Layered single-bonded nonmolecular phase of nitrogen from first-principles simulation

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A phase of nonmolecular nitrogen, found by first-principles density functional theory simulations at high pressures is reported. The phase has a $P2_1/m$ symmetry and consists of two-dimensional layers of fused N_6-rings where the rings are all in the boat conformation. The phase has been designated the layered boat or LB phase. Properties of LB are presented in comparison with other computationally studied polymeric phases of nitrogen. In particular, the structure of LB is compared to two other layered phases, black-phosphorus (BF) and α-arsenic ($A7$). A calculated enthalpy versus pressure phase diagram reveals that LB lies between BF and $A7$ in enthalpy at pressures less than 200 GPa. At pressures higher than this, the enthalpy of LB edges above that of $A7$. The metastability of LB at low pressures is probed by a few simple tests and the band structure is calculated.

I. INTRODUCTION

Metastable allotropes of molecular and nonmolecular nitrogen have been ardently pursued as potential future high energy-density materials (HEDMs).[1–5] The high energy content of polynitrogen candidates stems from the unusually strong triple bond in N_2 compared to the N-N single and double bonds. More specifically, the 4.89 eV/atom triple bond energy in N_2 is much more than three times the average N-N single bond energy of 1.42 eV/atom or three-halves the average N-N double bond energy of 2.65 eV/atom.[6] Thus, the decomposition of any polynitrogen compound into N_2 will be accompanied by a large release of energy.

On the molecular side, chemists have long sought to synthesize stable homoleptic polynitrogen compounds since the isolation of N_2 in 1772 and the discovery of the azide anion N_3^- in 1890. Despite numerous theoretical studies that have suggested that many polynitrogen compounds may be stable, it was only in 1999 that another stable homoleptic polynitrogen compound could be synthesized in macroscopic quantities—the N_5^+ cation.[3]

Synthesis of metastable nonmolecular forms of nitrogen have also long been sought after and again success has only come in recent years.[1,2,7–11] To date this has been achieved through high pressure compression of molecular nitrogen. First, in what is believed to be an amorphous form of nonmolecular polymeric nitrogen was produced at pressures above 150 GPa.[1,9] More recently, a crystalline form of nonmolecular polymeric nitrogen has been synthesized via pressures above 110 GPa and high temperatures.[2] This form was determined to have the so-called cubic gauche (CG) structure composed of a network of nitrogen atoms connected to three neighbors with single covalent bonds [Fig. 1(a)]. Interestingly, in the context of this study, the CG form of polymeric nitrogen was predicted theoretically in 1992 by the ground breaking work of Mailhiot, Yang, and McMahan.[8] Moreover, the agreement between the theoretical predictions and the measured properties of the CG form of polymeric nitrogen

are indeed impressive.[8] Theory also predicts that the CG phase may be metastable at ambient pressures,[12] but attempts to bring the CG phase to pressures lower than 42 GPa have not been successful due to current technological limitations.[2]

Theoretical calculations have also predicted other nonmolecular forms of polymeric nitrogen that are potentially metastable,[8] some of which are shown in Fig. 1. Many of these forms arise from distortions of the simple cubic (SC) form. For example, the α-arsenic structure, $A7$ [Fig. 1(b)], and the black phosphorus structure, BF [Fig. 1(c)], both based upon the expected analogies with arsenic and phosphorous, are rhombohedral and orthorhombic distortions of SC, respectively. Another commonly discussed theoretical phase is a chainlike phase, CH [Fig. 1(d)] consisting of nitrogen chains in alternating *trans* and *cis* configurations. The SC, CH, $A7$, and BF forms have not been observed experimentally and at pressures less than $\sim$200 GPa, they are all
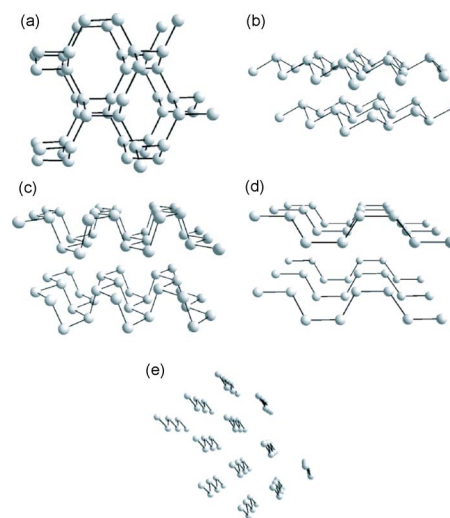

FIG. 1. (Color online) Structure of select predicted phases of polymeric nitrogen, (a) CG, (b) $A7$, (c) BF, (d) CH, and (e) zzCH.

predicted to be thermodynamically less stable than the cubic gauche form.

