Structural Transformation of Molecular Nitrogen to a Single-bonded Atomic State at High Pressures

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Introduction

Nitrogen exhibits characteristics of special interest as an archetypical molecular system. Diatomic molecular nitrogen has the greatest binding energy (after CO) and the shortest bond length, a unique elemental diatomic molecule with triple covalent bonds. First-principles theory [1] has predicted that under high compression, molecules dissociate so that each of the nitrogen atoms has three single covalent bonds to form a three-dimensional covalent solid. Moreover, Mailhiot et al. [2] predicted that the phase should crystallize in the cubic gauche (cg-N) structure where all nitrogen atoms are three-fold coordinated and the bond-lengths are the same for all pairs of bonded atoms. Due to its similarity to the diamond structure (which is four-bonded, however), cg-N could be called as a "nitrogen diamond."

Key properties of the polymeric form of nitrogen to be determined are its lattice parameters, compressibility, transformation pressure from the molecular state, metastability, and enthalpy [2-4]. The last (energy content) has been of special interest, as there is a large difference in average energy between the nitrogen single bond (0.83 eV/atom) and triple bond (4.94 eV/atom). Therefore, a very large energy should be released at the transformation from polymerized nitrogen to diatomic molecular nitrogen. Thus, nitrogen may form a high energy density material with energy content higher than that of any known non-nuclear material.

Experimentally, a transition to an opaque nonmolecular phase of nitrogen was identifying above 180 GPa at 80 K [5] and then at room and elevated temperatures [6-8]. Physical properties measured to date for the phase are close to those predicted for polymeric nitrogen. These properties include the value of equilibrium transformation pressure (about 100 GPa) and the large hysteresis indicating recoverability at ambient pressure and low temperatures [5]. Optical data indicated that the material formed on compression was disordered or amorphous [5-7]. The single-bonded nitrogen in a purely crystalline form of a cubic gauche structure (space group $I2_13$) has been recently synthesized at high pressures and high temperatures [9].

Detailed information on the crystal structure of molecular nitrogen is available only below approximately 50 GPa where the diatomic solid exhibits a rich phase diagram [10-11]. At higher pressures of ~60 GPa at room temperature, Raman and infrared absorption data indicate a transformation from the ε-N_2 (rhombohedral ($R\bar{3}c$) [12-13] to a ζ-N_2 [11,14,15]. This phase persists in the molecular state up to further transformation to the nonmolecular state at 150-180 GPa. The crystal structure of ζ-N_2 has not yet been determined. It was proposed as $R3c$ [15-16], but later it was found that this structure does not consist with Raman and IR data performed at low temperatures [11-14]. A low symmetry (orthorhombic or monoclinic) structure with two sites for atoms was proposed [14] In their x-ray studies of

nitrogen up to 65 GPa at room temperature, Jephcoat et al [17] observed a transition at ~60 GPa, but the signal was weak and the pressure was not high enough to separate the new phase and determine its structure. New molecular phases have also been synthesized at high pressures and temperatures (70-90 GPa and 600-1000 K); although x-ray diffraction data are sufficient to identify them as new phases, the crystal structures have not yet been determined [8]. Here we present x-ray diffraction measurements of molecular nitrogen up to 170 GPa and identify the structure of ζ-N_2 phase. The main results have been published in Ref. [18].

Methods and Materials

X-ray diffraction measurements of nitrogen at megabar (>100 GPa) pressures are challenging because it is a light element and a weak scatterer. We used diamond anvil cells with beveled anvils and flats 50-80 μm. An important feature was that a gasket was prepared from powder of cubic boron nitride mixed with epoxy. This gasket produced only few weak, well-defined diffraction peaks and provided a sample that is 1.5–2 times thicker than with typical hard metallic gaskets. The gasket hole was filled with fluid nitrogen at pressure about 0.2-0.3 GPa and then clamped for further pressurizing. A majority of the diffraction patterns of the molecular phases were collected at the Advanced Photon Source (APS, HPCAT at Sector 16), while the cg-N-phase and some patterns of molecular nitrogen were collected at the European Synchrotron Radiation Facility (ESRF, beamlines ID-9 and ID30). In all cases, we used an x-ray beam focused down to ~5x5 μm and angle dispersive diffraction techniques [9]. Pressure was determined from the ruby scale [19] and from the equation of state of c-BN [20].

Results

Diffraction patterns of nitrogen in the 60-150 GPa pressure range are shown in Fig. 1. At 60 GPa, several diffraction peaks of the previous ε-phase widen. At 69 GPa, these peaks are split but new peaks do not appear, which suggests that the ε-$N_2 \rightarrow \zeta$-N_2 transformation is not accompanied by a large lattice distortion. Above 80 GPa, diffraction patterns demonstrate only one phase which does not change up to 150 GPa, with the exception of the appearance of an amorphous halo above 100 GPa (Fig.1) and some redistribution of the intensity.

