

Novel High Pressure Structures of Polymeric Nitrogen

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The search for the stable monatomic forms of solid nitrogen is of great importance in view of its potential application as a high-energy-density material. Based on the results of evolutionary structure searches, we proposed two high-pressure polymeric structures to be stable beyond the stability field of the synthesized cubic *gauche* structure—the layered *Pba2* or *Iba2* (188–320 GPa) and the helical tunnel $P2_12_12_1$ structure (>320 GPa). We rule out the low-temperature stability of the earlier proposed black phosphorus structure. Stability fields of the newly predicted polymorphs are within the reach of current experimental techniques.

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The search for the nonmolecular single-bonded (polymeric) form of solid nitrogen under pressure has attracted much attention. The formation of such polymorphs involves the dissociation of the extremely strong triple $N \equiv N$ bond into three weaker single N-N bonds upon compression. The surprising feature is that the triple bond is much stronger than the single bonds—making the high-energy singly-bonded nitrogen compounds unrivalled explosives. While the triple $N \equiv N$ bond is the strongest homonuclear bond known, the triply bonded molecular state in nitrogen collapses at a surprisingly modest pressure of ~ 60 GPa [1–5]—compared to $\gg 250$ GPa for oxygen [6] and ~ 500 GPa for hydrogen [7] with much weaker molecules. Once the high-pressure polymeric nitrogen is synthesized, it may be metastably decompressed to ambient pressure as one of the best possible high-energy-density materials. Following the first theoretical prediction of simple cubic form of polymeric nitrogen by McMahan and Lesar [8], many other monatomic structures were proposed, including the cubic *gauche* (cg) [9], black phosphorus (BP), α -arsenic [10,11], *Cmcm* chain [12], $N_2 - N_6$ [12], cis-trans chain [13], layered boat [14], eight-member rings [15] and poly-N [16]. Among the proposed phases, the cg structure is energetically the most stable one after the breakdown of the molecular phases, but BP takes over at higher pressure above ~ 200 GPa [12,17,18].

Experimentally, the synthesis of polymeric nitrogen under pressure has turned out to be a challenging task. The very first successful attempts obtained only amorphous products [3–5], which are likely to be mixtures of small clusters of nonmolecular phases [19]. The purely singly-bonded crystalline form remained unclear until recently, when Eremets *et al.* made a breakthrough contribution by successfully synthesizing the cg structure at high pressure (110 GPa) and high temperature (2000 K) [20,21]. Later, their finding was confirmed by another independent work

[22]. These experimental achievements have greatly stimulated the theoretical exploration of other stable high-pressure structures of polymeric nitrogen, which could be synthesized by applying higher pressure or temperature or via yet unexplored experimental approaches such as chemical stabilization. Here, we have extensively explored the high-pressure crystal structures of nitrogen through the *ab initio* evolutionary algorithm [16,23,24]. We have confirmed the stability of the cg structure and unraveled two novel single-bonded structures—the layered *Pba2* stable in the range of 188–320 GPa and the helical tunnel $P2_12_12_1$ structure stable above 320 GPa. These two structures are much superior in enthalpy to the earlier proposed BP structure. Our predictions can be expected to greatly stimulate future experiments to synthesize these new phases.

Here we use *ab initio* evolutionary simulations to search for the structure possessing the lowest free energy (i.e., the stable structure) at zero temperature and different pressures; these searches were done without any experimental information. The details of this search algorithm and its several applications on exploring high-pressure structures can be found in the literature [6,16,23–26]. The evolutionary simulations were done with the USPEX code [16,23,24], and the underlying *ab initio* structure relaxations were performed using density functional theory (DFT) within the generalized gradient approximation (GGA) [27], as implemented in the VASP code [28]. The frozen-core all-electron projector-augmented wave (PAW) [29,30] method was adopted, with $1s$ -electrons treated as core. We used the plane-wave kinetic energy cutoff of 900 eV, which was shown to give excellent convergence of the total energies, energy differences, and structural parameters. Structure searches were done in the pressure range of 100–350 GPa. Analysis of our simulation results has confirmed the earlier predicted cg and BP structures.

