

AB-INITIO BASED SIMULATIONS OF HIGH-PRESSURE PHASES OF NITROGEN

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Abstract. Three new phases of polymeric nitrogen, found by first-principles DFT calculations at high pressure, are reported. The first, that has been labeled the "layered boat" (LB) phase consists of two-dimensional layers of periodically replicated N_6 -rings where the six-membered rings are all in a boat conformation. The other two new phases found are: i) a 3-dimensional web of chaired N_6 -rings (CW or chaired web), ii) quasi-one-dimensional chains of chaired N_6 -rings (CC or chaired chains). The energies, volumes and enthalpies of the new phases at 0GPa and 20GPa are listed and compared to the respective values of several other reported nitrogen phases.

Keywords: *Ab-initio*, polymeric nitrogen, cubic-gauche, high-energy material, high-pressure nitrogen, meta-stable phase.

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INTRODUCTION

In the last few years, single/double-bonded networks of nitrogen or polymeric nitrogen have received considerable attention for their potential use as future high-energy materials. The energy content of these materials is predicted to be very high due to the large energy differences between a single bond (1.42 eV/atom), a double bond (2.65 eV/atom) and a triple bond (4.89 eV/atom) - the diatomic triple bond being the second strongest bond in existence after CO. Starting from the molecular phase which consists of N-N triple bonds, both amorphous and crystalline forms of polymeric nitrogen have recently been synthesized that are believed to be composed of N-N single bonds. [1-3] High pressures and temperatures on

the order of hundreds of GPa and thousands of Kelvin, respectively, had to be applied to synthesize the material and more importantly the material was not stable under ambient pressures.

The extreme conditions needed for synthesizing these polymeric forms of nitrogen make it difficult to study, and would seem to cause concern over its practical applications. Nevertheless, polymeric nitrogen has several notable advantages over current energetic materials as a potential energy source. There is an abundant source of nitrogen, it makes up 78% of the Earth's atmosphere. Upon decomposing, the polymeric phase goes back to its original molecular phase, thus recovering its natural supply. Also, the decomposition yields no hazardous byproducts and is environmentally friendly. The predicted energy content of even the

most thermodynamically stable phases is predicted to be about ten-times that of conventional high-energy materials such as HMX.

It should be emphasized that the existence of polymeric phases of nitrogen under high pressure was first speculated in a number of theoretical articles starting in the 1980's [4-10]. A key feature of the new phases presented here is their hypothetical metastability [6,11], meaning the phases, once formed, are stable even at ambient conditions. Some physical properties of these polymeric nitrogens, such as symmetry and conductivity, have also been explored theoretically. [6] In a ground breaking work, Mailhot, Yang and McMahan[6] postulated a new phase of polymeric nitrogen, which they named *cubic gauche* (CG), whose structure had no known analogues in nature. Based on *ab-initio* calculations, the authors predicted that this structure is the most favorable form of nitrogen above ~20GPa. When the polymeric nitrogen was found experimentally in 2001, [2] measurements suggested that the newly found phase was amorphous. A subsequent experiment by Eremets et al.[1] confirmed the existence of the CG phase upon heating the sample to 2000K. This observation of CG in 2004 reiterates the enormous predictive power of first-principles calculations.

In this work we present three phases of polymeric nitrogen that have been found through first-principles density functional theory calculations.

TECHNICAL DETAILS

In this article we present the results of first-principle calculations using SIESTA[12], a local-basis set and pseudopotential based density-functional (DFT) program. The Perdew-Burke-Ernzerhof (PBE) [13,14] exchange-correlation DFT functional was used for all calculations. It should be noted that most first-principle calculations of solid nitrogen carried out so far, with the notable exception of Mattson et al[9] were using local-density approximation (LDA) types of functionals. Norm-conserving pseudopotentials [15,16] in the parametrization of Troullier-Martins[17] were used in the reference configuration of Nitrogen [He]2s²2p³ with cut-off radius of 0.98Å. A custom numerical 'double-zeta

with polarization' SEISTA basis set[18] was used. A 10Å cut-off for k-point sampling was utilized based on convergence of geometries and relative thermodynamic stabilities. The real-space mesh cut-off was set to 100.0 Rydbergs. The produced combination was tested on several nitrogen clusters, for which high level *ab-initio* data was available and its required transferability qualities confirmed. The local minima structures for CG and LB found in SIESTA were verified by performing calculations with the same PBE functional and a compatible pseudopotential using the plane-wave based DFT program VASP.[19]

A variable-cell-shape conjugate gradient method under constant pressure was used for the minimization of the geometries, and the standard Verlet integrator with Nose-Parinello-Raman method was employed for the molecular dynamics. The low-pressure calculations were done by performing an iterative minimization with a stepwise release of the pressure from the point the new phases were initially obtained. This technique carefully preserves the metastable phase for a wide range of conditions.

