Ammonium azide under hydrostatic compression

A C Landerville, B A Steele and I I Oleynik

University of South Florida, 4202 East Fowler Ave., Tampa, FL 33511

Email: alanderv@mail.usf.edu

Abstract. The properties of ammonium azide NH_4N_3 upon compression were investigated using first-principles density functional theory. The equation of state was calculated and the mechanism of a phase transition experimentally observed at 3.3 GPa is elucidated. Novel polymorphs of NH_4N_3 were found using a simple structure search algorithm employing random atomic displacements upon static compression. The structures of three new polymorphs, labelled as B, C, and D, are similar to those of other metal azides.

1. Introduction

Polymeric nitrogen compounds hold tremendous potential as energetic materials due to extremely high energy release upon conversion of singly-bonded material to triply-bonded N_2 molecules, with the expectation of exceeding the explosive performance of HMX by several times [1]. It has been proposed by Hu and Zhang [2] that hydro-nitrogen solid may offer a convenient pathway to polymeric nitrogen. Further, the computational study of Hu and Zhang suggests that hydro-nitrogen solid should be produced upon compression of ammonium azide (NH_4N_3) to 36 GPa [2]. However, experimental studies of NH_4N_3 have established that a polymorphic transition from Phase I to Phase II, referred to in this work as Phase A-I and A-II, occurs at ~3.3 GPa and Phase A-II of NH_4N_3 seems to persist at least up to 55 GPa [3–5]. Therefore, no phase transition to hydro-nitrogen solid has been detected so far with pressure loading at 300 K. Usually, the material transformation upon compression is experimentally probed using Raman spectroscopy, which deals with vibrational properties of the system under study. Although the analysis of vibrational spectra allows one to make some conclusions about changes of crystal structure upon compression, its indirect nature requires additional information to relate the observed spectrum and the underlying atomic structure. Therefore, density functional theory (DFT), which calculates both the atomic and electronic structures of the crystal upon compression from first principles, is a valuable tool to complement experimental studies by providing information that is difficult or sometimes impossible to obtain from experiment.

The goal of this work is to investigate the behavior of ammonium azide NH_4N_3 upon compression using first-principles density functional theory. This includes studies of crystal evolution upon compression, and the search for new polymorphs that may be obtained by subjecting NH_4N_3 crystal to high pressure and employing a simple atomic randomization algorithm. The possibility of new phases is envisioned due to the existence of multiple polymorphs in the case of metal azides such as LiN_3, KN_3, and NaN_3. Should other polymorphs of NH_4N_3 be found by experiment, a possibility then exists that one of these crystal phases may act as an intermediate for transition to hydro-nitrogen solid. In order to realize the existence of a proposed polymorph, however, it would be useful for experimentalists to have a priori knowledge of its structure at various pressures.

2. Computational Details

Plane-wave density functional theory calculations were performed using the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) [6] with norm-conserving pseudopotentials and the DFT-D2 van der Waals (vdW) correction of Grimme [7], as implemented in the Quantum Espresso package [8], to account for weak dispersive forces between molecules. The following parameters were carefully determined to give accurate forces and vibrational frequencies: an electronic kinetic energy cutoff of 100 Ry, Monkhorst-Pack [9] k-point sampling of the Brillouin zone with spacing 0.05 $Å^{-1}$ along each reciprocal lattice vector, and a maximum force convergence criterion of 10^{-4} Ry/a_0. The equation of state (EOS) was calculated by first determining the equilibrium unit cell volume of Phase A-I, and then sequentially compressing and expanding hydrostatically at $0.02 V_0^{A-I}$ increments within the interval $0.5 V_0^{A-I} < V < 1.1 V_0^{A-I}$. The geometry of each structure was optimized, followed by density functional perturbation theory calculation of the vibration spectrum. For comparison of the calculated equilibrium volume to that of experiment, as well as comparison of structural evolution through the Phase A-I to A-II transition, temperature and zero-point energy effects were incorporated into the EOS using the quasi-harmonic approximation, which was employed to calculate the free energy. The pressure contribution is calculated as the derivative of the free energy with respect to volume at 300 K. More details can be found in Ref. [10]. This contribution was then added to the cold pressure calculated by DFT. To investigate the possible existence of other NH_4N_3 polymorphs, we utilize a simple atomic randomization scheme by which the crystal is sequentially compressed by $0.02 V_0^{A-I}$, atomic positions are randomly displaced by no more than 0.1 Å, and the atomic positions and cell parameters are then relaxed under constant volume constraint. Once reordering of the crystal is found, each structure is sequentially expanded back to zero pressure without randomization to determine the lowest pressure at which a new phase is retained. For compactness, phases A-I, A-II, and A-III are referred to as simply Phase A with the correct phase implied by the given pressure.

