Cagelike Diamondoid Nitrogen at High Pressures

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Under high pressure, triply bonded molecular nitrogen dissociates into singly bonded polymeric nitrogen, a potential high-energy-density material. The discovery of stable high-pressure forms of polymeric nitrogen is of great interest. We report the striking stabilization of cagelike diamondoid nitrogen at high pressures predicted by first-principles structural searches. The diamondoid structure of polymeric nitrogen has not been seen in any other elements, and it adopts a highly symmetric body-centered cubic structure with lattice sites occupied by diamondoids, each of which consists of ten nitrogen atoms, forming a N_{10} tetracyclic cage. Diamondoid nitrogen possesses a wide energy gap and is energetically most stable among all known polymeric structures above 263 GPa, a pressure that is accessible to a high-pressure experiment. Our findings represent a significant step toward the understanding of the behavior of solid nitrogen at extreme conditions.

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Nitrogen exists abundantly in nature and stabilizes in the form of triply bonded diatomic molecules under ambient conditions. The nature of nitrogen is dramatically changed when subject to high pressure. The extremely strong triple $N \equiv N$ bond dissociates into three weaker single N-N bonds at a modest pressure >150 GPa [1–3]. In contrast, the molecular dissociation for oxygen is shown to happen at 1920 GPa [4,5] and for hydrogen at 500 GPa [6], even though these molecules have much weaker intramolecular bonds. Because of the exceedingly large difference in energy between the single N-N and triple $N \equiv N$ bonds, singly bonded polymeric nitrogen has the potential to become an excellent high-energy-density material for energy storage, propellants, and explosives. The search for polymeric forms of nitrogen upon compression has therefore attracted great attention.

The early attempts [7,8] to describe singly bonded polymeric structures of nitrogen focused on the simple cubic, black phosphorus, and α-arsenic structures, based on the known structures in group 15 (VA). Significant progress was made in 1992 by Mailhiot *et al.* [9], who predicted the *cubic gauche* (cg) structure. This remarkable cg structure was later found to be more energetically stable than all the previously proposed polymeric structures. Subsequently, numerous low-energy theoretical high-pressure structures of polymeric nitrogen were proposed (e.g., a *Cmcm* chain [10], a chaired web [11], N_2-N_6 [10], a cis-trans chain [12], a layered boat, eight-member rings, layered *Pba*2 [13], and the helical tunnel $P2_12_12_1$ structures [13,14]). It was established that the zero-temperature phase diagram of polymeric nitrogen at high pressures follows the transition sequence of cg → *Pba*2 (188–320 GPa) → $P2_12_12_1$(>320 GPa).

A great amount of experimental effort has been employed in synthesizing polymeric nitrogen, and evidence for nonmolecular phases of nitrogen at high pressures has been reported by several groups [1,2,15]. However, most samples are amorphous and likely to be mixtures of small clusters of nonmolecular phases. In 2004, the first crystalline form of singly bonded polymeric nitrogen was synthesized by Eremets *et al.* at high pressures (about 115 GPa) and high temperatures (above 2000 K) [16]. The obtained polymeric single crystal phase was found to be the long-sought cg structure, a finding that was confirmed by later independent experiments [17]. These experimental achievements greatly motivate the investigation of other crystalline forms of polymeric nitrogen under higher pressures.

In this Letter, we report an unexpected high-pressure stabilization of cagelike diamondoid nitrogen above 263 GPa, predicted jointly by the CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) algorithm [18,19] and the *ab initio* random structure searching method (AIRSS) [20,21]. The prediction of the diamondoid structure rules out completely the previously proposed helical tunnel phase [13,14] and narrows substantially the stable pressure range of the *Pba*2 phase. This is a unique case that an element heavier than C is found to be stable in a cagelike structure. Our findings provide a significant advance in the understanding of the behavior of solid nitrogen and other nitrogen-related materials under extreme conditions.

The CALYPSO structure searching approach [18,19] enables the global minimization of energy surfaces via *ab initio* total-energy calculations and the particle swarm optimization algorithm. This method has been successful in correctly predicting high-pressure structures for various systems [4,22,23]. The underlying *ab initio* structural relaxations and electronic band structure calculations were performed in the framework of density functional theory within generalized gradient approximation using Perdew-Burke-Ernzerhof functionals [24], as implemented in the VASP code [25]. Projector augmented wave [26] potentials are used to describe the ionic potentials. The cutoff energy (700 eV) for the expansion of the wave function into plane waves and Monkhorst-Pack [27] k meshes were chosen to ensure that all the enthalpy calculations are well converged to better than 1 meV/atom. The AIRSS structural search method has been described in detail in Refs. [24,25]. An ensemble of structures is chosen by first generating random unit cell translation vectors and renormalizing the resulting cell volumes to lie within some reasonable range. The atoms, or structural units, are then placed at random positions, possibly constrained by symmetry, and the cell shapes and atomic positions are relaxed at a fixed pressure to a minimum in the enthalpy. The structural optimizations and energy calculations for various structures have been performed by using the CASTEP code [28].

