K. Jha

Abstract Strain is an unavoidable factor which builds inherently during the synthesis of two-dimensional (2D) materials affecting the material's properties, whereas many times strain is also useful when it comes to tuning of material's properties. In recent years, arsenene and antimonene have been widely studied for their tunable bandgap with the application of strain. Therefore, characterizing and quantifying induced strain on arsenene and antimonene are of utmost importance in their experimental studies. In this work, we investigate the vibrational properties of arsenene and antimonene monolayer under biaxial strain using phonon dispersion curves and Raman spectral calculations. Both arsenene and antimonene are dynamically stable up to 10% stretching biaxial strain, whereas they are dynamically unstable under the compressive biaxial strain. The quadratic turned linear behaviour of ZA mode of arsenene and antimonene at 10% indicates that the removal of rippling under biaxial strain follows shell elasticity model. All the optical phonon modes of arsenene and antimonene are Raman active and sensitive to strain, and hence Raman spectral measurements can efficiently characterize strain in arsenene and antimonene. The Raman intensity of in-plane mode (E_{2g}) is less than that of out plane mode (A_{1g}) at strain-free condition, whereas the former becomes higher at large biaxial strain. The weakening of bond strength caused by increasing biaxial strain lowers the E_{2g} mode and A_{1g} mode of arsenene and antimonene. A_{1g} mode behaves linearly with the strain, whereas E_{2g} mode follows quadratic relation with biaxial strain.

29.1 Introduction

Two-dimensional (2D) materials have attracted a wide range of scientific communities due to their excellent, electronic, optical, vibrational and mechanical properties.

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Strain Effect on Mexican-Hat Dispersion and Electronic Band Gap of 2D α-CN

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Abstract. Two dimensional α-CN material with Mexican-hat-shaped quartic dispersions and its valence band edge position with respect to with redox potential of water makes it a potential candidate for thermoelectric and hydrogen generation. However, the large indirect band gap of α-CN limits its efficiency in water splitting reaction. We used first principles calculations based on density functional theory to alter the band gap and analyze the quartic dispersion of valence band under biaxial strain. The electronic band gap decreases with increasing biaxial strain and improving its efficiency for water splitting. The electronic band gap of α-CN becomes suitable for UV light applications at 6-12% strain. The changes in Mexican-hat dispersion were analyzed by determining strain induced changes in the Mexican-hat coefficient. Valence band follows quartic dispersion preserving the Mexican-hat at VBM under compressive and tensile strains preserving the thermoelectric performance of α-CN.

INTRODUCTION

Intensive search for two dimensional (2D) materials with novel properties has been a common goal of every material researcher. Successful synthesis of two dimensional (2D) monolayers following graphene have paved the way for computational prediction and testing the dynamical stability of a large number of 2D materials. Among them, materials with energy-momentum relation in the form of a 'Mexican' hat has gained much attention due to their enhanced thermoelectric figure of merit which arises due to Van-Hove singularity[1] in the density of states (DOS) near their valence band maximum (VBM)[2]. Single layer group-III monochalcogenides are such materials which are mostly known for their thermoelectric properties owing to Mexican-hat-shape dispersion at their VBM[3-4]. Recently, sixteen stable phases of group IV-V binary monolayers were shown to exist in hexagonal symmetry with a wide range of band gap values between 0.35–5.14 eV[5]. Among them, VBM of α-phase structures of CN, SiN, SiP, GeN, GeP, SnN, SnP, SnAs, PbP, PbAs resembles Mexican hats which may give rise to interesting thermoelectric performance[6-7] and magnetic transitions[6,8]. However, for sustaining large scale device manufacturing, exploiting novel 2D materials composed of earth abundant elements is of utmost important. α-CN being such a 2D material possess quartic dispersion of valence band. Further, the compatible band edge position with a redox potential of water in different pH environments makes α- CN suitable for water splitting and gives an extra dimension to its potential application[5]. However, the wide band gap of α- CN limits its efficiency in water splitting. Robust tools for modifying the electronic properties of 2D materials are pressure and strain which can be used to tune the wide band gap of α- CN for improving efficiency in water splitting for hydrogen generation. Hence

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Strain Effect on Electronic and Lattice Dynamical Behaviour of Two Dimensional Bi, BiAs and BiSb

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Abstract. The present study investigates the electronic band structure and lattice dynamical stability of 2D monolayer sheet of Bi, BiAs and BiSb using density functional theory based on first principles calculation. All these systems are semiconductor with direct bandgap. Under tensile strain the bandgap reduces and no bandgap closing is observed upto +5% strain whereas a direct-indirect-metal transition is observed for compressive strain in all these systems. The lattice dynamical stability of these materials has been studied under strain.

