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Prediction of a new layered phase of nitrogen from first-principles simulations

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Abstract

A new phase of nonmolecular nitrogen has been suggested by first-principles density functional theory simulations at high pressures. The phase has zigzag chains similar to the BP, A7 and LB phases, but the zigzag chains in the PP phase are connected by two atoms with double bonds with *Pmna* symmetry, which we designated as the PP phase. Properties of PP are presented in comparison with other polymeric phases of nitrogen discussed previously. The calculated enthalpy versus pressure reveals a similarity between the PP and CH phases. The equation of state of nitrogen in the PP, CG and ϵ phases shows that an ϵ transition to the PP phase happens at 90 GPa. The band structure and bulk modulus of PP phase are also calculated.

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

1. Introduction

Among the diatomic molecular solids, nitrogen has been widely studied. Nitrogen usually consists of molecules in which two atoms are strongly triple-bonded under usual conditions, but high external pressure will destabilize the triple molecular bonds and lead to various nonmolecular polymeric structures, in which each of the nitrogen atoms has single or single and double covalent bonds with neighbors [1–4]. Because of the large energy difference between the N–N single and triple bonds, when the single-bonded nitrogen transforms into a N₂ molecule, about 1 eV/atom of energy can be released. The calculated results show that the energy density of single-bonded polymeric nitrogen is at least 0.4 eV cm⁻³ [5], which is about three times that of the most powerful energetic materials known today. So it is an extremely powerful high-energy-density material (HEDM), potentially for use in energy storage systems, propellants and explosives.

Much important progress has been made in theoretical and experimental research on the nature of nitrogen at high pressure. Several polymeric structures have been suggested

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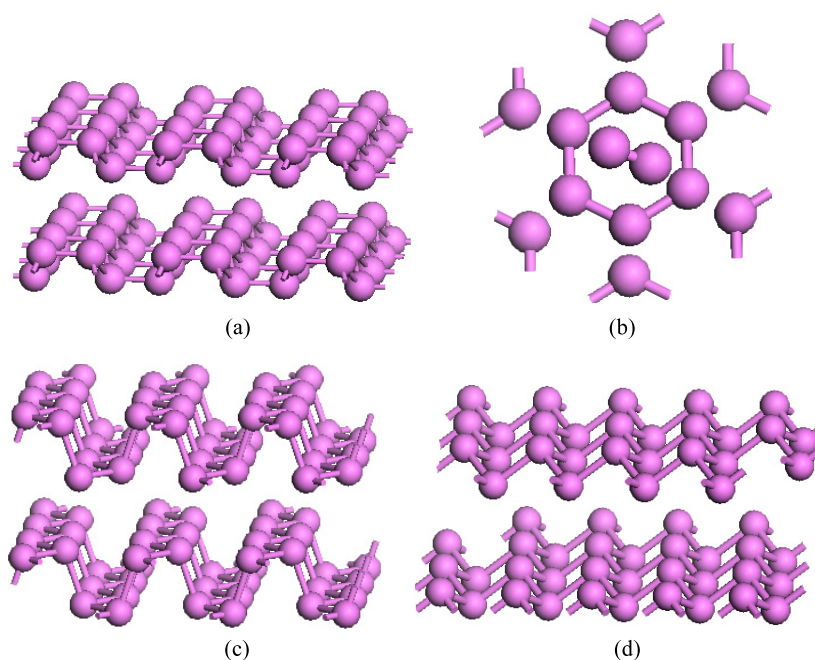


Figure 1. Structures of (a) the LB, (b) the N₂-N₆, (c) the A7 and (d) the BP phases.