3. Results

The equilibrium volume for the NH_4N_3 crystal was calculated by optimizing the experimental structure determined by Prince and Choi [11]. The comparison of calculated and experimental equilibrium volumes is shown in table 1. DFT alone over-predicts the equilibrium volume by 2.7%, whereas DFT with the D2 vdW correction by Grimme [7] under-predicts the volume by 6.5%, and DFT with vdW plus thermal correction at 300 K results in an equilibrium volume 3.3% below the experimental volume. The disagreement with experiment is likely due to an inadequate description of dispersive interactions, such as hydrogen bonding, despite the use of the DFT-D2 vdW correction. For completeness, the thermally corrected EOS is compared to the cold curve for NH_4N_3 in figure 1.

   Medvedev *et al.* [3] identified a phase transition from Phase A-I to A-II (Phase I to II in their work) at ~3.3 GPa based on abrupt changes in the Raman spectrum. They proposed that these changes were due to the rotation of azides causing the weakening of hydrogen bonds under compression [3]. To confirm this, hydrostatic compression calculations were performed using DFT, which subsequently showed the rotation of the azides along the c lattice vector within the c–b plane; see figure 2. The calculated structure at pressure 3.4 GPa reveals that the azides oriented along the c-lattice vector within the c–b plane make an angle of 14˚ with the c–a plane; though experiment suggests this angle should be closer to 20˚ [5]. The abrupt changes in Raman spectrum Medvedev *et al.* [3] had observed involved mode discontinuities and splitting with prominent red-shifting of the N-H stretch modes, all of which being attributed to the weakening of hydrogen bonding between the ammonium and azide ions. The red-shifting of the N-H stretch modes with pressure continued up to ~10 GPa, at which point these modes appear to begin blue-shifting with pressure [3]. Interestingly, our compression calculations show the azides flattening out along the c lattice vector and reversing orientation at 10.9 GPa. The calculations show that by 27.1 GPa the azides once again make a 14˚ angle with the c–a

plane, which may indicate a transition into a new Phase A-III as hydrogen bonding is expected to once again be enhanced by the azide orientation.

Table 1. Comparison of calculated and experimental equilibrium volumes for ammonium azide.

	Volume (Å^3)	% Error
Experiment	295.1	–
PBE	300.6	+2.7%
PBE–D2	275.9	-6.5%
PBE–D2+300K	285.4	-3.3%

Figure 1. EOS for Phase A of NH_4N_3 with and without thermal correction. Red line is Birch-Murnaghan fit of thermally corrected EOS with parameters V_0, B_0, and B'_0 shown.
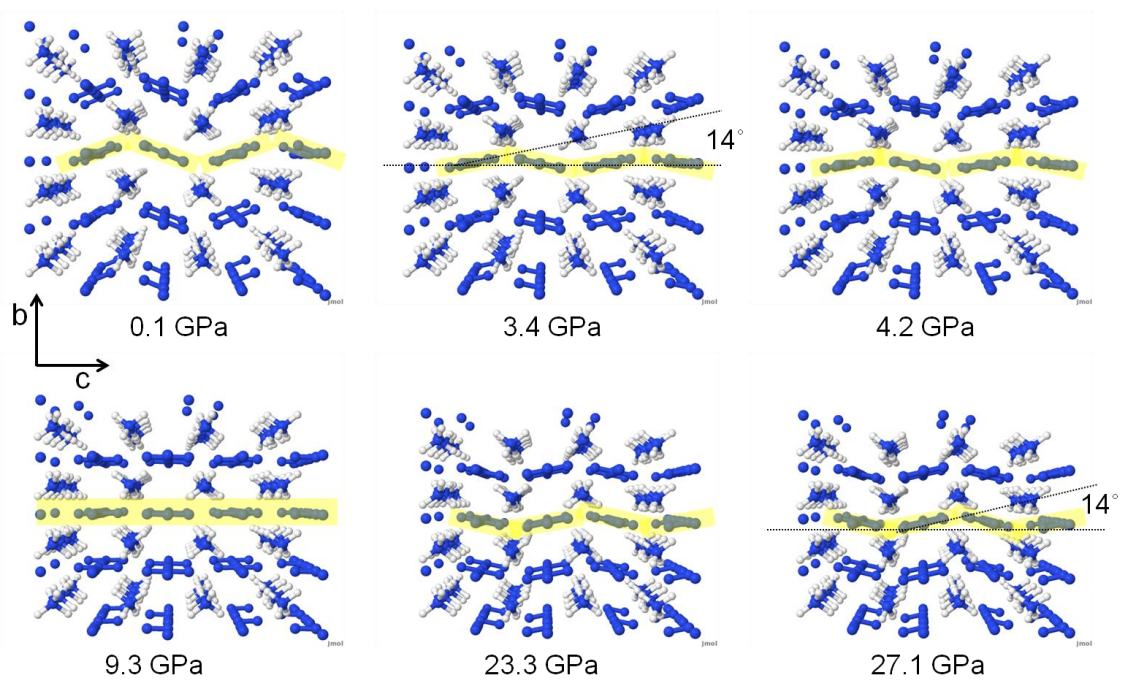