64-atom supercells were used for all calculations except for CW which had a 48 atom supercell.

RESULTS AND DISCUSSION

Three new phases of polymeric nitrogen that we have labeled the layered boat (LB), chaired web (CW) and chaired chains (CC) phases have been found by first-principles DFT calculations at high pressure. The lattice structure of these three phases is shown in Figure 1. LB has a simple monoclinic unit cell and *P2₁/m* symmetry. The structure of LB can be described as a layered phase composed of fused six-membered rings, where each ring is in a boat conformation. All the nitrogen atoms are three-fold connected through single bonds, forming two-dimensional layers similar to that in α -arsenic, A7, and black phosphorus, BF, structures. CW has a rhombohedral unit cell and *R-3m* symmetry. CW consists of six-membered rings in a chair conformation forming a 3-dimensional web. The structure of CW is shown in Figure 1b. All the nitrogen atoms are three-fold connected with single bonds. CW has a highly symmetric structure where each six-membered ring is connected with three

six-membered rings above and three six-membered rings below, the bonds pointing up and down from it in an alternating fashion. The third new phase chaired chain, *CC*, has a primitive orthorhombic unit cell and *Pbam* symmetry. *CC* consists of chains formed by fused six-membered rings in a chair conformation as depicted in Figure 1C. The peculiarity of this phases is that half of the nitrogens are three-fold connected, while the other half are two-fold connected.

The structures of *LB*, *CW* and *CC*, initially obtained at high pressures, remained qualitatively unchanged when re-optimized at different pressures in the range of 0GPa to 300GPa. This is an indication that, along with other known polymeric phases of nitrogen, they are meta-stable for a wide range of pressures including the ambient pressure.

In Table 1, the energies, volumes and enthalpies of the new phases are compared with

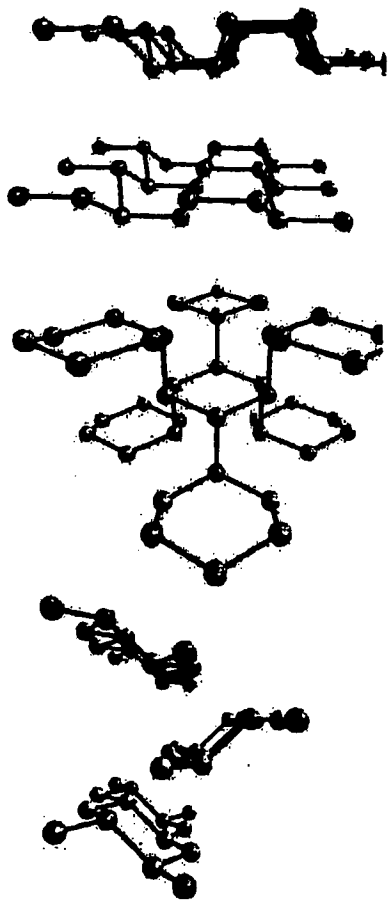


Figure 1. Lattice structure of a) the layered boat, *LB*, b) chaired web, *CW*, and c) chaired chain, *CC*, phases.

those of α -molecular phase, cubic gauche (*CG*), black phosphorus (*BP*) and α -arsenic (*A7*) at 0GPa and 20GPa. The energy (and enthalpy) of α -molecular phase at 0GPa was chosen as a reference and all the other energies and enthalpies are relative to its value. The choice of reference is physically motivated as after destabilization at ambient conditions, a metastable phase will decompose to a molecular phase. Although the final form after decomposition is likely to be gaseous, the α -molecular phase at 0GPa is a reference that is reasonably close to that of the final product of such a decomposition. As a by-product of our choice of reference the relative energy values are simultaneously estimates of the energy content of the phases.

