

Combined X-ray Diffraction and Raman Study of Molecular and Nonmolecular Phases of Nitrogen at High Pressure

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Introduction

The evolution of molecular solids under pressure constitutes an important problem in condensed matter physics. Under compression, delocalization of electronic shells and eventual molecular dissociation is expected, leading to the formation of a framework or closed packed structures. However, this process may not necessarily be simple and direct, because of the large barriers of transformation between states with different types of bonding and molecular structures with various types of orientational order, including possible associated and charge transfer intermediate states. Nitrogen is an archetypal homonuclear diatomic molecule with a very strong triple bond. The phase diagram of nitrogen is complex at moderate pressures and temperatures. Until recently, it had not been studied much over a wider range [1]. A theoretically proposed dissociation of nitrogen molecules under pressure [2] was recently confirmed experimentally [3-5]. Here we report on the existence of two new molecular phases called ι and θ , which have exceptionally large regions of stability and metastability extending through the P - T region where ϵ and ζ have been thought to be the only stable phases of nitrogen. This observation establishes a new class of dense molecular nitrogen phases.

Methods and Materials

X-ray and Raman experiments were performed with an externally heated diamond anvil cell with two heaters [6]. Rhenium was used as a gasket material. Samples were loaded at room temperature under a pressure of 0.2 GPa. The temperature was measured by a thermocouple attached to the gasket to be within ± 1 K below 600K and ± 5 K above 600K. To determine the pressure, we used *in situ* fluorescence measurements of ruby and Sm:YAG chips loaded in the sample chamber. We performed more than 20 experiments ranging from 15 to 1050K and up to 150 GPa by using *in situ* visible and Raman spectroscopy, synchrotron infrared spectroscopy, and synchrotron x-ray diffraction. For Raman spectroscopy, we used 514.5, 487.9 nm lines of an Ar-ion laser as excitation sources. A wavelength λ of $+0.4246 \text{ \AA}$ was used for the angle-dispersive (AD) diffraction experiments. The 2-D

diffraction patterns were recorded by a MAR charge-coupled device (CCD) detector. Additional x-ray measurements were performed by using the energy-dispersive (ED) technique at the X-17C beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.

Results

When compressed at 300K, nitrogen transforms from the ϵ phase to the ζ phase at around 60 GPa (see Fig. 1). When heated at pressures higher than 60 GPa, the material first back transforms from ζ to ϵ along a boundary that we find to be on the extension of the line established in Ref. 1 at lower temperatures. At 90 GPa, when the temperature reaches ≈ 625 K, the transition to θ takes place. The transition can be observed visually, since ϵ to ζ -N₂ normally shows substantial grain boundaries, and since after the transition to the θ phase, the sample looks uniform and translucent. In most cases, the transition happens instantaneously and goes to completion within seconds, as determined by Raman spectroscopy. If ϵ -N₂ is heated at even lower pressures (e.g., 60-70 GPa), it transforms at temperatures above 750K to ι -N₂. It is also possible to access the ι phase from θ . We observed the transformation from the θ to the ι phase upon pressure release at ≈ 850 K at 69 GPa.

Raman and ir measurements clearly indicate phonon and vibron spectra of θ and ι modifications distinct from all other known nitrogen phases [9]. Synchrotron x-ray diffraction (Fig. 2) confirms the existence of two new structures. First, the data show good agreement with previously reported results for the ϵ -phase [10, 11], although only a few reflections could be observed above 50 GPa because of strong sample texture (see below), as found in previous studies. The highly textured nature of the sample above 50 GPa could result in a substantial change in intensities of x-ray diffraction peaks from ideal powder intensities and even prevent observations of some of them (i.e., a peak that is observable on the ED pattern in Fig. 2 is not present on the AD spectrum). For the θ phase results presented here, we combined the ED and AD measurements for three samples with presumably different preferred orientations of crystallites.