CALYPSO structure predictions were performed for simulation cells containing up to 40 N atoms at a pressure range from 100 to 800 GPa. Besides the earlier predicted cg, $Pba2$, $P2_12_12_1$, and $P\bar{4}21/m$ structures, our structural searches identified a highly symmetric body-centered cubic (bcc) structure (20 atoms/cell, space group $I\bar{4}3m$), as depicted in Fig. 1(a). This cubic structure has a lattice parameter of $a = 4.287$ Å with N atoms sitting at two inequivalent crystallographic sites $12e$ (x, 0, 0) and $8c$ (y, y, y) with $x = 0.3532$ and $y = 0.6745$ at 300 GPa (3.939 Å^3/atom). Inspection reveals that the structure consists of identical N_{10} cages at the bcc sites, each of which contains 10 N atoms forming a tetracyclic cage [Fig. 1(b)] and is covalently bonded with its six next-nearest-neighboring N_{10} cages, i.e., bonding between center cages or between vertex cages. There is no covalent bonding between the nearest-neighboring cages [29]; i.e., no bonding exists between center and vertex cages. Within each cage, there are 6 "bridge" N atoms (shaded in light gray) and 4 "cage" N atoms (shaded in brown), as displayed in Fig. 1(a). Although all the N atoms form three single N-N bonds with their neighbors, bridge and cage N atoms are distinct. Each cage N bonds equally with three bridge N atoms, forming a triangular pyramid with a cage N sitting at the apex. In contrast, each bridge N bonds with two cage N atoms and one bridge N, forming a trigonal plane, and the bridge N sits at the center. Analysis of electron localization functions (ELFs) [Fig. 1(d)] and partial densities of states [Figs. 2(b) and 2(c)] suggests that the cage N atoms are sp^3 hybridized, with lone pair lobes pointing opposite to the pyramid, whereas the bridge N atoms are in sp^2 hybridization with lone pair lobes (p_z) at both sides of the triangular plane. As shown in Fig. 1(d), the lone pairs are arranged in a way that their lobes avoid each other by pointing to the perpendicular directions at neighboring N atoms. Following the prediction of the N_{10} structure by CALYPSO, an independent structural search at 300 GPa was performed using the AIRSS method, with no prior knowledge of the structure beyond the number of atoms required to describe it. The N_{10} structure was found and confirmed to be the most stable. Six new metastable structures were also identified [29] and included in the enthalpy curves (Fig. 3). Further attempts on structural design by using different combinations of N_{10} units and applying symmetry did not yield any better structures.

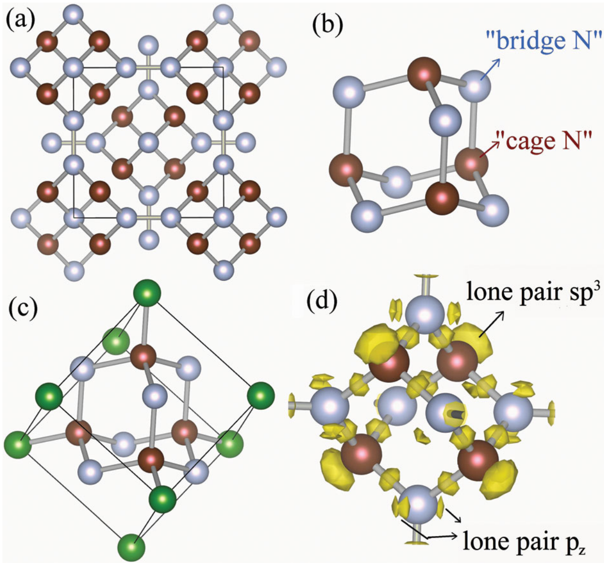

FIG. 1 (color online). (a) Top view of the N_{10}-cage structure. (b) Side view of one N_{10} cage to compare with the diamondoid. (c) Side view of the cubic diamond structure. The N_{10} cage can be derived by cutting out the eight green vertex atoms of the cubic diamond. (d) The calculated ELF isosurface within one N_{10} cage at ELF = 0.83.