Recently, two new zig-zag chainlike phases, possibly metastable, have been proposed[13,14] from theoretical calculations. One of these phases that we will label zzCH, is predicted to be thermodynamically competitive with the cubic gauche phase at low pressures. Interestingly, these phases (as well as others) were found by virtual experiments, in the sense that the authors started from known molecular phases and compressed them. These were followed by either high temperature molecular dynamics and/or geometry optimization.

In this paper, we present a phase of polymeric nitrogen determined from first principles, gradient-corrected, density functional theory simulations. The phase consists of layers of fused six-membered rings. Since all of the rings are in a boat conformation, we have named this phase the layered boat or LB phase. The phase is related to the BF and $A7$ structures, and, to the best of our knowledge, has not been reported in the literature yet. The structural, thermodynamic and electronic properties of the phase are examined and compared with the SC, $A7$, BF, CG, and zzCH (Ref. 13) phases.

II. TECHNICAL DETAILS

Kohn-Sham density functional theory calculations with the gradient-corrected exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE)[15,16] were used to determine all of the energies and structures presented. It should be noted that most first-principle calculations of solid nitrogen carried out so far, with the notable exception of Mattson *et al.*[13] have used the local-density approximation (LDA) type of functional. LDA and generalized gradient approximation (GGA) functionals give markedly different results when calculating simple bond lengths and binding energies of nitrogen.[10,17,18] A number of studies suggest that when applied to covalently bonded systems, GGA functionals are more accurate than LDA functionals for a wide range of systems, with nitrogen clusters being one of them.[19–31]

The SIESTA[32] local-basis, pseudopotential, density-functional (DFT) program was used for all presented calculations. Norm-conserving pseudopotentials[33,34] of Troullier-Martins[35] were used in the reference configuration of nitrogen $[He]2s^2 2p^3$. A short cutoff radius of 0.98 Å was selected for the pseudopotential to allow for a greater transferability of the pseudopotential, especially at high pressures. A custom SEISTA-type numerical double-zeta with polarization basis set[36] with a 3.5 Å cutoff was developed for these simulations. The produced combination of basis and pseudopotential was tested on several nitrogen clusters, for which high level *ab initio* data was available and its required transferability qualities confirmed. Similar calculations on polymeric nitrogen using SEISTA have also recently been reported.[13] The real-space mesh cutoff was set to 100.0 Rydbergs. A 10 Å cutoff for k-point sampling was utilized based on convergence of geometries and relative thermodynamic stabilities. For the phase, local minima for the entire pressure range found in SIESTA were verified by performing calculations using the projector-augmented[37] plane-
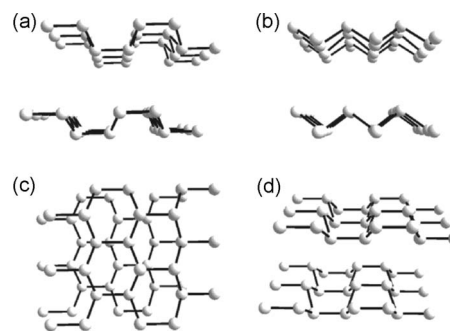

FIG. 2. The lattice structure of LB from different viewing angles, (a) along [100]-direction, (b) along [010]-direction, (c) perpendicular to the (001)-plane [note, the [001]-direction is skewed versus the (001) plane as the unit cell is monoclinic], (d) a perspective view.

wave based DFT program VASP[38] using the same functional and a comparable pseudopotential.

For optimization of the structures used in the construction of the enthalpy versus pressure diagrams, both the cell shape and nuclear geometries at a given pressure were simultaneously optimized. Simulations were performed with a variable-cell-shape conjugate gradient method under constant pressure for the minimization of geometries. NPT molecular dynamics simulations were performed using the Parinello-Raman variable cell method[39] and Nosé-Hoover thermostating.[40] A 1 fs time step was used.