Figure 2. Evolution of azides upon compression through Phase A-I to Phase A-II transition as seen from the c–b plane. 2x2x2 super cells are shown.

To determine the existence of novel NH_4N_3 polymorphs we employ the atomic randomization scheme explained above. At pressures above 64 GPa (T = 0 K) we find a new polymorph labeled Phase B, in which the azides are reoriented, see figure 5, and which is retained upon decompression to 0 GPa. The crystal structure evolution upon randomized compression and non-randomized decompression is shown in figure 3, which displays the relative enthalpy $H = E^{DFT} + PV$ at zero temperature for each phase found, all referenced by that of Phase A. Following the randomization process, Phase A is retained until 50 GPa where the evolution of the "randomized" structure diverges

from the horizontal reference line for Phase A. Decompression of any structure up to 64 GPa will result in full recovery of Phase A. Decompression of any structure at or above 64 GPa results in a path connecting the compressed point with the line corresponding to Phase B (one such segment is shown connecting the perturbed structure at 64 GPa to the Phase B line at 45 GPa. The decompression then follows the Phase B line back to 0 GPa. Finally, continued compression with randomization eventually results in the structure coinciding with Phase B above 80 GPa. Interestingly, the enthalpy of Phase B is lower than that of Phase A beyond ~5 GPa, indicating that Phase A should be metastable at high pressure. As the actual energy barrier for the transition from A to B is unknown it is difficult to make any conclusion on whether Phase B is accessed under conditions of diamond anvil cell experiments.
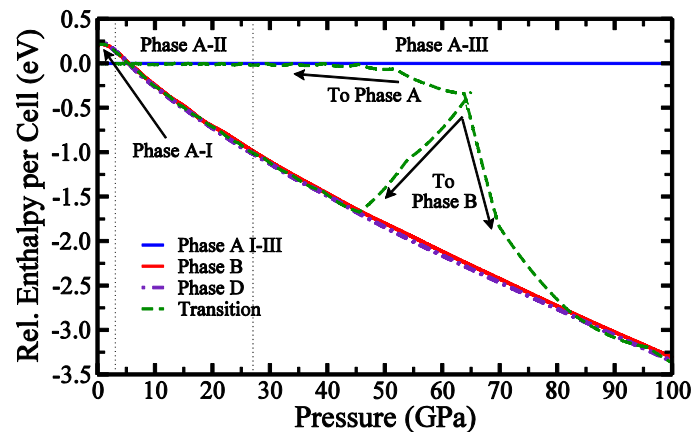

Figure 3. Relative enthalpy (T = 0 K) plots of Phases A, B, D, and transition from A to B via atomic randomizations referenced by Phase A. Phase C not shown as its range is limited to 1.5 GPa.
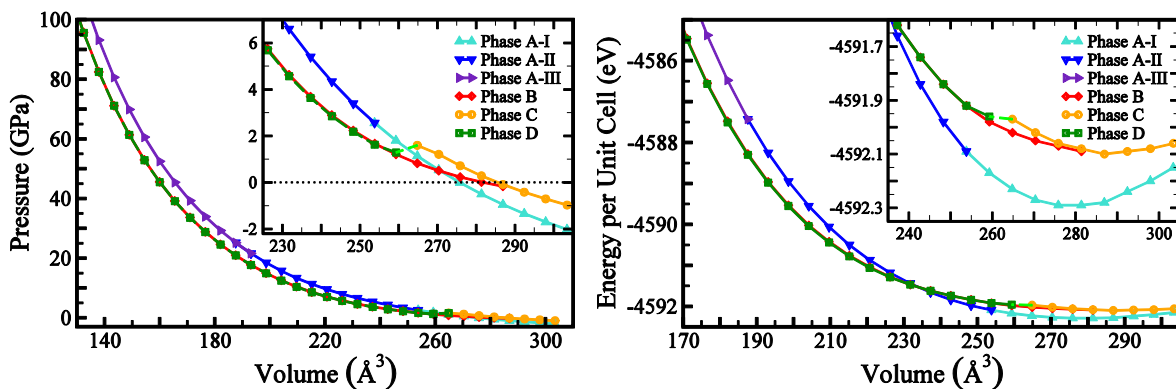

