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Stability, elastic and electronic properties of palladium nitride

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Abstract

The crystal structure, stability, elastic constants and electronic properties of PdN₂ for four polymorph structures: pyrite, marcasite, CoSb₂ and ST_{AA}, have been investigated using first-principles calculations. At zero pressure all four polymorphs are metallic and thermodynamically unstable but mechanically stable. Pyrite PdN₂ is found to be the lowest energy phase. It is metallic at ambient pressure but becomes a semiconductor at pressures higher than 18 GPa. The calculated phonon band structures of pyrite PdN₂ show the structure is dynamically stable up to 60 GPa. Good agreement between calculated and observed Raman frequencies was found, indicating that the recently synthesized palladium nitride at high pressure is likely to have a pyrite structure.

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

1. Introduction

Metal nitrides have attracted increasing attention from both experimental and theoretical investigations since they exhibit many useful properties such as hardness, superconductivity, photoluminescence and many types of magnetism [1–8]. Most recently, four noble metal nitrides of Pt, Ir, Os and Pd have been synthesized under extreme conditions (in the range of 60 GPa and 2000 K, respectively) [9–12]. Except for PdN₂, all these high pressure forms can be recovered at ambient conditions. Due to potential practical applications, there is considerable interest in investigating the crystalline structure, stability, elasticity and electronic structures of novel noble metal nitrides [13–30], and by now a consensus has been reached concerning the observed crystal structures and stoichiometry (one metal atom for every nitrogen dimer). It is confirmed that PtN₂, OsN₂ and IrN₂ have pyrite [10, 18, 20], marcasite [23–27] and CoSb₂ structures [23, 28, 29], respectively. However, it was found that PdN₂ decomposes at pressures below ~13 GPa. Therefore, the correct stoichiometry could not be determined using electron

microprobe or x-ray photoelectron spectroscopy [12]. Until now the crystalline structure of this new synthesized palladium nitride has not been determined. In this study, the stability, electronic structure and elastic constants of PdN₂ with four possible structures: pyrite, marcasite, CoSb₂ and ST_{AA} [30], were investigated by first-principles calculations. The ST_{AA} structure is reported by Åberg *et al* [30]. They showed that the ST_{AA} structure at low pressure is thermodynamically more stable than the other crystal phases that have been synthesized experimentally up to now or calculated from theory for noble metal nitrides. In view of the similarity of the chemical properties, most likely PdN₂ could adopt one of those structures with competitive energetic stability. The theoretical results conclusively support the recently synthesized palladium nitride at high pressure adopting the pyrite structure at pressures higher than 18 GPa. Moreover, it is shown that, due to thermodynamic instability, PdN₂ is metastable and will dissociate under ambient conditions.

2. Computational details

Most of the calculations were performed using the CASTEP code [31] based on the density functional theory. Interactions

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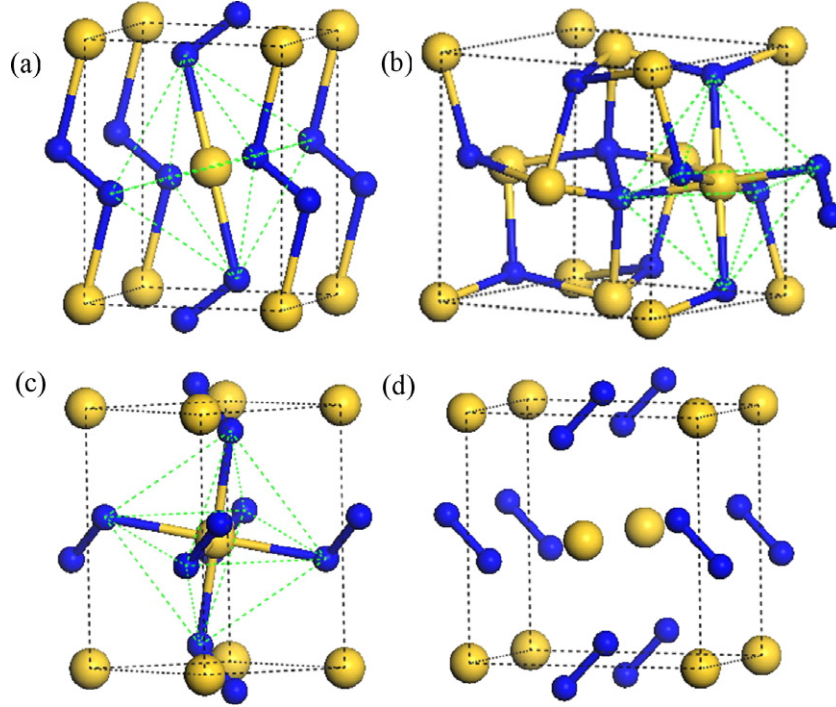