Remarkably, we have uncovered four new structures—tetragonal $P-42_1/m$ (8 atoms/cell) [31], orthorhombic $Pba2$ (16 atoms/cell, or $Iba2$ structure [32] with 32 atoms/cell), monoclinic $P2_1/c$ (12 atoms/cell) [31], and orthorhombic $P2_12_12_1$ (8 atoms/cell), and these are reported here for the first time. Enthalpy difference curves (relative to BP structure) for the various structures are presented in Fig. 2. For the polymeric phases, the cg structure is most stable below 188 GPa and the BP structure becomes preferable with respect to cg at 201 GPa, in excellent agreement with previous calculations [12,17,18]. However, with the prediction of the four new structures, BP structure is not favorable any more in the whole pressure range studied. We have estimated the temperature contributions to the Gibbs free energy by explicitly calculating the entropy term (TS) based on the quasiharmonic model [33]. It turns out that inclusion of entropy contribution does not affect the phase transition order, but slightly changes the transition pressures between different phases. For example, at 350 GPa and 300 K (2000 K) the calculated TS contributions are 8.4 (708.0) meV/atom for $Pba2$ and 7.8 (700.0) meV/atom for $P2_12_12_1$. This results in a negligible change in the transition pressure of $Pba2 \rightarrow P2_12_12_1$ at 300 K, but a higher transition pressure (~ 340 GPa) at 2000 K. Among the newly proposed structures, the orthorhombic $Pba2$ structure is stable in the pressure range of 188–320 GPa and above 320 GPa the $P2_12_12_1$ structure is the ground state. Below we focus on these two polymorphs which represent new structure types, not known in any other systems.

At 250 GPa ($4.27 \text{ \AA}^3/\text{atom}$) the $Pba2$ structure (Fig. 1) has the optimized lattice parameters $a = 4.17 \text{ \AA}$, $b = 4.15 \text{ \AA}$, and $c = 3.95 \text{ \AA}$, with N atoms occupying four inequivalent Wyckoff $4c$ positions: (0.2933, 0.2172, 0.6608) (0.7852, 0.2167, 0.3403), (0.0209, 0.3363, 0.177), and (0.8381, 0.0171, 0.8219). This is a layered structure,

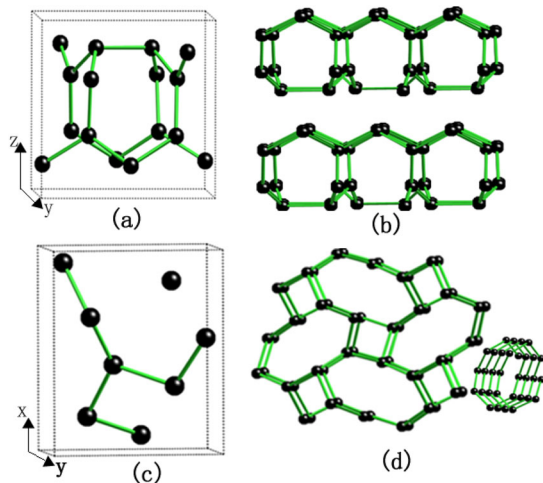


FIG. 1 (color online). Primitive cells and the extended structures of $Pba2$ (a),(b) and $P2_12_12_1$ (c),(d), respectively. The inset figure in (d) represents the helical tunnel feature.

which can be regarded as consisting of N_4 units (one central N atom being covalently bonded to three others, among which two of such N-N single bonds are equivalent). Interestingly, all the N_4 units are confined within the layers and form large building blocks along c axis. This packing arrangement is in stark contrast with that in the cg structure, where three N-N single bonds in N_4 unit are perfectly equivalent and form a highly symmetric 3D framework.

In contrast to the layered $Pba2$ structure, the orthorhombic $P2_12_12_1$ structure (Fig. 1) adopts a fully 3D packing consisting of intriguing helical tunnels connected to each other by N-N covalent bonds. At 350 GPa ($3.96 \text{ \AA}^3/\text{atom}$), the optimized lattice parameters are $a = 4.01 \text{ \AA}$, $b = 3.31 \text{ \AA}$, $c = 2.39 \text{ \AA}$ with atomic positions: N1 at $4a$ (0.8298, 0.261, 0.2384) and N2 at $4a$ (0.5704, 0.3963, 0.5025). In this structure, each N atom also forms three single covalent bonds with three neighbors, but these three N-N bonds are all nonequivalent. While the dimensionality of the covalent bond network oscillates from 3D to 2D and then again to 3D as pressure increases, there is a clear trend of decreasing local symmetry of nitrogen atoms in the structural sequence $cg \rightarrow Pba2 \rightarrow P2_12_12_1$.