The enthalpies of the N_{10}-cage structure together with other known and our newly predicted structures are plotted as a function of pressure in Fig. 3. It shows clearly that the cg structure is most stable up to 188 GPa, beyond which the $Pba2$ structure is favored. The results are in excellent agreement with the previous calculations [10,13,30]. However, the prediction of the N_{10}-cage structure being stable at pressures higher than 263 GPa narrows the stability range of the $Pba2$ structure and rules out the $P2_12_12_1$ structure completely. Furthermore, it is seen that the enthalpy difference between N_{10}-cage and $P2_12_12_1$ structures becomes increasingly larger with pressure, and our thorough structural searches could not find any better metastable structures energetically sitting in between N_{10} and

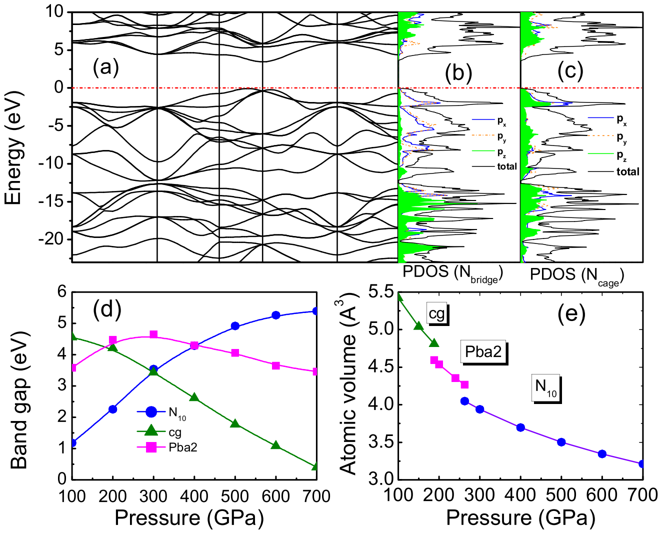

FIG. 2 (color online). Electronic properties of the N_{10}-cage structure at 300 GPa. (a) Band structure; (b),(c) partial densities of states (PDOS) of the bridge and the cage N, respectively; (d) band gaps calculated as a function of pressure for the N_{10}-cage, cg, and *Pba*2 structures; (e) atomic volume as a function of pressure for the cg, *Pba*2, and N_{10}-cage structures.

$P2_12_12_1$. Our current prediction has modified the earlier phase transition sequence into cg → *Pba*2 → N_{10} and illustrates that polymeric nitrogen should become highly ordered at extreme pressures. The calculated equation of states [Fig. 2(e)] suggested that the two phase transitions of cg → *Pba*2 → N_{10} have a first order nature with an increased packing efficiency at 26.11% → 27.24% → 28.97%.

The electronic band structure calculations showed that the N_{10}-cage phase is an insulator. We plot the band structure at 300 GPa [Fig. 2(a)] and the band gap as a function of pressure [Fig. 2(d)]. Interestingly, the band gap of N_{10}-cage structure increases significantly with pressure, reaching 5.47 eV at 800 GPa (3.096 Å^3/atom), in contrast to those in the *Pba*2 and cg phases. Because density functional calculations usually lead to a considerable underestimation of the energy gap, the actual band gaps are expected to be much larger. The insulating state is the result of the complete localization of valence electrons, similar to the monatomic O_4 phase of oxygen [4,5]. The increase of the N_{10}-cage band gap with pressure is the result of the competition of two effects: (i) on one hand, the compression and the consequent shortening of the bond length will widen both valence and conduction bands, and therefore tend to reduce the gap; (ii) on the other hand, the stronger coupling of the sp^2 (or sp^3) orbitals at the neighboring N atoms will lower the energy of the bonding states (valence bands) and increase the energy of the antibonding states (conduction bands), therefore leading to an increase of the gap. In the case of the N_{10}-cage structure, the gap increases with increasing pressure.

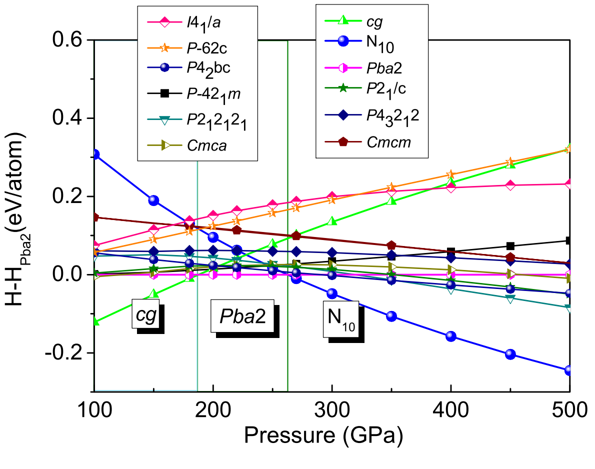

FIG. 3 (color online). Enthalpy curves (relative to the *Pba*2 structure) of various polymeric structures as a function of pressure.