Figure 1. Crystal structures of marcasite (a), pyrite (b), CoSb₂ (c) and ST_{AA} (d). The large and small spheres represent Pd and N atoms, respectively.

Table 1. Lattice constants a , b and c (Å), bond lengths of M–N (M presents the noble metal) and N–N (Å) and cell volume per formula unit V (Å³) for noble metal nitrides at 0 and 18 GPa. P, pyrite structure; m, marcasite structure; c, CoSb₂ structure and s, ST_{AA} structure. For pyrite, marcasite and CoSb₂ structures, bond lengths of M–N in MN₆ octahedra are given and, for the ST_{AA} structure, only the shortest Pd–N bond length is reported.

	0 GPa						18 GPa					
	a	b	c	M–N	N–N	V	a	b	c	M–N	N–N	V
p-PdN ₂	4.975			2.184	1.269	30.8	4.789			2.075	1.320	27.1
m-PdN ₂	3.911	4.975	3.133	2.154	1.259	31.0	3.845	4.805	3.006	2.069	1.288	27.8
				2.201						2.102		
c-PdN ₂	5.071	5.005	5.071	2.163	1.260	31.3	4.881	4.802	4.881	2.068	1.290	27.8
				2.201						2.101		
s-PdN ₂	4.868		3.097	2.042	1.245	36.7	4.767		2.720	1.993	1.243	30.9
p-PtN ₂	4.874			2.112	1.401	29.0	4.791			2.072	1.389	27.5
	Exp. [10]	4.804										
m-OsN ₂	4.116	4.915	2.686	2.053	1.416	27.2	4.071	4.849	2.633	2.022	1.403	26.0
				2.091						2.061		
	Exp. [24]	4.102	4.910	2.714								
c-IrN ₂	4.873	4.920	4.912	2.051	1.413	28.0	4.805	4.850	4.845	2.022	1.401	26.8
				2.069						2.042		
				2.072						2.047		
				2.100						2.065		
				2.107						2.074		
				2.124						2.086		

Table 2. Elastic constants c_{ij} (GPa) and bulk modulus B (GPa) for PdN₂ polymorphs.

	c_{11}	c_{22}	c_{33}	c_{44}	c_{55}	c_{66}	c_{12}	c_{13}	c_{15}	c_{23}	c_{25}	c_{35}	c_{46}	B
Pyrite	289			40			58							135
Marcasite	165	235	164	43	37	65	49	78		46				100
CoSb ₂	157	259	143	66	48	56	67	86	-23	59	-16	-29	-15	93
ST _{AA}	452		44	10		103	38	-36						26