The electronic band structure calculations (Fig. 3) have demonstrated the insulating nature of both $Pba2$ and $P2_12_12_1$ phases. The layered crystal structure of the $Pba2$ phase is responsible for the flat bands along $Y-T$ and $X-U$ directions. This is in strong contrast to the more dispersive bands in the three-dimensional $P2_12_12_1$ structure. The DFT band gaps of the $Pba2$ and $P2_12_12_1$ structures are ~ 5.2 eV at 250 GPa and ~ 2.64 eV at 350 GPa, respectively. It is well-known that present-day DFT func-

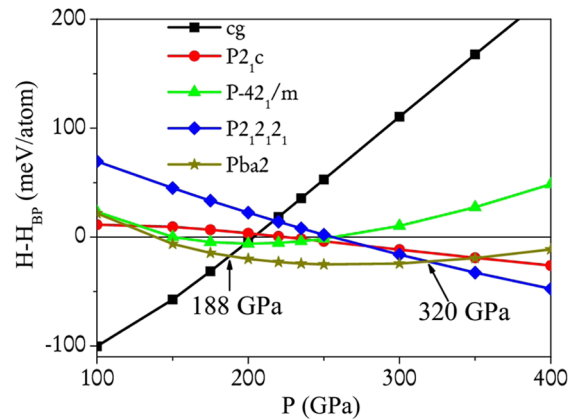


FIG. 2 (color online). Enthalpy curves (relative to BP structure) of cg and the newly predicted structures. The Monkhorst-Pack k meshes of $12 \times 12 \times 12$, $12 \times 16 \times 12$, $16 \times 12 \times 16$, $12 \times 12 \times 12$, $8 \times 12 \times 12$, and $12 \times 12 \times 16$ for cg, $P2_1/c$, $P-42_1/m$, $P2_12_12_1$, BP, and $Pba2$, respectively, were used and shown to give excellent convergence of the total energies (within 1 meV/atom). Although the structural searches are performed in the range of 100–350 GPa, enthalpy curve calculations have been extended up to 400 GPa to show that $P2_12_12_1$ becomes more preferable at higher pressures.

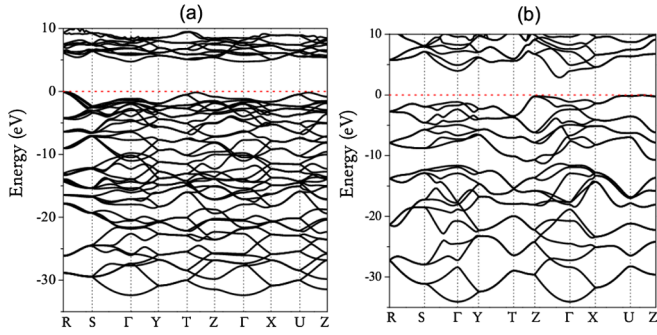


FIG. 3 (color online). Electronic band structures for $Pba2$ at 250 GPa (a) and $P2_12_12_1$ at 350 GPa (b).

tionals (LDA or the GGA used in this work) lead to a large underestimation of the energy gap. The actual band gaps can be expected to be ~ 2 times larger, and the resulting metallization pressures should be significantly higher than DFT predictions. We find that the DFT band gap of the $P2_12_12_1$ structure has only a weak dependence on pressure and decreases from 2.64 to 2.57 eV as pressure increases from 350 to 500 GPa. This suggests that the metallization pressure of crystalline polymeric nitrogen should be much higher than 500 GPa. In contrast, for amorphous nitrogen metallization was suggested to occur at around 280 GPa [5], i.e., a much lower pressure—probably due to the filling of the band gap by localized states that result from disorder. The high metallization pressure of nitrogen is in contrast to the relatively low values for its neighbors oxygen (~ 100 GPa) [34] and boron (~ 160 GPa) [35]. It is noteworthy that DFT band gap for carbon was predicted to close at ~ 1000 GPa [36]. Metallization of nitrogen can be interesting from the standpoint of superconductivity—both metallic oxygen [37] and boron [35] are superconductors.

Phonon calculations give a criterion for the crystal stability and indicate, through soft modes, structural instability. Therefore, we calculated phonon dispersion curves for the $Pba2$ and $P2_12_12_1$ phases using the supercell method [38]. No imaginary phonon frequencies are found in the pressure ranges of 180–320 GPa for $Pba2$ and above 320 GPa (e.g., at 350 GPa) for $P2_12_12_1$ in the whole Brillouin zone (Fig. 4), indicating that these two structures are dynamically stable. Phonon dispersion curves of the $P2_12_12_1$ phase are very curious and differ from other stable phases—all phonon modes can be clearly split into three groups (separated by gaps in the density of states)—acoustic (and related to them low-frequency optic) modes at 0–17 THz, framework optic modes (19–49 THz), and pseudomolecular vibrations (53–57 THz). The existence of “pseudomolecular” modes can be related to the peculiar topology of this structure and the strongly distorted local coordination of N atoms in the $P2_12_12_1$ phase. The primitive cells of $Pba2$ and $P2_12_12_1$ structures contain 16 and 8 atoms, giving 48 and 24 phonon branches, respectively. The calculated zone-center (Γ) phonon eigenvectors were used to deduce the symmetry labels of phonon modes. The