before, such as black-phosphorus (BP), α -arsenic (A7), *cmcm* chain (CMCM), *cis-trans* chain (CH), and *cubic gauche* (CG), as shown in figures 1 and 2; details can be found in [1]. The BP and A7 structures were at first suggested to be that of the known single-bonded forms of group 15 elements phosphorus and arsenic. Then Alemany and Martins found that the BP phase would transform into the CH phase [6] at 20 GPa through geometry optimization. By analogy with carbon in diamond, Mailhot *et al* [1] predicted that the phase should crystallize in the *cubic gauche* (CG) structure, where all nitrogen atoms are threefold coordinated and the bond lengths are the same for all pairs of bonded atoms, as shown in figure 2(d). Due to its similarity to the diamond structure (which is four bonded, however), CG could be called a ‘nitrogen diamond’. Theoretical calculations [4, 7] have shown that an infinite CG structure is mechanically metastable under ambient pressure and room temperature. On the other hand, on the experimental side, Nellis’ shock wave experiments have indicated dissociation of the N₂ molecules to form monatomic nitrogen at a high temperature (6000 K) and modest pressure (30 GPa). After a long search for monatomic nitrogen phases, in 2004 Eremets and co-workers successfully synthesized single-bonded polymeric nitrogen in the CG phase under a pressure greater than 110 GPa and a temperature of 2000 K [8]. Although the CH, BP and CMCM phases shown in figure 2 have so far not been observed experimentally at pressures less than 200 GPa, they are all predicted to be thermodynamically less stable than the CG phase. Indeed, it is possible that other metastable phases of polymeric nitrogen may exist at ambient pressure or that they may be synthesized easily. So, exploration of the new polymeric nitrogen structure is a yet more interesting topic in theoretical and experimental research. Recently, two new nonmolecular phases have been predicted. One is the layered boat (LB) [9] shown in figure 1(a), which has all six-membered rings in a boat conformation. The other is the N₂-N₆ structure [10] shown in figure 1(b), in which three molecules rotate and bond to form a

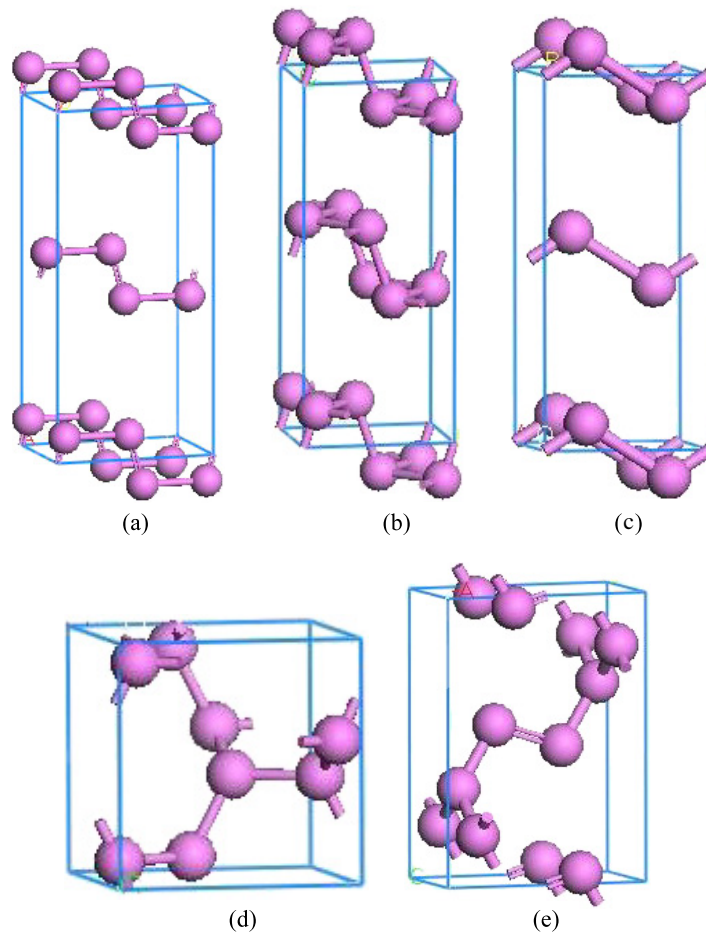


Figure 2. The primitive cell of several phases of polymeric nitrogen: (a) CH, (b) BP, (c) CMCM, (d) CG, and (e) PP.

hexagon and the molecules in the center of the projection remain diatomic. The methods of both geometry optimization and molecular dynamics simulation have been used to obtain these structures.

In this paper, we suggest a new nonmolecular phase (PP), which is similar to the LB, A7 and BP structures, but the method of connection between zigzag chains of these structures is different. The zigzag chains in LB, A7 and BP structures are singly bonded, as shown in figure 3, and the zigzag chains in the new phase are connected by two atoms with double bonds, as shown in figure 4(d). The electronic, mechanical and thermodynamic properties compared with the BP, CG, CH, CMCM, SC and LB phases are reported.