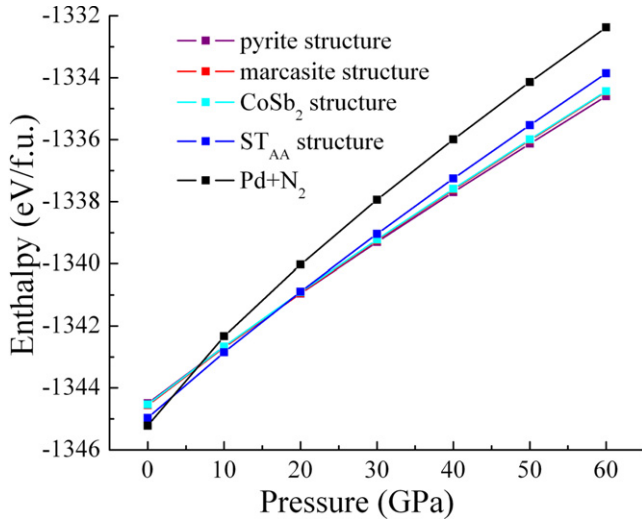


Figure 2. Enthalpy versus pressure for PdN₂ with four structures: pyrite structure, marcasite structure, CoSb₂ structure and ST_{AA} structure, together with their constituents at $T = 0$ K.

between the ions and electrons were described by using the Vanderbilt ultrasoft pseudopotential [32]. The generalized gradient approximation (GGA) [33] was used for the exchange–correlation potentials. The calculations were performed using an energy cutoff of 500 eV for the plane wave basis set. Integrations in the Brillouin zone (BZ) were performed using Monkhorst–Pack k -point meshes $10 \times 10 \times 10$ for pyrite, $7 \times 5 \times 8$ for marcasite, $8 \times 8 \times 8$ for CoSb₂ and $5 \times 5 \times 8$ for ST_{AA}. Test calculations have shown that the energy convergence is better than 5 meV/PdN₂ with the k -meshes employed. The phonon band structures of pyrite PdN₂ were obtained with the small-displacement frozen-phonon method [34, 35] implemented in the PHONON code [36]. Hellmann–Feynman forces were calculated with the VASP code [37–39] on $2 \times 2 \times 2$ supercells and $4 \times 4 \times 4$ k meshes in the first BZ for the interpolation of the force constants. A geometry optimization was regarded as converged if both the difference in total energy and the gradient on the Hellmann–Feynman forces is less than 1×10^{-7} eV/atom and 1×10^{-5} eV \AA^{-1} , respectively. To ensure reliability on the calculated interplanar force constants, results from two sets

of calculations with atomic displacements of 0.01 and 0.02 \AA were compared. The structure of the supercell and the k -mesh convergence was checked against more extensive calculations on the conventional cell with k -point meshes up to $16 \times 16 \times 16$. Owing to the relatively large unit cell size and the large demand on computational resources, even using linear response theory, a $2 \times 2 \times 2$ supercell is deemed to be satisfactory.

3. Results and discussion

The structures of pyrite, marcasite, CoSb₂ and ST_{AA} of PdN₂ are depicted in figure 1. The pyrite structure has a $P\bar{a}3$ space group with Pd atoms occupying the 4a Wyckoff positions and N atoms occupy the 8b positions. The marcasite structure has the $Pnmm$ space group and the Pd and N atoms occupy the 2a and 4g sites, respectively. The CoSb₂ structure is monoclinic $P2_1/c$ with all of the atoms occupying Wyckoff 4e positions. These three structures are composed of PdN₆ octahedra. In the pyrite structure, the octahedra are corner-shared while in the marcasite structure and CoSb₂ structure the octahedra are both edge- and corner-shared. In $P4/mbm$ ST_{AA}, the Pd atoms occupy 2a Wyckoff positions and N atoms are located at the 4g positions. ST_{AA} has a layer structure with the layers stacked along the c axis. Each layer is composed of Pd atoms occupying the square lattice sites with face-centered nitrogen dimers pointing towards the edges of the squares and perpendicular to the four nearest-neighbor dimers.