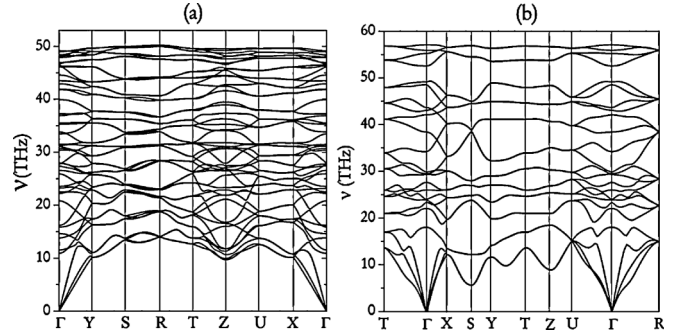


FIG. 4. Phonon dispersion curves for $Pba2$ at 230 GPa (a) and $P2_12_12_1$ at 350 GPa (b).

group theory analysis shows that the 48 vibrational modes of $Pba2$ at the zone center have the irreducible representations $\Gamma_{Pba2} = 12(A_1^{I+R} + A_2^R + B_1^{I+R} + B_2^{I+R})$, while the 24 phonon modes of $P2_12_12_1$ have the irreducible representations of $\Gamma_{P2_12_12_1} = 6(A^R + B_1^{I+R} + B_2^{I+R} + B_3^{I+R})$. The Raman active modes are labeled by superscript R and infrared active by I . It is interesting to note that all the phonon modes of the two phases are Raman active. The infrared and Raman frequencies of the two structures (zone-center phonons in Fig. 4) could be useful for the future experiments to identify the two phases as in the case of the cg structure [20].

With the current prediction of the high-pressure structural sequence $cg \rightarrow Pba2 \rightarrow P2_12_12_1$ in polymeric nitrogen, the trend of losing order in local symmetry is clearly evidenced on compression. This is in somewhat accordance with the experimental observations of amorphous nitrogen [3–5]. We have calculated the infrared frequencies of $P2_12_12_1$ structure at 170 GPa to compare with the measured data (two broad infrared peaks at 900 and 1400 cm^{-1}) characterized for amorphous nitrogen [3]. It turns out that the experimental data are well within the infrared frequency range 467–1668 cm^{-1} of $P2_12_12_1$ structure.

In conclusion, we have extensively explored the high-pressure crystal structures of polymeric nitrogen by *ab initio* evolutionary algorithm in crystal structure prediction. We discovered four novel polymorphs of tetragonal $P = 42_1/m$, monoclinic $P2_1/c$, orthorhombic $Pba2$ or $Iba2$, and orthorhombic $P2_12_12_1$, reported here for the first time. In particular, the layered $Pba2$ and helical tunnel $P2_12_12_1$ structures are found to be most stable at low temperature in the pressure ranges of 188–320 GPa, and above 320 GPa, respectively, ruling out the low-temperature stability of the previously proposed BP structure. In view of the successful synthesis of cg phase, it is greatly desirable to synthesize the uncovered two stable structures under higher pressure or temperature or via yet unexplored experimental approaches (e.g. stabilization in thin films or interfaces, and/or by impurities). It is worth mentioning that due to the small enthalpy differences between the proposed metastable phases and the stable

structures, the $P - 42_1/m$ and $P2_1/c$ phases might be also possible to be synthesized at very high temperature (e.g., 2000 K).

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- [32] $Iba2$ structure can be viewed as a c axis doubled $Pba2$ structure with two $Pba2$ units slightly c axis rotated each other. The lattice parameters at 200 GPa for $Iba2$ structure are $a = 4.1890 \text{ \AA}$, $b = 4.1843 \text{ \AA}$, and $c = 7.9967 \text{ \AA}$ with N atoms occupying four inequivalent $8a$ positions (−0.4812, 0.1636, 0.1594), (−0.7822, 0.7915, 0.2405), (−0.7161, 0.7850, 0.3995), and (−1.1628, 0.9802, 0.4801). Enthalpy calculations at 220 GPa gave nearly identical results on $Iba2$ and $Pba2$ structures within the calculation errors.
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