2. Technical details

All calculations reported in this paper are based on the first-principle plane-wave pseudopotential density functional theory, completed by using the CASTEP code [11]. An ultrasoft pseudopotential is used. The exchange and correlation effects are described by the generalized gradient approximation (GGA) PW91 (Perdew Wang (1991)) [12] instead of the

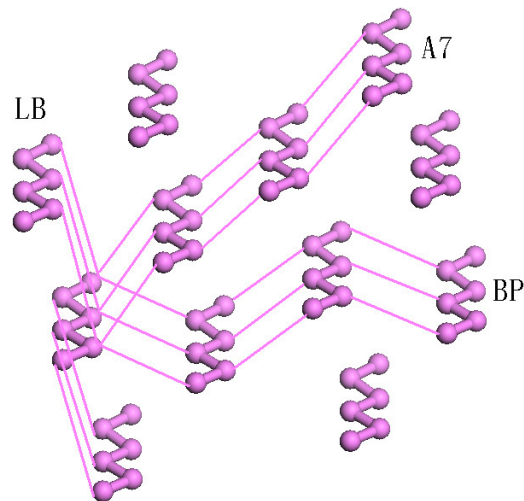


Figure 3. All three of the phases LB, A7 and BP have zigzag chains; connection between two zigzag chains is single-bond, with different arrangements of the zigzag chains.

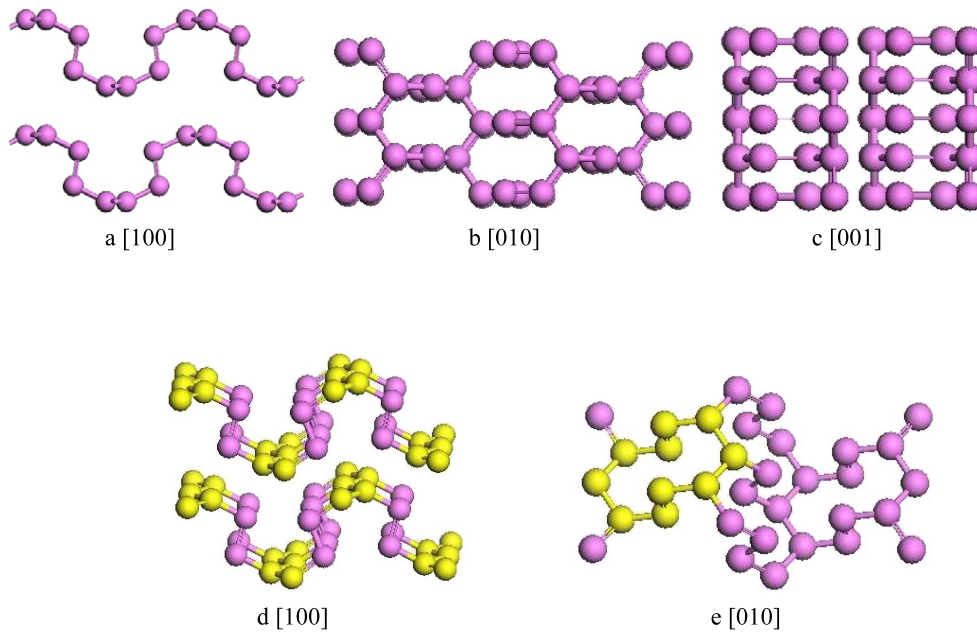


Figure 4. Structure of the PP phase from different viewing angles.

local-density approximation (LDA), since a number of studies suggest that, when applied to covalently bonded systems, GGA functionals are more accurate than LDA functionals, with nitrogen clusters being one of them [13–15]. The convergence tests give kinetic energy cutoffs of 500 eV, with $11 \times 6 \times 6$, $9 \times 9 \times 9$, $10 \times 10 \times 12$, $12 \times 12 \times 8$, $10 \times 10 \times 7$, $9 \times 7 \times 9$ and $7 \times 7 \times 7$ Monkhorst–Pack grids for the electronic Brillouin zone (BZ) integration for the PP, CG, CCM, BP, CH, LB and SC phases, respectively. It is found that the convergence of the total energies is better than 2 meV/atom.