Structures of the four candidate polymorphs were optimized at zero pressure. The optimized structural parameters are tabulated in table 1. To examine the mechanical stability, elastic constants were calculated and checked against Born stability conditions [40] for cubic (pyrite), tetragonal (ST_{AA}), orthorhombic (marcasite) and monoclinic (CoSb₂) structures (table 2). The calculated elastic moduli are summarized in table 2. All four polymorphs of PdN₂ are mechanically stable at zero pressure. It is noteworthy that the bulk moduli of all four candidate structures are very low. The pyrite structure of PdN₂ has the largest bulk modulus of 135 GPa while the ST_{AA} structure has the lowest bulk modulus of 26 GPa. Since the ST_{AA} structure resembles a simple combination of Pd and N₂, the very low bulk modulus is not too surprising. By comparing with other noble metal nitrides, OsN₂ (358 GPa), IrN₂ (428 GPa) and PtN₂ (354 GPa) [9–12],

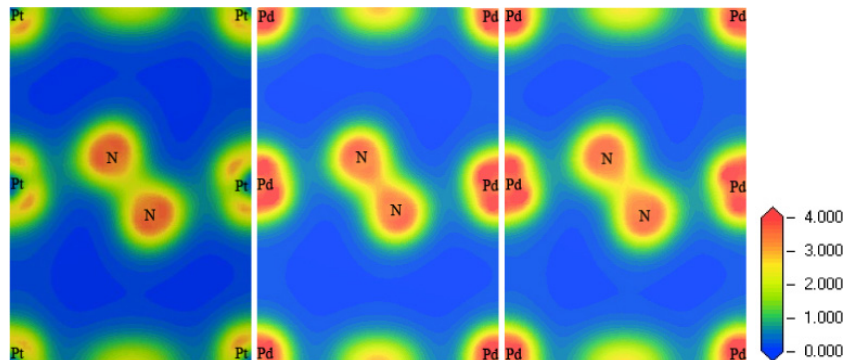


Figure 3. Charge density of pyrite PtN₂ at 0 GPa (left), pyrite PdN₂ at 0 GPa (middle) and at 18 GPa (right) for the $(1\bar{1}0)$ plane.

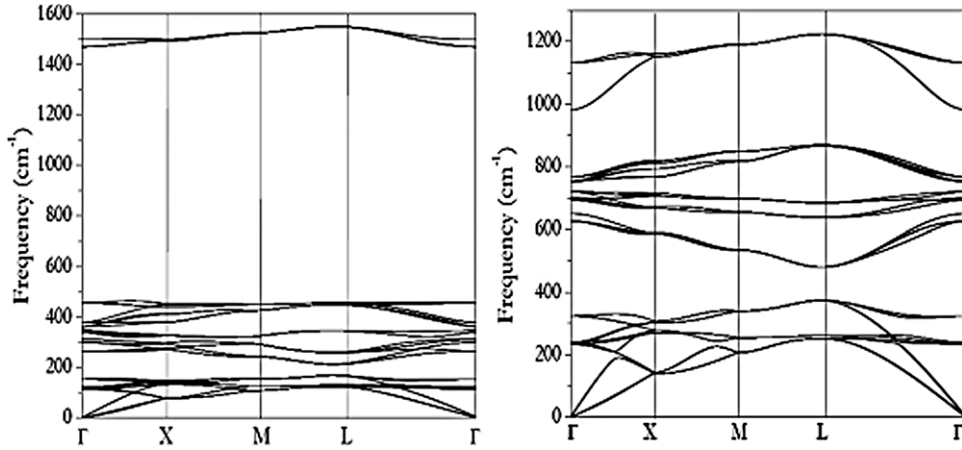


Figure 4. Phonon dispersion of pyrite PdN₂ at zero pressure (left) and 60 GPa (right).