The stability of a structure cannot be determined exclusively by comparing enthalpy, since the structure might be subject to dynamic instabilities. Therefore, we calculated phonon dispersion curves for the N_{10}-cage phase using the supercell method [31]. No imaginary phonon frequencies are found in the pressure range of 250–800 GPa in the whole Brillouin zone (Fig. 4), indicating that the N_{10}-cage structure is dynamically stable in this pressure range. The primitive cell of the N_{10}-cage structure contains 10 atoms, giving 30 phonon branches. The calculated zone-center (Γ) phonon eigenvectors can be used to deduce the symmetry labels of phonon modes [29]. Both infrared and Raman frequencies [29] of the structure can provide useful information for future experiments to identify the N_{10}-cage phase, as that was done in the case of the cg structure.

The N_{10}-cage structure reported here is unique and has not been seen in any other elements. Together with the facts that the earlier attempts to search for structures of polymeric nitrogen among known phases in group VA elements were not successful, it reveals a fundamental difference between N and other group VA elements in forming singly bonded extended structures. N has a very small $1s$ core which is capable of forming very short bonds,

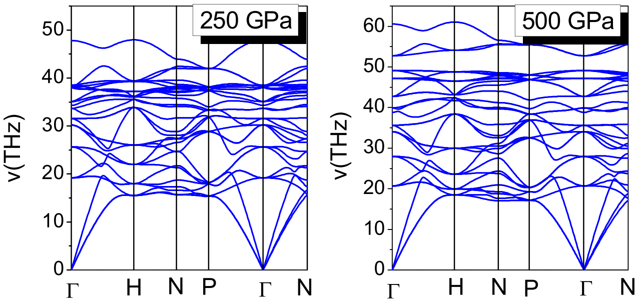

FIG. 4 (color online). Phonon dispersion curves for the N_{10}-cage structure at 250 and 500 GPa, respectively.

in contrast to the much larger $2p$ core in P or the $3d$ core in As. As a result, the low-pressure forms of black phosphorus, α-arsenic, and simple cubic phases adopted by P and As are not stable for nitrogen. Taking another view, if we consider a N_{10} age as a pseudoatom, the phase adopts indeed a bcc structure, which was also taken by P and As at very high pressures of 262 and 110 GPa [32–34], respectively. In this regard, a N_{10} unit might be seen as a superatom of group VA. The novelty of the N_{10}-cage structure lies in a compromise between atomic cores and atomic volumes tuned by external pressures.

Cagelike structures are rare in the elements and compounds. Besides the known B cage in α boron or γ boron [35], C cages in C_{60} or C_{70} [36], and Si/Ge cages in clathrates (e.g., in Ba_8Si_{46} [37]), we have also found a H cage in a hydrogen sodalite structure in CaH_6 [38]. C has the right number of electrons and forms conjugated π bonds. B is electron deficient and therefore forms multicenter bonds. The current discovery of the N_{10} cage adds a surprising new member to the cage family and extends the cage structures to group VA elements. However, compared with B and C, N has too many electrons and must develop a structure that is best in packing the lone pairs whose Coulomb repulsion excluded the stabilization of planar triangle, square, pentagon, or hexagon faces in the cages seen in other elements and render the irregularly puckered-hexagon faces in N_{10}.

More strikingly, one single N_{10} tetracyclic cage [Fig. 1(b)] can be derived by cutting out the eight vertex atoms of one unit cell of cubic diamond [Fig. 1(c)] and is the simplest possible nanoform of diamond, a so-called "diamondoid" [39], by the removal of H from adamantane. In this regard, the N_{10} structure is a basic cage structure of a diamond lattice, a *nitrogen diamond*. We tried larger cages cut from cubic or hexagonal diamonds, but no better structure was found. There is no surprise since the diamondoid structure is evidently denser. Intuitionally, a cage structure is not the preferable choice for achieving the best packing efficiency, but the diamondoid structure as a compromise adopts a mathematically perfect structure, forming puckered tetracyclic cages to optimize the volume.

In summary, we have reported for the first time a strikingly cagelike diamondoid structure for polymeric nitrogen under high pressures. Based on thorough structural searches and accurate density functional calculations, we predict that the diamondoid structure is stable in the pressure range >263 GPa accessible to the high-pressure experiment. Our findings provide an unexpected example created by compression of a molecular solid and represent a significant step toward the understanding of the behavior of solid nitrogen and other nitrogen-related materials at extreme conditions. In view of the successful synthesis of the cg phase, it would be of great interest to experimentally synthesize the predicted diamondoid structure above 260 GPa and at a temperature higher than 2000 K. It will be necessary to consider the synthetic kinetics which has been found to be large in synthesis of the cg phase.

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