Figure 4. P-V (left) and E-V (right) curves (T = 0 K) for Phases A, B, C, and D.

It is important to note that Phase B has a monoclinic crystal structure similar to that of α-NaN$_3$ [12]. One might expect that as seen with the α to β transition in NaN$_3$, induced by thermal expansion, Phase B should transition into another polymorph upon expansion. In fact, this is precisely what is seen for the EOSs in figure 4 as Phase B transitions to Phase C when expanded to a volume of ~287 Å^3 ($1.04V_0^{A-1}$). However, Phase C does not have the same hexagonal symmetry as β-NaN$_3$; rather it is orthorhombic and appears similar to AgN$_3$ with azides arranged in a criss cross pattern offset by an angle of 155° when viewing the *c-b* projection; see figure 5. As Phase C is compressed, the azides push against each other along the *c* lattice vector up to ~1.5 GPa, at which point the crystal suddenly transforms into yet another polymorph, Phase D, resulting in reduction of the energy; see EOS in figure 4. This new, triclinic phase D has azide orientation similar to that of α-NaN$_3$ with all azides oriented in parallel. Surprisingly, the energy and pressure as functions of volume for Phase D are

almost indistinguishable from those of Phase B despite the different structures; see figure 5 for structure comparison. As a consequence, Phases B and D have nearly the same enthalpies as seen in figure 3. We believe it entirely possible that if Phase B were present at zero pressure, heated, and then compressed, a mixture of Phases B and D would be formed and retained at high pressures.
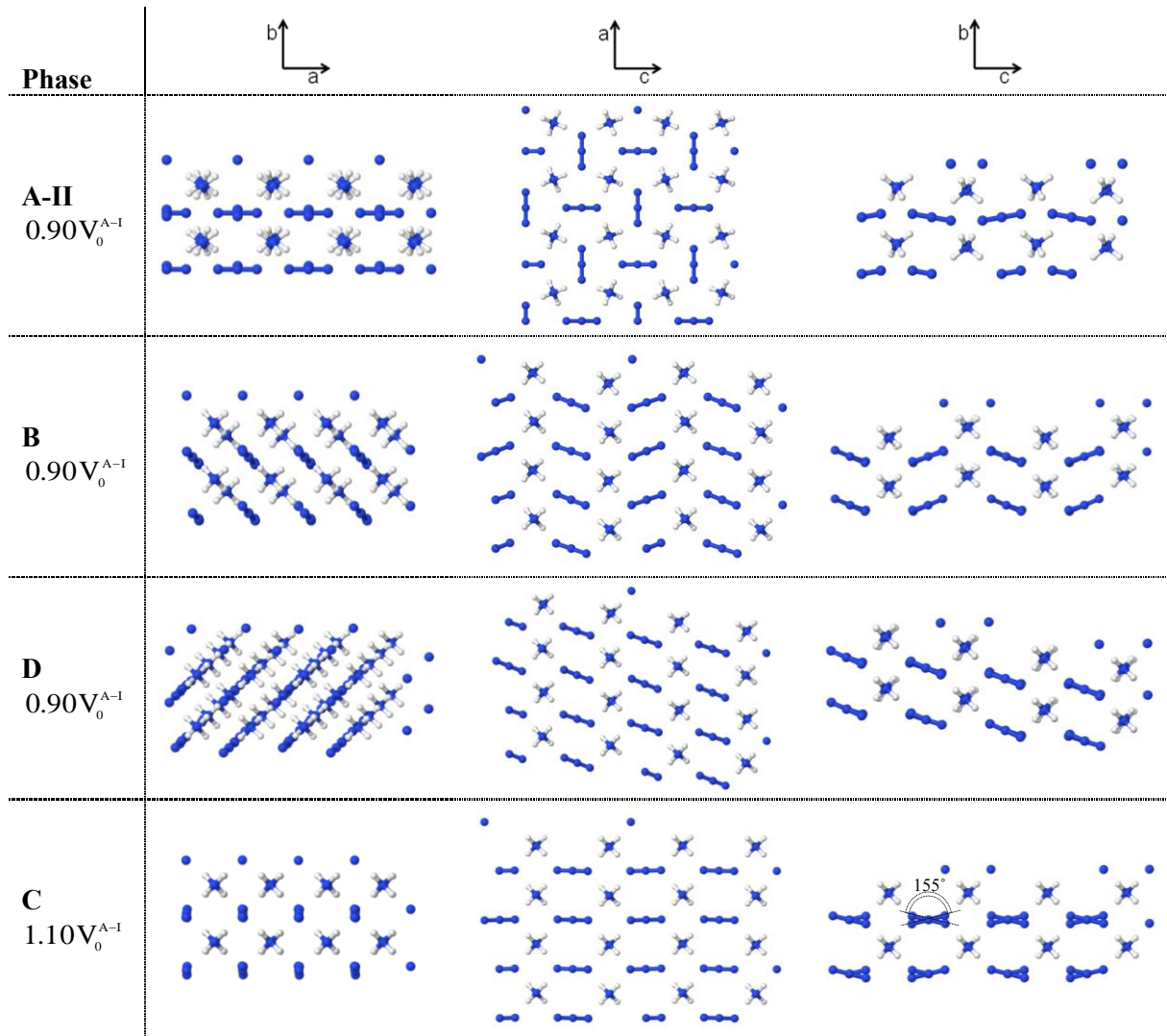