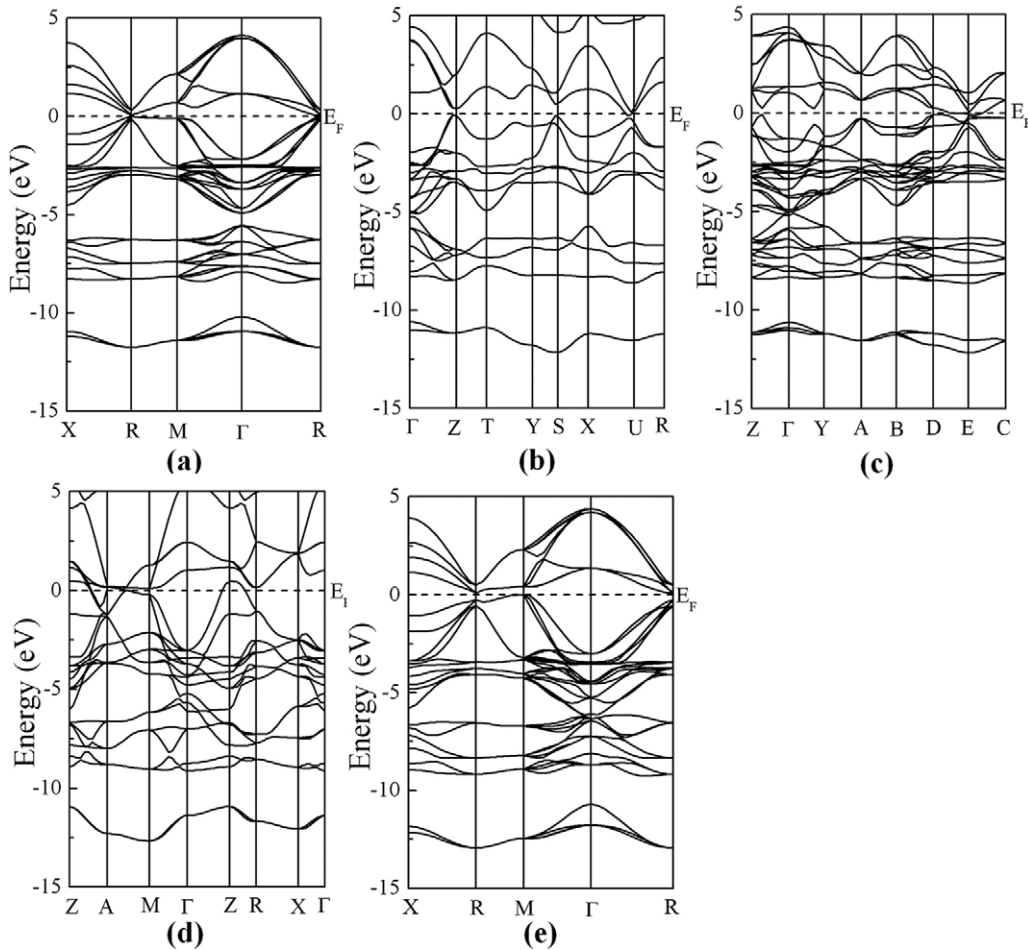


Figure 5. Electronic band structures of PdN₂ with pyrite structure (a), marcasite structure (b), CoSb₂ structure (c) and ST_{AA} structure (d) at zero pressure and with pyrite structure at 18 GPa (e).

PdN₂ is clearly not a hard material. The pressure dependence of the enthalpies calculated at 0 K is shown in figure 2. The enthalpy of the solid N₂ phase is calculated assuming the ϵ -N₂ structure. It is found that all four PdN₂ structures are thermodynamically metastable with respect to Pd metal and solid N₂ at low pressures. However, the ST_{AA}, marcasite,

pyrite and CoSb₂ structures become thermodynamically stable with dissociation into Pd metal and solid N₂ at 3.5, 6.5, 7 and 7 GPa, respectively. At pressures up to 18 GPa, the ST_{AA} structure is the lowest enthalpy phase with a formation energy of approx. 0.3 eV/f.u. at ambient pressure. Above 18 GPa, the pyrite structure becomes the most stable polymorph. The