64-atom supercells were used for all the simulations. More specifically, the following unit cell multiplicities were used for each phase, $2 \times 2 \times 2$ for the α-molecular phase, $4 \times 4 \times 4$ for SC, $4 \times 4 \times 2$ for $A7$, $4 \times 2 \times 2$ for BF, $4 \times 2 \times 2$ for CG, $4 \times 2 \times 2$ for CH, $4 \times 4 \times 2$ for zzCH, and $4 \times 2 \times 2$ for LB.

III. RESULTS AND DISCUSSION

In the following we will first briefly describe how LB was obtained in the simulations. After this a more detailed description of the lattice structure will be given with a comparison to other computationally studied phases of polymeric nitrogen. A discussion of the energetic contribution of *gauche*, *trans*, and *cis* dihedral angles in the phase is also discussed. A pressure versus enthalpy phase diagram is presented with a discussion of how LB compares with the other phases in terms of thermodynamic stability. We end with a brief analysis of the band structure and the phase's metastability.

The layered boat (LB) phase was obtained in the following manner. Beginning with a $2 \times 2 \times 2$ supercell of the α-molecular phase, for which the coordinates are known experimentally,[41–43] geometry optimization at ~50 GPa resulted in the formation of structure, not necessarily stable, that resembled the ε-molecular phase.[41–45] Further optimization of the ionic coordinates and cell at elevated pressures (80–140 GPa) resulted in the zig-zag chainlike phase, zzCH [Fig. 2(d)], previously reported by Martin and co-workers.[13] The LB phase was formed from zzCH after further structural optimization at 150 GPa. The phase was also formed in a
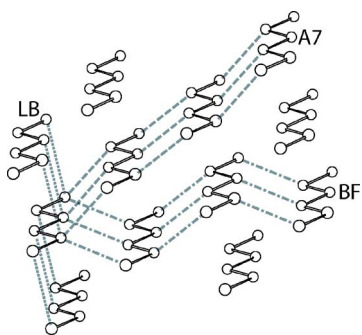
FIG. 3. (Color online) The zzCH phase with the possible interchain bonding drawn, BF (dashed-dotted lines), $A7$ (dashed lines), and LB (dotted lines).

FIG. 4. Newman projections of the R_2N-NR_2 fragment in various conformations. lp represents the lone pair.

simulation run beginning from the chainlike phase ch [Fig. 2(d)] following optimization at 120 GPa.

The structure of the phase, LB, can be described as a layered phase composed of fused six-membered rings, where each ring is in a boat conformation. The structure of LB is shown from various viewing angles in Fig. 2. The boat conformation of the rings can most easily be seen in the perspective view of Fig. 2(d). All the nitrogen atoms are threefold connected with single bonds, forming two-dimensional layers similar to that in $A7$ and BF [Figs. 1(a) and 1(b), respectively]. The unit cell of LB at 150 GPa is a simple monoclinic cell with vector lengths of $a=3.183$ Å, $b=2.295$ Å, $c=2.310$ Å. There are four nitrogen atoms in a unit cell at (0.00, 0.00, 0.00), (1.25, 0.00, 0.00), (1.59, 0.93, 0.84), and (2.84, 0.93, 0.84). The symmetry group of the phase is $P2_1/m$.

The structure of LB is related to the BF and $A7$ phases in that they are also composed of layers of fused six-membered rings, however, in the latter two the rings are in the chair conformation. The relationship between LB and the BF and $A7$ phases can be made more extensive. For example, all three phases can be thought of as different arrangements of the zig-zag chains coming close together along given directions in the zzCH phase and forming interchain bonds. This is shown in Fig. 3 where the zzCH phase is depicted with possible interchain bonds that would result in the formation of the LB, BF, and $A7$ phases. The two-dimensional layers emerge with a periodic six-ring pattern as result of the chains in zzCH coming close together and forming bonds in between them.