We begin with an analysis of the diffraction pattern of the ζ-phase obtained at 80 GPa. First, we tried the hexagonal indexing to verify the $R3c$ structure. The structure was found not to be rhombohedral structure; only hexagonal indices fit the data, verifying that the ζ-phase does not have the $R3c$ structure. To identify this low-symmetry structure, we took into account additional considerations. We assumed that the structure of the ζ-phase retains some properties of the lower pressure ε-phase, consistent with the diffraction and earlier spectroscopic data. It

is also possible that it exhibits features of the denser nonmolecular phase (cg-N). Accordingly, we began by assuming that the rhombohedral structure of ε-N_2 transforms into a rectangular structure with screw axes and without an inversion center as in the cg-N cubic space group $I2_13$. Indeed, the best indexing was found with an orthorhombic unit cell. Systematic extinctions showed the best correlation with a primitive space group without an inversion center and with only even indices for axis reflections. There are three such space groups: $P222_1$, $P2_12_12$, and $P2_12_12_1$. The volume for one atom of nitrogen in the ζ-phase should be between those in the ε-phase (8 $Å^3$ at 69 GPa) and those in the cg-phase (5.15 $Å^3$ at 115 GPa [9]). We also examined correlations in cell parameters of the ζ-, and ε- and cg-phases. It is possible to represent the unit–cell parameters of the orthorhombic ζ-phase as a derivation of ε-N_2 and the cubic phase: c_ζ (5.039 Å) is almost equal to a_ε (5.08 Å) and taking into account that a_{cg-N} = 3.454 Å [9], $a_{cub.}$ ~ $c_\zeta/\sqrt{2}$=3.81 Å, $a_{cub.}$ ~ $b_\zeta\sqrt{2}$=3.91 Å. There are common directions in these structures and the transformations may be represented as a result of diagonal displacements of atoms from threefold axes of the rhombohedral ε-phase. The screw axes of the space group $P222_1$ are in the same crystallographic direction as those in space group $I2_13$, which leads to a choice of $P222_1$ for the space group of the ζ-phase structure. The atom positions – 4e (x y z) are general for both atoms of nitrogen. The volume change of the $\varepsilon \to \zeta$ transition is ~6% at 69 GPa. The Rietveld

carried out with an R–factor (Bragg angle) = 0.08, and RF (structural factor) = 0.05 The unit–cell–dimensions and atomic positions were refined.

In the ζ-phase, the shortest distance between nitrogen atoms in the molecule N1–N1=0.982 Å (pressure 80 GPa), and the shortest intermolecular distance N1–N2=1.93 Å indicates that the ζ-phase retains a diatomic structure. However, the intramolecular and intermolecular distances significantly change
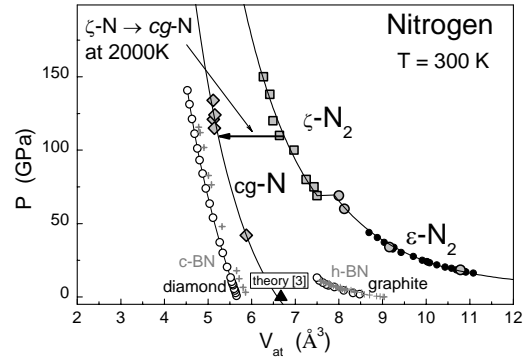
Figure 2. Pressure-volume equation of state (EOS) of nitrogen. Our experimental data for ε-N_2 are shown with open circles. Solid circles are data from Ref. [13]. Both sets of data were fitted with a third-order Birch-Murnahgan (BM) equation of states (EOS) with parameters determined at 16.3 GPa: V= 11.00 $Å^3$, B= 64.78 GPa, B′= 5.445. The volume drop at ~60 GPa identifies the transition to the ς-N_2 phase. The B-M EOS fit for this phase is described by parameters determined at 69 GPa: B= 310 GPa, B′= 4.0, V= 7.5 $Å^3$. On room temperature compression, the ς-phase remains stable at pressures up to ~150 GPa, whereupon it transitions to a nonmolecular phase with an amorphous-like structure. ς-N_2 can be directly transformed to the cubic gauche structure (cg-N) with laser heating above 2000 K at ~110 GPa [9]. The EOS of this phase has been measured with increasing pressure up to 134 GPa, and then on releasing pressure down to 42 GPa where the sample escaped the cell. The experimental points were fitted with B-M EOS with B_{42}= 460.72 GPa, $B′_{42}$= 4.0, V_{42}= 5.878 $Å^3$ taken at 42 GPa. Extrapolation of this EOS to zero pressure gives a volume of cg-N structure about 6.6 $Å^3$ (in excellent agreement with theoretical predictions of 6.67 $Å^3$ [2]), B_0= 298 GPa, B′= 4.0. The zero-pressure bulk modulus B_0 calculated using other EOS forms was found to lie in the range ~300-340 GPa. This result is also in a good agreement with theoretical predictions ~340 GPa [2]. The EOS for carbon (graphite [29] and diamond [30]) and BN (hBN and cBN [31]) are also presented to show the proximity of these covalent bonded materials with nitrogen.
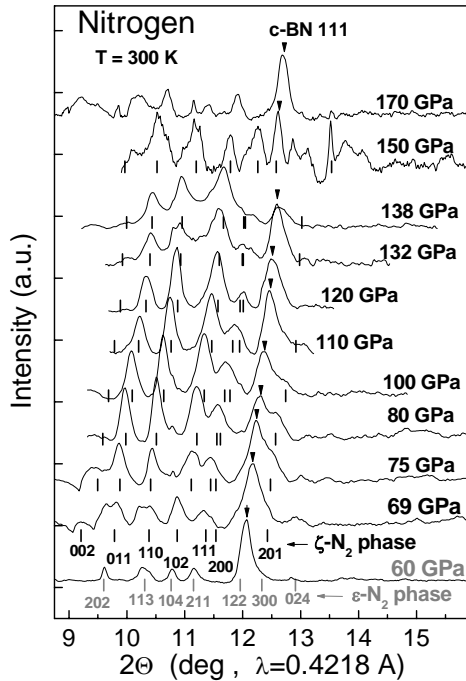