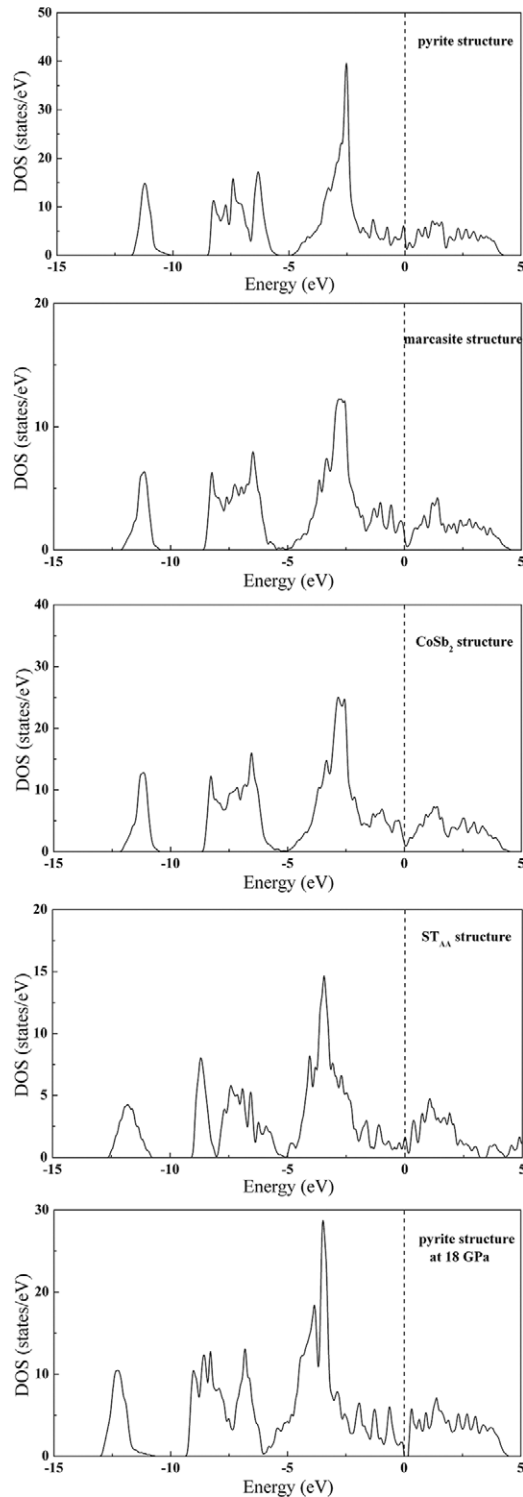


Figure 6. Density of states of PdN₂ with pyrite structure, marcasite structure, CoSb₂ structure and ST_{AA} structure at zero pressure and with pyrite structure at 18 GPa. The Fermi energy is set to zero.

theoretical results are consistent with experiment [12] that no stable PdN₂ compound was observed below 13 GPa.

It is important to note that the calculated N–N bond lengths in PdN₂ approx. 1.25–1.27 Å in these four structures are almost the same (table 1). These values are close to the double-bonded N=N distance of 1.25 Å. At 18 GPa, the N–

N bonds lengthened substantially and the distances are closer to N–N single-bonded. Andrea *et al* [20] have proposed that pressure-induced changes in the bonding character of nitrogen (triple to single) are keys to understand the synthesis of PtN₂. The change from triple-bonded molecular N₂ to double-bonded at ambient pressure and then to single-bonded at high pressure enhances the Pd–N interactions and stabilizes PdN₂ at high pressure. Plots of the charge density distribution of pyrite–PdN₂ at 0 and 18 GPa are shown in figure 3 and clearly reveal strong covalent interaction in the di-nitrogen units while Pd–N bonds are very weak as compared to M (M = Pt, Os, Ir)–N bonds in PtN₂, OsN₂ and IrN₂. Consequently, the bulk modulus for PdN₂ is much lower than those for PtN₂, OsN₂ and IrN₂. As the pressure increases, the N–N double bond becomes weaker and, at the same time, the Pd–N bond becomes stronger, which results in the existence of the pyrite–PdN₂ phase at high pressure.