In this representation, the chains of $A7$ are aligned parallel to each other, and all of them are simultaneously tilted to one side. In Fig. 3 the chains are depicted tilted to the left. A complementary right tilted form of $A7$ could be constructed from zzCH by choosing a different direction along which the zig-zag chains come together. In the same spirit, LB could be characterized as an arrangement of zig-zag chains tilted to the left and right in an alternating fashion. The relationship between the layered phases and the zzCH phase outlined here, by no means proves this is how the layered phases are most favorably formed from the zzCH phase. Nonetheless, it does provide possible pathways for the formation of the layered phases from the zzCH phase that do no require significant structural rearrangement. We note that both BF and LB
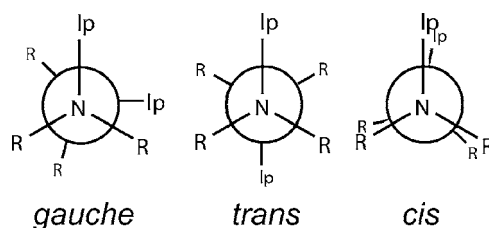
can also be considered in terms of *cis-trans* chains of the CH phase [Fig. 2(c)] coming close together and forming interchain bonds.

The three layered phases, $A7$, BF, and LB all consist of fused six-membered rings composed of nitrogen atoms that are sp^3 hybridized. The local structure of the three phases is distinct, for example, the rings in $A7$ and BF are in the chair conformation whereas they are in the higher energy boat conformation in LB. Here we examine the relationship between the local structure and the relative internal energies of the phases by considering the dihedral angles between N-N single bonds.

Quantum chemical calculations of small molecules of the form R_2N-NR_2 (R=H, CH$_3$, etc.) show that they have two minimum energy conformers—*gauche* and *trans* as depicted in Fig. 4. The *gauche* structure of R_2N-NR_2 is not ideal in that the lp-N-N-lp dihedral angle, θ, is not 60° but 90°. The 90° dihedral angle of the *gauche* conformer can be accounted for by the fact that this θ angle minimizes the two-orbital/four-electron destabilizing interaction between the two lone-pair orbitals of the adjacent N atoms. (We note that *gauche* definition sometimes used is somewhat different than the convention used here. For example, the lp-N-N-lp dihedral angle, in the cubic *gauche* phase is 107° with a lp-N-N-R dihedral angle being close to zero.) For a later discussion we also introduce the *cis* conformation where the lp-N-N-lp $=0°$. This is actually not a minimum energy structure but the maximum energy conformation as the lp-N-N-lp is rotated through 360°.

The energy of the N-N moiety, depends on the mutual orientation of two adjacent lone pairs as defined by the lp-N-N-lp dihedral angle. The structure of CG was postulated[8] with the above fact in mind as a solid phase of nitrogen that has all of its single bonds in a *gauche* dihedral conformation. Indeed, our calculations as well as many others[8,13,14,46] demonstrate that above 50GP, CG has the lowest enthalpy among all the nitrogen phases known so far.