Figure 5. Comparison of super-cell structures shown for projections of *a-b*, *c-a*, and *c-b* planes for Phases A-II, B, and D at $0.90 V_0^{A-I}$, as well as for Phase C at $1.10 V_0^{A-I}$ for completeness.

4. Summary

Equations of state and enthalpies were calculated for the known phases of ammonium azide (A-I, II, and III) and three new phases (B, C, and D), which were found using a simple randomized atomic displacement algorithm applied upon static compression. We find that the transition from A-I to A-II reported by Medvedev *et al.* [3], and verified by Wu *et al.* [5] using x-ray diffraction, coincides with the rotation of azides within the *b–c* plane through less than a 14° angle with the *c–a* plane, thus weakening hydrogen bonding. We further classify a new Phase A-III as occurring near ~27 GPa, where the azides exceed a 14° angle with the *c–a* plane in reverse orientation along the *c* lattice vector. When randomized atomic displacements are included in the compression of Phase A-III, a new Phase B with symmetry similar to that of α-NaN$_3$ is retained. Upon expansion, a new Phase C is formed at

$1.04V_0^A$, which appears similar to AgN_3. Compressing Phase C to ~1.5 GPa induces yet another transition into Phase D, which has an azide arrangement similar to that of α-NaN_3, and nearly the same enthalpy as Phase B. We predict that should Phase B ever be produced it should coexist with Phase D.

References
[1]   Talawar M B and Sivabalan R 2005 *Combust. Explo. Shock+* 264
[2]   Hu A and Zhang Fan 2010 *J. Phys-Condens. Mat.* **23** 022203
[3]   Medvedev S A, Eremets M I, Klapötke T M, Palasyuk T and Trojan I A 2011 *Chem. Phys.* **386** 41
[4]   Medvedev S A, Palasyuk T, Trojan I A, Naumov P G, Evers J, Klapötke T M and Eremets M I 2012 *Vib. Spectrosc.* **58** 188
[5]   Wu X, Cui H, Zhang J, Cong R, Zhu H and Cui Q 2013 *Appl. Phys. Lett.* **102** 121902
[6]   Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[7]   Grimme S 2006 *J. Comput. Chem.* **27** 1787
[8]   Giannozzi P *et al.* http://www.quantum-espresso.org
[9]   Landerville A C, Oleynik I I and White C T 2010 *Appl. Phys. Lett.* **97** 251908
[10]   Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
[11]   Prince E and Choi C S 1978 *Acta. Crystallogr. B* **34** 2606
[12]   Zhu H, Zhang F, Ji C, Hou D, Wu J, Hannon T and Ma Y 2013 *J. Appl. Phys.* **113** 033511