INTRODUCTION

The identification of 2D sheets of semiconductors particularly the layered compounds of group-V elements with different bandgap energies is of utmost importance for their particular applications in optoelectronic and spintronic devices[1-2]. However, their properties are sensitive to biaxial strain induced from the substrate which is inherent while dealing with 2D materials in practical situations[3]. The semimetal-semiconductor and semiconductor-to-topological transitions under strain have been subjects of active studies [2, 4]. Recent studies on bismuthene includes the finding of Rashba-type spin splitting due to strong spin orbit coupling (SOC) in Bi and dependence of surface states on film thickness[1, 5]. Recently, the interfacial properties of the bismuthene−metal contacts have been studied in detail where it was shown that the bismuthene on the metal surface undergoes metallization, and Ohmic contact occurs in the vertical direction [6]. However, the effect of strain induced on Bi monolayer by the metal substrate has not been considered which is of utmost important since the change in bandgap of bismuthene or bismuthene compounds due to strain will alter the choice of metal electrodes in monolayer bismuthene devices. Strain dependence of electronic band structure Bi, BiAs and BiSb has been studied recently but the stability of free standing BiAs and BiSb is in question[1, 2] due to imaginary frequency of out of plane acoustical branch (ZA) near zone centre. Further, the lattice dynamical property of these materials under strain has not been considered yet which makes the study of these materials incomplete. In the present work, we systematically calculated the electronic band structure of two dimensional Bismuth (Bi), bismuth arsenide (BiAs) and bismuth antimonide (BiSb) and investigated the dynamical stability of these materials by studying phonon dispersion curves using density functional theory calculations. The objective is to understand the modification of electronic band structure of 2D Bi, BiAs and BiSb with compressive and tensile strain, to know the stability limit of monolayer Bi, BiAs and BiSb under strain and occurrence of any transition or unusual behaviour of phonon modes with the application of strain.

METHODS

The structural, electronic and lattice dynamical properties of Bi, BiAs and BiSb were studied using first principle calculations based on Density Functional Theory within the plane wave pseudopotentials as implemented in Quantum Espresso code[7]. The exchange correlational functional of Perdew-Burke-Ernzerohf (PBE)[8] for the Generalised Gradient Approximation was adopted. To mimic the 2D system, vacuum of about 15 Å is used along Z

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Strain induced changes in phonon band structure of antimony monolayer using density functional theory calculations

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Abstract. The present paper reports the study of phonon properties of a two dimensional antimony nanosheet under the biaxial strain using first principles calculation based on density functional theory. Our calculations shows that the strain turns the quadratic dependence of wave vector on frequency to the linear dependency which can be linked with the removal of rippling in nanosheets.

Keywords: **A**ntimony nanosheets, Density Functional Theory, phonon, strain
PACS: 31.15.A-, 81.05.zx, 68.65.-k, 81.05.ue

INTRODUCTION

In recent years graphene like 2D materials have attracted lots of interest due to their fascinating mechanical, electronic and transport properties. Monolayer of BN has been successfully fabricated and subjected to extensive studies with promising application on electronic and energy storage[1-2]. Monolayer sheets of various inorganic layered materials such as MoS_2, WS_2, $MoTe_2$, $MoSe_2$, $NbTe_2$ and $NbSe_2$ has been efficiently produced[3-4]. Lots of 2D carbon allotropes, nitrogen-graphene alloys and group III-IV compounds have been predicted using structural search methods and first principles calculations[5-6] which shows different properties ranging from semi metal to wide band gap semiconductors. Furthermore, a novel 2D boron structures with massless dirac fermions has been predicted and investigated[7]. These studies motivate interest in seeking new nanosheets of other elements. Efforts have been made to have one atom thick honeycomb lattices of group IV elements and compounds of III-IV and II-VI group elements[8-9]. Further the application of strain to a material is expected to change the strength of inter atomic bonding and hence the strength of the material. This suggests that the strain engineering can be an effective way of tuning the electronic properties of any material.