The internal energy of the $A7$, BF, and LB phases can be related to the ratio of *gauche*, *trans*, and *cis* N-N bonds there are in each phase. There are six such dihedral angles in each six-membered ring of these phases. BF has a ratio of 4-*gauche*/2-*anti*/0-*cis*, while $A7$ has a ratio of 0-*gauche*/6-*anti*/0-*cis* and LB has a ratio 0-*gauche*/4-*anti*/2-*cis*. With the *gauche* conformation being the most stable, followed by the *anti* conformation and the *cis* conformation being the least stable, it is clear that this simple structural analysis predicts the following ordering of the three layered six-membered ring phases, BF$<A7<$LB. Our first-principles computations
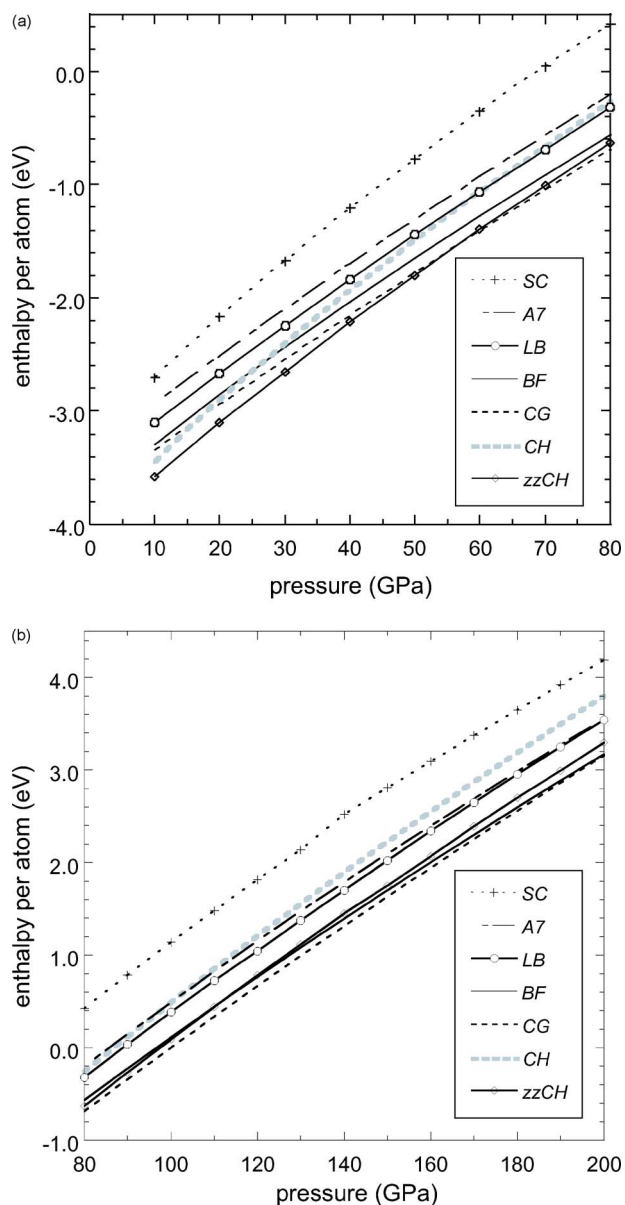
FIG. 5. (Color online) Phase diagram of various polymeric nitrogen phases. The enthalpy per atom is relative to the enthalpy per atom of CG at 100 GPa. For clarity, the phase diagram is split into two pressure regions, (a) 0–80 GPa and (b) 80–200 GPa.

of the three phases are in agreement with this. The calculated internal energy per atom of the phases is -268.6710 eV $<$ -268.6103 eV < -268.5912 eV at 20 GPa. Of course, the overall enthalpy of the phases contains a volume factor, which has substantial contribution at elevated pressures.

The structure of LB, initially obtained at high pressures, remained qualitatively unchanged when reoptimized at different pressures in the range of 0 GPa to 300 GPa, indicating that, along with other polymeric phases of nitrogen, LB is also metastable for a wide range of pressures. An enthalpy versus pressure phase diagram for LB and various other phases is shown in Fig. 5 for pressures less than 200 GPa. At low pressures, from 0 GPA to 50 GPa, zzCH is predicted to be the lowest in enthalpy, in agreement with the work of Mattson *et al.*[13] At pressures greater than 50 GPa and less

than 200 GPa, CG becomes the lowest in enthalpy, and BF becomes lowest at even higher pressures. The phase, LB, is higher in enthalpy than CG and zzCH for all observed pressures and is between *A*7 and BF for pressures up to 210 GPa. At pressures above 210 GPa, LB becomes slightly higher in enthalpy than *A*7. SC is the least favorable phase among all the phases discussed here. CH has the fastest growth of enthalpy with respect to the increasing pressure, and quickly becomes less favorable than all except SC as the pressure is increased.

The band structure of LB depicted on Fig. 6 reveals that LB is a semiconductor. The direct band gap at the gamma point is around 1.3 eV. For comparison the band gap of Si is 1.12 eV and of GaAS is 1.43 eV. The band gap is larger around *Y*, *A*, *B* indicating that it is essentially an insulator in the direction perpendicular to the layered sheets, something that one might expect due to the relatively weak electronic interaction between them.

For applications in HEDM, the mestability of polymeric nitrogen at low pressures is of interest. As a preliminary exploration of this, we have performed molecular dynamics (MD) runs on the LB phase at 0 and 1 GPa pressures. At zero pressure and temperatures up to 30 K, LB is stable after 2.0 ps of simulation time, while above this temperature the phase quickly disintegrates. At 1 GPa pressure LB was stable at 200 K but disintegrated at 300 K during the 2.0 ps MD runs. It is important to note that these short time-scale molecular dynamics simulations are only adequate to show that the phase is unstable at the given conditions.