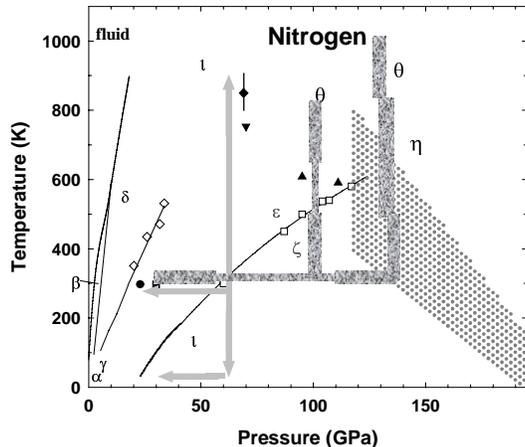


FIG. 1. Phase and reaction diagram of nitrogen at high pressures and temperatures. Open symbols and thick solid lines are from this work and Refs. 5 and 7. The shaded area shows the region where transformation to η -nitrogen takes place and is considered a kinetic boundary. The arrows show thermodynamic paths used to reach θ and τ phases and paths taken to investigate their stability. Phase boundaries at low P - T are from Refs. 1 and 8. The phase boundaries for the α , γ , δ , and δ_{loc} phases are not shown.

No major changes in the x-ray diffraction patterns were observed at 60 GPa and room temperature, corresponding to the ϵ - ζ transition (see also Ref. 12). This observation is consistent with vibrational spectroscopy, which shows only moderate changes identified as a further distortion of the cubic unit cell of the δ phase [7, 13]. In contrast, x-ray diffraction patterns of the samples after ϵ - θ and ϵ - τ transformations differ substantially from those of the ϵ and ζ phases and from each other (Fig. 2).

Indexing of the peaks of θ -nitrogen shows that its unit cell is orthorhombic (e.g., with the lattice parameters $a = 6.797(4)$, $b = 7.756(5)$ and $c = 3.761(1)$ Å. The systematic absences, lack of inversion center, and presence of high-symmetry sites (see above) are consistent with space groups $Pma2$, $Pmn2_1$, $Pmc2_1$, $Pnc2$, and $P2_12_12$. The a/c is close to $\sqrt{3}$, which suggests that the lattice is derived from a hexagonal structure (compare with hydrogen in phase III). By using the equation of state of ϵ - N_2 [10], we can determine the volume when a pressure-induced (density-driven) transition is assumed. The unit cell volume (198 \AA^3) has 16 molecules, giving 12.4 \AA^3 per molecule and 11% volume collapse at the ϵ - θ transition. The number of molecules is in agreement with the vibrational spectroscopy, although it is possible to describe the vibrational spectra with a smaller number (up to 8) [9].

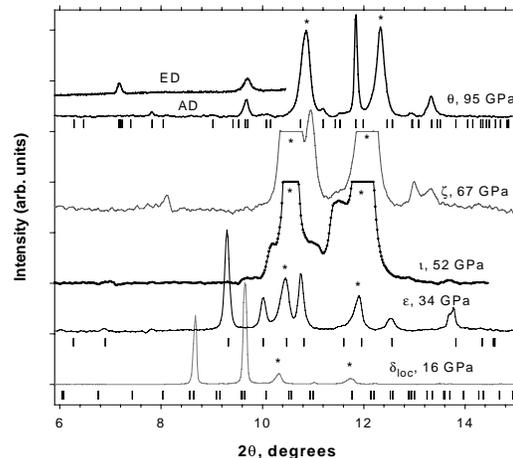


FIG. 2. Representative x-ray diffraction patterns of θ , τ , ζ , ϵ , and δ_{loc} phases measured at different pressures and 297K. Asterisks denote diffraction from Re gasket. AD and ED stand for angle-dispersive and energy-dispersive techniques. For the ED pattern, energy was recalculated to 2θ by using $\lambda = 0.4246 \text{ \AA}$. Ticks show the calculated positions of the x-ray reflections according to the proposed symmetry of phase θ (see text). For δ_{loc} and ϵ structures, ticks are according to known symmetries of those phases.

In order to understand better the provenance of new phases in the phase diagram and their relationships with other phases of nitrogen (Fig. 1), we made extensive observations in different parts of the phase diagram. The new phases were found to persist over a wide P - T range. As noted above, both phases could be quenched to room temperature. Upon subsequent heating, the θ phase remained stable when heated above 1000K between 95 and 135 GPa, but it transformed to τ - N_2 when releasing pressure at 68 GPa at 850K. In view of the relatively high temperature of this transformation and its absence at room temperature, this observation implies that the transformation point is close to the θ - τ equilibrium line (Fig. 1). At room temperature, θ -nitrogen remains metastable as low as 30 GPa upon unloading. Similarly, τ -nitrogen remains metastable to 23 GPa; at these pressures, both phases transform to ϵ - N_2 upon unloading. The τ - N_2 was found to be stable at low temperatures (down to 10K) at pressures as low as 30 GPa. We note that η nitrogen so far has been accessed only from ζ - N_2 (Fig. 1). The apparent kinetic boundary (shaded area on Fig. 1) that separates these phases can be treated as a line of instability of ζ - N_2 . On the other side, the τ and θ phases can be reached only from ϵ (and possibly δ). We observed that upon further increases in pressure and temperature, the θ phase does not transform to the nonmolecular η

phase (to at least 135 GPa and 1050K). We suggest that it might instead transform to a (perhaps different) nonmolecular crystalline phase upon compression. By this argument, this phase is not easily reached by compression at 300K because of a kinetic barrier separating it from ζ -N₂.