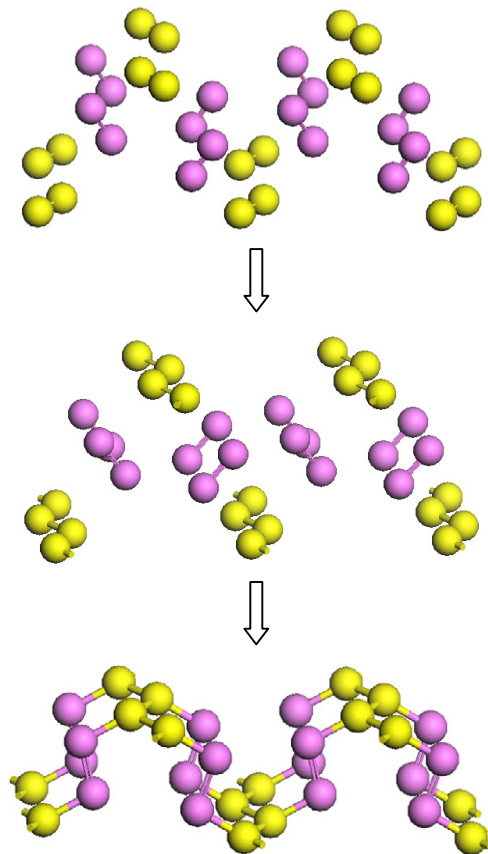


Figure 5. The evolution from the molecular phase ζ to the atomic phase PP.

Table 1. The unit-cell parameters and atomic positions of the PP nitrogen phase.

Pressure phase (GPa)	Space group	a (Å)	b (Å)	c (Å)	Z	Atoms	x	y	z
20	$Pmna$	2.287	4.281	5.975	4	N ₁	-0.5000	0.8049	0.3153
					4	N ₂	-0.5000	0.6537	0.5193

3. Results and discussion

The PP phase has been obtained by full geometry optimization, including atomic position and lattice constants from the ζ phase at 114 GPa [16]. The evolution of the molecular ζ phase to the atomic phase PP is shown in figure 5. The PP phase can be described as a layered structure composed of fused 10-member rings, which is shown in figure 4 from different angles of view. The unit cell of PP is an orthorhombic cell, inside which there are eight nitrogen atoms. The cell parameters and atomic positions of the PP nitrogen phase are listed in table 1.

The bulk modulus and Young's modulus of PP are obtained and given in table 2; the experimental values and the calculated values for CG are also listed for comparison. We can see that the calculated CG structural parameters in our case are in good agreement with the previously calculated results and also compare reasonably with the experiments. The CG bulk

Table 2. The lattice constant, bulk modulus and Young's modulus of the PP phase at 20 GPa. The CG phase values are listed for comparison.

	Bulk modulus (GPa)	Young's modulus (GPa)	Lattice constant (Å)	Atom position	Bond length (Å)
PP (20 GPa)	163	X 133 Y 738 Z 137			1.385 1.336 1.380
CG	280 (0 GPa)	471 (0 GPa)	3.49 (115.4 GPa)	0.073 (115.4 GPa)	1.335 (115.4 GPa)
CG	281 ^a (0 GPa)	452 ^a (0 GPa)	3.50 ^b (115.4 GPa)	0.071 ^b (115.4 GPa)	1.350 ^b (115.4 GPa)
CG	298 ^c (0 GPa)		3.45 ^c (115.4 GPa)	0.067 ^c (115.4 GPa)	1.346 ^c (115.4 GPa)

^a Reference [17].^b Reference [7].^c Reference [8].

modulus is excellently consistent with the experimental result, which sufficiently proves the accuracy of our calculations. Also, the Young's modulus along the a axis of the PP phase is very large, displaying the high capability of resistance to strain along the a axis.

The structure of PP, initially obtained at high pressures, remained qualitatively unchanged when reoptimized at different pressures in the range 0–360 GPa, indicating that, along with other polymeric phases of nitrogen, PP is also metastable for a wide range of pressures. In order to explore the stability of this phase, we have performed two tests similar to those used by Mattson *et al* [10]. In the first test, we randomly select one atom in a eight-atom cell, and move it away from its equilibrium positions within 1%, 2%, 3%, 4%, 7%, 13% and 20% of the bond length at 10 and 20 GPa; this procedure will make every atom in the cell move when performing geometry optimization. The second test was performed in such a way that a favored bond was chosen in the cell and its bond length was decreased or increased by 4%, 7%, 13% and 20%. Both tests show that the structure returns to the initial PP structure after optimization. Above 360 GPa, the PP structure immediately transforms into a fully connected structure.