In terms of enthalpy *LB* is between *BP* and *A7*, while *CW* and *CC* are below *BP* for both pressures reported. At 0GPa *CC*'s enthalpy is just slightly higher than that of *CG*. On the otherhand, *LB* has the highest energy content

Preliminary molecular dynamics simulations and geometry optimization runs following random distortions of the structure suggest that phases are expected to be stable at high pressures and possibly metastable at near ambient pressures but only at extremely low temperatures.

CONCLUSIONS

In this article three new polymeric phases of nitrogen are presented that were found from first-principle DFT calculations at high pressure. Their energies, volumes and enthalpies at 0GPa and 20GPa are calculated and compared with those of known phases. The calculations show a large energy difference between the new phases and the α -molecular phase, showing they possess a very large energy content. This last property in combination with the meta-stability property has drawn considerable attention to similar polymeric nitrogen phases as potential high-energy materials. A detailed phase diagram of the three new phases with calculated band structure and stability properties will be a subject of further publications.

TABLE 1. Energies (eV), volumes (\AA^3) and enthalpies (eV) of known and new phases at 0GPa and 20GPa. All of the values are per atom. The energies and enthalpies of the phases are relative to the energy (and enthalpy) of α -molecular phase at 0GPa.

	α -mol	CG	BF	A7	LB	CW	CC
<i>0 GPa</i>							
energy	0.0	1.34	1.71	1.88	1.79	1.47	1.35
volume	22.34	6.77	7.47	8.07	8.08	7.54	8.52
enthalpy	0.0	1.34	1.71	1.88	1.79	1.47	1.35
<i>20 GPa</i>							
energy	1.56	1.36	1.77	1.95	1.85	1.50	1.47
volume	15.54	6.41	6.60	6.89	6.95	5.12	7.91
enthalpy	1.95	2.16	2.59	2.81	2.72	2.35	2.46

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REFERENCES

- Eremets, M. I. et al., "Single-bonded cubic form of nitrogen," *Nature Materials* 3 (8), 558-563 (2004).
- Eremets, M. I. et al., "Semiconducting non-molecular nitrogen up to 240 GPa and its low-pressure stability," *Nature* 411 (6834), 170-174 (2001).
- Eremets, M. I. et al., "Polymerization of nitrogen in sodium azide," *Journal of Chemical Physics* 120 (22), 10618-10623 (2004).
- McMahan, A. K. and LeSar, R., *Phys. Rev. Lett.* 54, 1929 (1985).
- Martin, R. M. and Needs, R. J., *Phys. Rev. B* 34, 5084 (1986).
- Mailhot, C. et al., "Polymeric nitrogen," *Phys. Rev. B* 46 (22), 14419-14435 (1992).
- Mailhot, C. et al., "Polymeric nitrogen," *AIP Conference Proceedings* 309 (High-Pressure Science and Technology-1993, Pt. 1), 221-224 (1994).
- Yarkony, D. R., "Theoretical studies of spin-forbidden radiationless decay in polyatomic systems: insights from recently developed computational methods," *J. of the Amer. Chem. Soc.* 114 (13), 5406-5411 (1992).
- Mattson, W. D. et al., "Prediction of New Phases of Nitrogen at High Pressure from First-Principles Simulations," *Phys. Rev. Lett.* 93 (12), 125501/125501-125501/125504 (2004).
- Alemary, M. M. G. and Martins, J. L., "Density-functional study of nonmolecular phases of nitrogen: metastable phase at low pressure," *Phys. Rev. B* 68 (2), 024110/024111-024110/024114 (2003).
- Barbee III, I. W., "Metastability of atomic phases of nitrogen," *Physical Review B* 48, 9327-9330 (1993).
- Soler, J. M. et al., *J. Phys.: Cond. Matt.* 14, 2745 (2002).
- Perdew, J. P. et al., *Phys. Rev. Lett.* 77, 3865 (1996).
- Perdew, J. P. et al., *Phys. Rev. Lett.* 78, 1396(E) (1997).
- Bachelet, G. B. et al., *Phys. Rev. B* 26, 4199 (1982).
- Hamann, D. R. et al., *Phys. Rev. Lett.* 43, 1494 (1979).
- Troullier, N. and Martins, J. L., *Phys. Rev. B* 45, 1993 (1997).
- Junquera, J. et al., "Numerical atomic orbitals for linear-scaling calculations," *Phys. Rev. B* 64, 223511-235119 (2001).
- Kresse, G. and Furthmuller, J., "Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set," *Comput. Mat. Sci.* 6 (1), 15-50 (1996).

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