We also performed two other tests similar to those used by Mattson *et al.*[13] (i) optimization runs after random Cartesian displacements of atoms from their equilibrium positions within 1%, 3%, 5%, and 7% of the bond length, and (ii) optimization runs after random Peierls deformation of bonds (each atom is chosen to participate in only one favored bond being deformed), by 2%, 6%, 10%, and 14%. 20 random displacement runs were performed at each condition. At 0 GPa, all of the 1% random Cartesian displacement runs and all of the 2% Peierls deformation runs successfully optimized back to the LB structure, while Cartesian displacements at 3% and Peierls deformations at 6% or greater resulted in most runs destroying structure during the geometry optimization. At 1 GPa pressure, LB was stable following the 5% Cartesian displacements and 10% Peierls deformations, but at larger displacements not all runs return to the LB structure upon optimization. These tests suggest that LB is metastable at high pressures, and may be metastable at near ambient pressures but only at very low temperatures.

IV. CONCLUSION

A phase of polymeric nitrogen that we have named the layered-boat (LB) phase has been discovered from density functional theory based first-principles simulations. The phase arose from a high pressure ($\sim$150 GPa), variable cell simulation of the known α-molecular phase of nitrogen following molecular dynamics and geometry optimization. The key structural feature of LB is that it is a layered phase composed of fused six-membered rings similar to the BF and
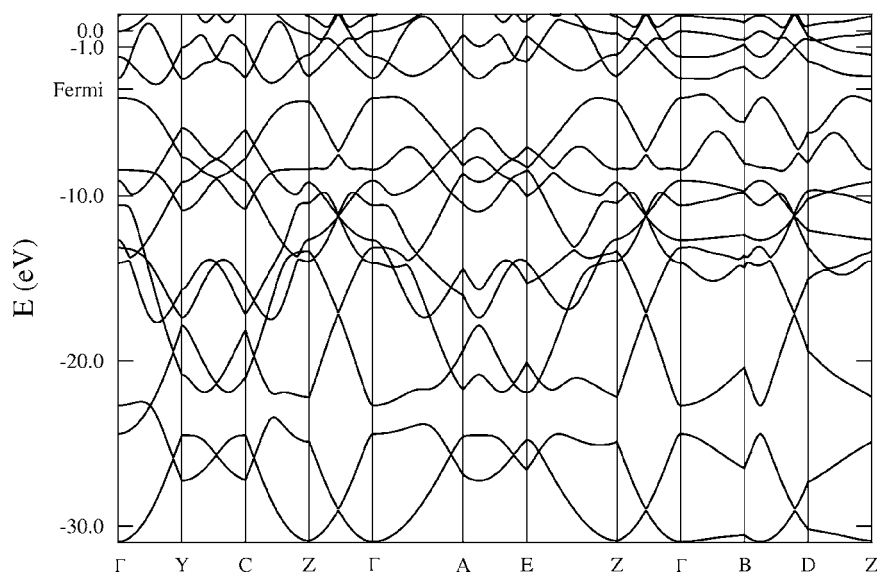
FIG. 6. The band structure of LB using the special points for the primitive monoclinic unit cell.

A7 phases such that each nitrogen atom forms a single bond with three neighbors. Unlike BF and A7, however, the phase has all six-membered rings in a boat conformation. The structural similarities between the three layered (LB, BF, and A7) has been examined with a particular emphasis on how they can be formed by simple distortions of the zig-zag chainlike (zzCH) phase recently discovered computationally by Martins and co-workers.[13] Additionally, the internal energy of the three layered phases have been related to the lp-N-N-lp (lp=lone pair) dihedral angles within the six-membered rings that make up the layers. An enthalpy versus pressure phase diagram was calculated in the range 0–300 GPa for the LB, SC, BF, A7, CH, and zzCH phases. At pressures below 210 GPa, the enthalpy of LB lies between BF and A7 and above 210 GPa it rises slightly above A7. A band-structure calculation reveals the semiconducting nature of the two-dimensional layers of LB. Molecular dynamics simulations and geometry optimization runs following random distortions of the structure suggest that LB is expected to be stable at high pressures and possibly metastable at near ambient pressures but only at extremely low temperatures.

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