The enthalpy–pressure curve is given in figure 6. The enthalpies of the seven structures are all increased as the external pressure is increased. When the external pressure is lower than 220 GPa, the CG phase has the lowest enthalpy among these phases in our calculations, and it is in good agreement with the previous work of Zahariev *et al* [9], which suggested a transition pressure of 200 GPa. Moreover, the phase CMCM has lower enthalpy than the CH and PP phases for all pressures. The enthalpies of PP and CH have almost the same trend, changing with increasing pressure. At pressures greater than 140 GPa, PP becomes lower in enthalpy than CH. SC is the least favorable phase among all the phases discussed here.

Figure 7 shows the energies as a function of volume of nitrogen in the ϵ , CG and PP phases. ϵ is a molecular phase and is stable at higher pressure with a hexagonal structure. The common tangent between the two theoretical curves suggests that a transition from the ϵ phase to the PP phase occurs at a pressure of 90 GPa, and that the ϵ -to-CG phase transition pressure is at about 32 GPa, in agreement with the previous works of Mattson *et al* [10] and Mailhiot *et al* [1].

In figure 8, the calculated electronic energy bands of the five structures at 20 GPa are shown, in which the PP structure shows a direct band gap feature. It is important to note that the Fermi level crosses the energy band, so the PP and CH, CMCM, LP phases are metallic, but the BP and CG phases have indirect band gaps of about 0.24 eV and 4.5 eV, respectively.

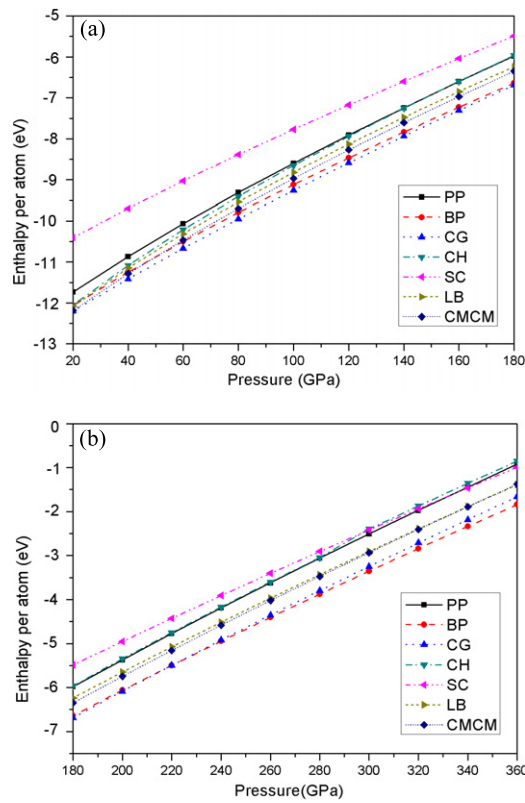


Figure 6. Calculated enthalpies of the various polymeric nitrogen phases at (a) 20–180 GPa and (b) 180–360 GPa.

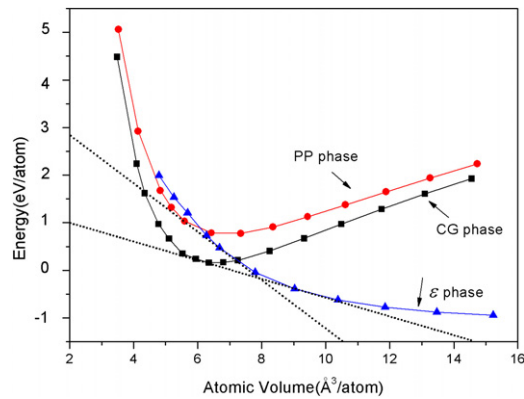


Figure 7. The common tangent between the two theoretical curves suggests a transition pressure of 32 GPa from ε to CG, and about 90 GPa from ε to PP.