Figure 1. X-ray diffraction patterns of nitrogen taken at room temperature. (a) Evolution of diffraction patterns with pressure. Nitrogen at 60 GPa was identified as the ε-N_2 phase. The onset of ζ-phase occurs at 69 GPa. Vertical bars indicated Bragg angle positions, and indices of diffraction reflections are shown for the ε-phase at 60 GPa and for the ζ-N_2 phase at 69 GPa and higher. They were calculated for each pressure using a Rietveld refinement.

profile analysis of the diffraction pattern obtained at 80 GPa was

in comparison with the ε-phase, where the shortest intermolecular distance is equal to 2.38 Å (at 69 GPa). Between 60 and 138 GPa, the intermolecular distances further shorten from 2.38 Å to 1.73 Å. Importantly, intramolecular distances extend from 0.9684 Å to 1.002 Å in this pressure range. This expansion indicates a weakening of the (intramolecular) bonds and can explain the softening of the vibron frequencies [21], which starts at the same pressure as the transformation to ζ-N_2. These changes in intra- and intermolecular distances are favorable for the later transformation of ζ-N_2 to the cg-N phase,

where distances between atoms (bond lengths) are the same for all pairs of bonded atoms.

Discussion

It is interesting to compare transitions between differently bonded phases in nitrogen and carbon (and its analogue BN). There is a striking similarity in both volume drop (Fig. 2) and metastability. The volume drop at the ζ-N$_2$ to cg-N transition at 110 GPa is 22%, comparison to 24% for hBN $\rightarrow$ cBN and 27 % for the graphite $\rightarrow$ diamond transition at 10 GPa. At zero pressure, the energy difference between cubic diamond and hexagonal graphite is nearly zero [24]. The energetic barrier between these degenerate phases is ΔE = 0.33 eV/atom and 0.38 eV/pair for BN [24-25]. For nitrogen, a larger barrier of ~0.86 eV ^{2} is calculated for the cg-N and β-O$_2$ molecular phases. This implies metastability of cg-N even at zero pressure [2,26]. Experimentally, the diffraction experiment showed that the phase can be stabilized down to at least 25 GPa [9]. The disordered nonmolecular phase created on cold compression can be recovered to near ambient pressure at low temperatures (<100 K) based on spectroscopy [5].

There may also be similarities in the microscopic mechanisms of these transformations in nitrogen and carbon (and BN). Transitions between the carbon and BN phases are reconstructive diffusion-type phase transformations where growth of a new phase can be accompanied by the fragmentation of the parent crystal and the creation of a disordered amorphous layer between crystallites, as has been reported for the hBN $\leftrightarrow$ cBN transitions [27]. Similarly, it has been proposed recently that such transformations can occur through virtual melting along interfaces in the material [28]. This general picture of fragmentation of phases and creation of amorphous material is consistent with the disordered state of the nonmolecular nitrogen.

Acknowledgments

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