In this study we perform density functional theory (DFT) calculations to study the complete phonon behaviour of antimony sheets subjecting them to a biaxial strain. The objective is to know whether monolayer of Sb shows electronic and phonon properties similar to graphene and other 2D like materials and any structural transition and unusual behaviour of phonon modes with the application of strain. The rippling in Sb monosheet has been analysed by monitoring the behavior of out of plane acoustic (ZA) mode under strain. It is known that the loss of two dimensional ordering resulting from rippling is associated with the movements of constituent atoms in the out of plane direction.

METHODS

All calculations were performed using first principle calculations based on Density Functional Theory within the plane wave pseudopotentials as implemented in Quantum Espresso code[10]. We adopt the exchange correlational functional of Perdew-Burke-Ernzerohf (PBE) for the Generalised Gradient Approximation. Kohn Sham wave functions were represented with a plane wave basis with an energy cutoff of 50Ry. The Brillouin Zone integration was sampled on uniform Monkhorst pack guides 9x9x1. The structures were optimized until the maximum force allowed on each atom is less that 10^{-4}eV/Å. A vacuum spacing of 15Å was applied to reduce interaction between layers. Lattice dynamical calculations were performed within the frame work of

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First Principles Calculation Of Two Dimensional Antimony And Antimony Arsenide

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Abstract. This work focuses on the strain dependence of the electronic properties of two dimensional antimony (Sb) material and its alloy with As (SbAs) using density functional theory based first principles calculations. Both systems show indirect bandgap semiconducting character which can be transformed into a direct bandgap material with the application of relatively small strain.

Keywords: Two dimensional antimony, Density Functional Theory, band structure, indirect-direct band gap, strain.
PACS: 31.15.A-, 81.05.zx, 68.65.-k, 81.05.ue

INTRODUCTION

The excellent properties such as high electron mobility, heat conduction and mechanical strength in graphene[1] a great deal of attention is being diverted to other two dimensional (2D) materials such as silicene, germanene[2], boron nitride (BN)[3-4], dichalcogenides (XY_2; X=Mo and W and Y=S and Se))[5-6] monolayer and few layer black phosphorus[6-7]. However, the electronic band structure of graphene, silicene and germanene shows zero band gap, which reduces their ability to switch current on and off in transistors even though the functonalization, electric field and strain can create a gap. The identification of 2D semiconductors with different bandgap energies for their particular applications in light emitting and optoelectronic devices is of utmost importance.

Recently, after successful experimental studies on phosphorene[8-9], the atomically thin 2D arsenic and antimony known as arsenene and antimonene respectively have received great attention and been actively studied[10-11]. These systems exist in three structural configurations namely planar, buckled and puckered among which the later two configurations are found to be stable by investigation [10]. The arsenene and antimonene both have indirect bandgap which limits their use in light emitting and optoelectronic devices. However the application of strain to arsenene makes indirect to direct bandgap transition [12]. In this work, we investigate the electronic properties of 2D planer and buckled antimonene by employing density functional theory (DFT) based electronic structure calculations. We also study the effect of strain to see and study the effect of strain on band structure of these 2D systems to find out any possible indirect-direct band transition.

METHODS

The computational approach to gain insight into the energetic, structural and electronic properties of layered antimony and antimony arsenide has been studied using first principle calculations based on Density Functional Theory within the plane wave pseudopotentials as implemented in Quantum Espresso code[12].The exchange correlation interaction was treated within the generalised gradient approximation (GGA) given by Perdew-Burke-Ernzerhof (PBE)[14]. Both materials are periodic in X and Y directions and to mimic 2D system, vacuum of about $15A^0$ is used along Z direction to avoid interaction between adjacent models. An energy cutoff of 45Ry and 180Ry were used for electronic wave function and charge density respectively. The reciprocal space for both was sampled by a grid of 25x25x1 and Brillouin zone integration was performed using Monhorst-Pack scheme. Both energy cutoff and k-point sampling value are determined by performing extensive convergence analysis. The energy convergence value between two consecutive steps was chosen as 10^{-5}eV

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