Discussion

The data presented provide important new insights about the behavior of solid nitrogen at high pressures and temperatures. The τ phase appears to represent a different kind of lattice consisting of disk-like molecules, presumably packed more efficiently when compared with the mixed disk-like and sphere-like δ -family structures. The θ phase is more complex. Its striking vibrational properties are interesting and indicate that it is characterized by strong intermolecular interactions, perhaps with some analogy to H₂ phase III [14], ϵ -O₂ [15], or CO₂ II [16]. If the interactions are strong enough, the phase may be related to theoretically predicted polyatomic species [17], but this requires further investigation. Our data show that the new phases are thermodynamically stable, high-pressure phases, since they are formed irrespective of the thermodynamic path. Indeed, our data indicate that ζ -N₂ may be metastable in much of the P - T range over which it is observed, since it can be obtained only as a result of compression at a temperature of <500K of the ϵ -N₂ (see also Refs. 3 and 7). An important general conclusion of this work is that the definitive determination of the equilibrium phase relations of nitrogen is more complex than previously thought because of the presence of substantial transformation barriers between different classes of structures. These structures include the well-known phases based on weakly interacting N₂ molecules [18], the recently observed nonmolecular phase [3, 5], and the strongly interacting molecular phases documented here.

Acknowledgments

Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy

Sciences. We acknowledge excellent support from GSECARS. Infrared spectroscopy and additional x-ray diffraction measurements were performed at X-17C and U2A (NSLS). This work was also supported by the National Science Foundation and W. M. Keck Foundation.

References

- [1] R. Bini et al., J. Chem. Phys. **112**, 8522 (2000).
- [2] A. K. McMahan and R. LeSar, Phys. Rev. Lett. **54**, 1929 (1985).
- [3] A. F. Goncharov, E. Gregoryanz, Z. Liu, H. K. Mao, and R. J. Hemley, Phys. Rev. Lett. **85**, 1262 (2000).
- [4] M. Eremets, R. J. Hemley, H. K. Mao, and E. Gregoryanz., Nature (London) **411**, 170 (2001).
- [5] E. Gregoryanz, A. F. Goncharov, R. J. Hemley, and H. K. Mao, Phys. Rev. B **64**, 052103 (2001).
- [6] Y. Fei, in *Mineral Spectroscopy: A Tribute to Roger G. Burns*, edited by M. D. Dyar, C. McCammon, and M. W. Schafer (Geochemical Society, Houston, TX, 1966), p. 243.
- [7] A. F. Goncharov, E. Gregoryanz, H. K. Mao, and R. J. Hemley, Low Temp. Phys. **27**, 866 (2001).
- [8] D. A. Young et al., Phys. Rev. B **35**, 5353 (1987).
- [9] E. Gregoryanz, A. F. Goncharov, R. J. Hemley, H.-K. Mao, M. Somayazulu, and G. Shen, Phys. Rev. Lett. (submitted).
- [10] H. Olijnyk, Chem. Phys. **93**, 8968 (1990).
- [11] M. Hanfland et al., Rev. High Pressure Sci. Technol. **7**, 787 (1998).
- [12] A. P. Jephcoat et al., Bull. Am. Phys. Soc. **33**, 522 (1988).
- [13] R. Reichlin et al., Phys. Rev. Lett. **55**, 1464 (1985).
- [14] R. J. Hemley, Z. Soos, M. Hanfland, and H. K. Mao, Nature (London) **369**, 384 (1994).
- [15] F. Gorelli, L. Ulivi, M. Santoro, and B. Bini, Phys. Rev. Lett. **83**, 4093 (1999).
- [16] V. Iota and C. S. Yoo, Phys. Rev. Lett. **86**, 5922 (2001).
- [17] R. Bartlett, Chem. Ind. **4**, 140 (2000).
- [18] *Physics of Cryocrystals*, edited by V. G. Manzhelii and Y. A. Freiman (AIP, Woodbury, NY, 1997).