Since the pyrite structure is stable above 18 GPa, it is interesting to investigate whether this structure would still be stable if it could be recovered at ambient pressure. The dynamical stability of pyrite PdN₂ was investigated with phonon calculations. The calculated phonon dispersions at zero pressure and 60 GPa are shown in figure 4. The absence of an imaginary vibrational mode indicates that the pyrite structure is dynamically stable at ambient pressure and at least up to 60 GPa. The vibrational profiles can be divided into three distinct regions. At zero pressure, Pd and N atoms are weakly interacting. Therefore the translation vibrations are well separated from the much higher energy N–N stretch vibrations and resulted in a large energy gap in the vibrational band structure. This unusual vibrational profile is a consequence of the weak chemical interaction between the Pd and N₂, which is also shown in the electronic band structure (see below). The low-frequency vibrations below 180 cm⁻¹ can be assigned to collective translational vibrations of Pd and N atoms. Vibrations at 210–470 cm⁻¹ correspond to molecular-like librations of the N–N units. The high-frequency band at 1470–1550 cm⁻¹ arises from N–N stretches. At 60 GPa, the gap between 500 and 1400 cm⁻¹ is filled due to the change of N=N to N–N bonding. Under compression, the Pd now interacts more strongly with the N₂. This effect is evident in the decrease of the N–N stretch frequencies from 1500 to 1200 cm⁻¹. This is compensated by the enhancement of Pd–N bonding as indicated by the appearance of a new band from 600 to 800 cm⁻¹ and the concomitant disappearance of the N₂ librational vibrations. The calculated zone center Raman-active modes at 770, 980 and 1138 cm⁻¹ at 60 GPa are in accord with observed Raman peaks at 770, 970 and 1040 cm⁻¹ [12]. The good agreement with experiment strongly suggests the recently synthesized palladium nitride at high pressure should have the pyrite structure.

To investigate the electronic properties of PdN₂, the electronic band structures and density of states (DOS) of pyrite, marcasite, CoSb₂ and ST_{AA} PdN₂ were calculated and are shown in figures 5 and 6, respectively. At zero pressure, all the polymorphs are metals with very low density of states at the Fermi level (figure 6). However, as shown in figure 5 there are several dispersive electron bands crossing the Fermi level. The

layered crystal structure in ST_{AA} is clearly reflected in the lack of electron band dispersion in the $R \rightarrow M$ direction (figure 5). As the pressure increases, the valence band width and the energy gap between the valence and conduction bands becomes larger. At 18 GPa, pyrite PdN_2 becomes the lowest enthalpy phases and a semiconductor having an indirect energy gap of 0.25 eV (figure 5(e)) between the valence band maximum at M and the bottom of the conduction band at R. The opening of an energy gap helps to stabilize the pyrite structure at high pressure. This scenario has been invoked previously to rationalize the stable structure of IrN_2 [23, 28]. A net energy reduction results from occupation of the states with lowered energy, while the states with higher energy are empty.

4. Conclusions

The crystal structure, electronic structure, mechanical and dynamical stability, and elastic constants of PdN_2 of four candidate structures: pyrite, marcasite, $CoSb_2$ and ST_{AA} , have been investigated using first-principles calculations. From the calculated energies and Raman vibrational frequencies, it is suggested that the recently synthesized PdN_2 is a semiconductor and should possess the pyrite structure at pressures higher than 18 GPa. On the other hand, at low pressure, PdN_2 is dynamically stable but thermodynamically unstable and may decompose into metallic Pd and solid N_2 at ambient pressure.