4. Conclusion

One new layered phase of polymeric nitrogen named PP is suggested in this paper. The phase has zigzag chains similar to the BP, A7 and LB phases, but the zigzag chains in the PP phase

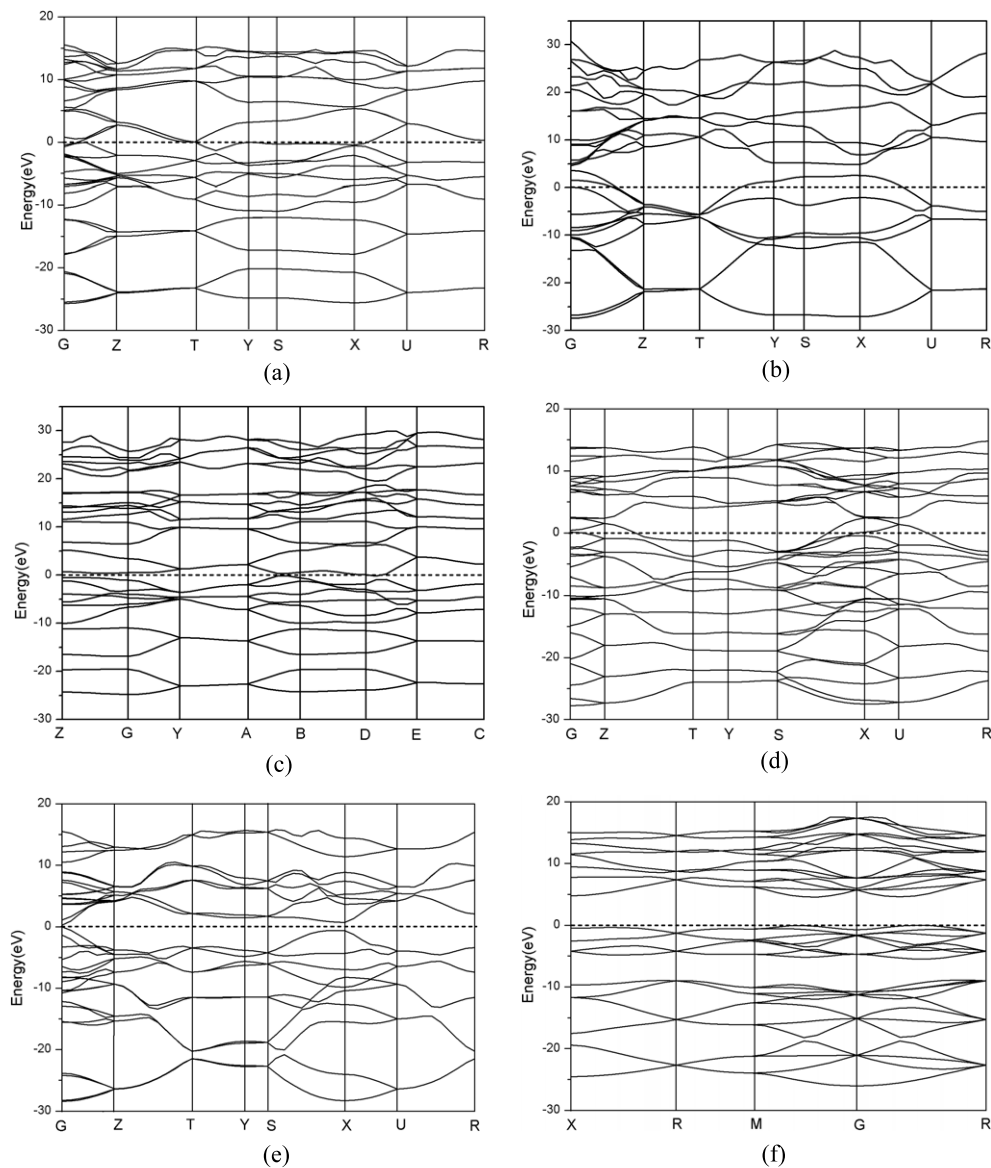


Figure 8. The electronic energy bands of (a) CH, (b) CMCM, (c) LB, (d) PP, (e) BP, and (f) CG phases at 20 GPa. The Fermi level is given by the dashed line at $E = 0$.

are connected by two atoms with double bonds. The calculated results of enthalpy versus pressure show that the PP phase and the CH phase have almost the same trend, changing with increasing pressure. At pressures greater than 140 GPa, the enthalpy of the PP phase becomes smaller than that of the CH phase. The band-structure calculations suggest that the PP phase is metallic. The equation of state of nitrogen in the PP, CG and ϵ phases gives that the transition from the ϵ phase to the PP phase is at 90 GPa. Young's modulus along the a axis is very large, revealing the high capability of resistance to strain along the a axis.

Acknowledgments

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