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References

- [1] Jhi S H, Ihm J, Louie S G and Cohen M L 1999 *Nature* **399** 132
- [2] McMillan P F 2002 *Nat. Mater.* **1** 19
- [3] Maruyama T and Morishita T 1996 *Appl. Phys. Lett.* **69** 890
- [4] Yamanaka S, Hotehama K and Kawaji H 1998 *Nature* **392** 580
- [5] Zerr A, Miehe G and Boehler R 2003 *Nat. Mater.* **2** 185
- [6] Chhowalla M and Unalan H E 2005 *Nat. Mater.* **4** 317
- [7] Leineweber A, Jacobs H and Hull S 2001 *Inorg. Chem.* **40** 5818
- [8] Wu Z G, Chen X J, Struzhkin V V and Cohen R E 2005 *Phys. Rev. B* **71** 214103
- [9] Gregoryanz E, Sanloup C, Somayazulu M, Badro J, Fiquet G, Mao H K and Hemeley R 2004 *Nat. Mater.* **3** 294
- [10] Crowhurst J C, Goncharov A F, Sadigh B, Evans C L, Morrall P G, Ferreira J L and Nelson A J 2006 *Science* **311** 1275
- [11] Young A F, Sanloup C, Gregoryanz E, Scandolo S, Hemley R J and Mao H K 2006 *Phys. Rev. Lett.* **96** 155501
- [12] Crowhurst J C, Goncharov A F, Sadigh B, Zaug J M, Aberg D, Meng Y and Prakapenka V B 2008 *J. Mater. Res.* **23** 1–5
- [13] Sahu B R and Kleinman L 2005 *Phys. Rev. B* **71** 041101
- [14] Uddin J and Scuseria G E 2005 *Phys. Rev. B* **72** 035101
- [15] Kanoun M B and Goumri-Said S 2005 *Phys. Rev. B* **72** 113103
- [16] Yu R and Zhang X F 2005 *Appl. Phys. Lett.* **86** 121913
- [17] Yu R and Zhang X F 2005 *Phys. Rev. B* **72** 054103
- [18] Yu R, Zhan Q and Zhang X F 2006 *Appl. Phys. Lett.* **88** 051913
- [19] Patil S K R, Khare S V, Tuttle B R, Bording J K and Kodambaka S 2006 *Phys. Rev. B* **73** 104118
- [20] Young A F, Montoya J A, Sanloup C, Lazzeri M, Gregoryanz E and Scandolo S 2006 *Phys. Rev. B* **73** 153102
- [21] Gou H Y, Hou L, Zhang J W, Sun G F, Gao L H and Gao F M 2006 *Appl. Phys. Lett.* **89** 141910
- [22] Fan C Z, Zeng S Y, Li L X, Zhan Z J, Liu R P, Wang W K, Zhang P and Yao Y G 2006 *Phys. Rev. B* **74** 125118
- [23] Yu R, Zhan Q and De Jonghe C 2007 *Angew. Chem. Int. Edn* **46** 1136
- [24] Montoya J A, Hernandez A D, Sanloup C, Gregoryanz E and Scandolo S 2007 *Appl. Phys. Lett.* **90** 011909
- [25] Wang Y X, Arai M and Sasaki T 2007 *Appl. Phys. Lett.* **90** 061992
- [26] Chen Z W, Guo X J, Liu Z Y, Mao M Z, Jing Q, Li G, Zhang X Y, Li L X, Wang Q, Tian Y J and Liu R P 2007 *Phys. Rev. B* **75** 054103
- [27] Wu Z J, Hao X F, Liu X J and Meng J 2007 *Phys. Rev. B* **75** 054115
- [28] Wang Y X, Arai M, Sasaki T and Fang C Z 2007 *Phys. Rev. B* **75** 104110
- [29] Wu Z J, Zhao E J, Xiang H P, Hao X F, Liu X J and Meng J 2007 *Phys. Rev. B* **76** 054115
- [30] Aberg D, Sadigh B, Crowhurst J and Goncharov F 2008 *Phys. Rev. Lett.* **100** 095501
- [31] MATERIALS STUDIO 2002 *Version 2.1.5* Accelrys Inc.
- [32] Vanderbilt D 1990 *Phys. Rev. B* **41** 7892
- [33] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [34] Kresse G, Furthmüller J and Hafner J 1995 *Europhys. Lett.* **32** 729
- [35] Alfè D, Price G D and Gillan M J 2001 *Phys. Rev. B* **64** 045123
- [36] Alfè D 1998 Program available at http://chianti.geol.ucl.ac.uk/_dario.
- [37] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** R558
- [38] Kresse G and Hafner J 1994 *J. Phys.: Condens. Matter* **6** 8245
- [39] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
- [40] Nye J F 1985 *Physical Properties of Crystals* (Oxford: Oxford University Press)