X-ray Diffraction Study of Nitrogen at Megabar Pressures

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Introduction

The phase diagram of molecular nitrogen is complex at moderate pressures and temperatures and until recently has been little studied over a wider range. The non-molecular semiconducting nitrogen (η) has been characterized only quite recently by combined Raman, infrared and visible spectroscopy methods [1,2] and by electrical conductivity measurements [3]. The transformation occurs at 150 GPa at room temperature and shifts to higher pressures at lower temperatures. The transformation reveals a considerable hysteresis at low temperatures [3]. Optical spectroscopy techniques show some evidence for highly disordered (amorphous) structure of the high-pressure phase [2], but unambiguous structural characterization is still missing.

In the lower pressure range (below 100 GPa) at elevated temperatures (above 550 K) nitrogen forms two molecular phases, ι and θ (Ref. [4] and Fig. 1). The lower pressure phase ι is the only nitrogen diatomic phase with orientationally equivalent molecules above 5 GPa. The most remarkable is a higher-pressure phase θ which striking vibrational properties indicate that it is characterized by strong intermolecular interactions, perhaps with some analogy to H_2 phase III, ε-O_2 or CO_2-II. If the interactions are strong enough, the phase may be related to theoretically predicted polyatomic species (e.g. N_4) [5] which can be tested by x-ray diffraction study. Both phases can be quenched to room temperature and are observed over a wide P-T range from 20 to 100 GPa and 30 to 1000 K. The discovery of these phases suggests a major revision of the phase relations of nitrogen at high pressures and temperatures (Fig. 1).

In the present study we investigated the crystal structure of the newly discovered [1-3] molecular and nonmolecular high-pressure high-temperature phases of nitrogen. The main goal of this particular experiment was to characterize the crystal structure of the high-pressure phase ζ stable above the ε-N_2 phase, where no structural information has been available so far.

Methods and Materials

All experiments were conducted in the externally heated diamond anvil cells. Nitrogen gas was loaded in a 50-100 μm diameter hole of a rhenium gasket. To determine the pressure, we used *in situ* fluorescence measurements of ruby chips placed in the sample chamber. Pressure was measured before and after heating and usually did not change much. For Raman spectroscopy we used 514.5, 487.9 nm lines laser as excitation sources. Nitrogen, being a light element, has small cross section in x-ray diffraction; also due to its low bulk modulus (~120 GPa at 40 GPa [6]) it is very soft material at elevated pressures leading to considerable x-ray lines broadening with pressure, thus preventing precise determination of the line positions. In order to circumvent this problem we used a resistive heating technique to anneal the sample. The annealing process was monitored by Raman spectroscopy and lasted from 10 to 90 minutes, sometimes reaching temperatures above 1000 K. The changes in the sample were easily noticeable in Raman and x-ray patterns: *e.g.* the width of the most intense Raman vibron sometimes decreased by factor of 3 and x-ray diffraction peaks that appeared as shoulders became split. The annealing though neither improved or worsened the preferred orientation of the sample at pressures above ~60 GPa. The diffraction data were collected at the 16-ID beam line of HPCAT at the APS. A focused, monochromatic beam of different wavelength was used while the data were recorded on a MAR CCD (calibrated with a CeO_2 standard). Two-dimensional diffracted patterns were angularly integrated with the Fit-2D program.

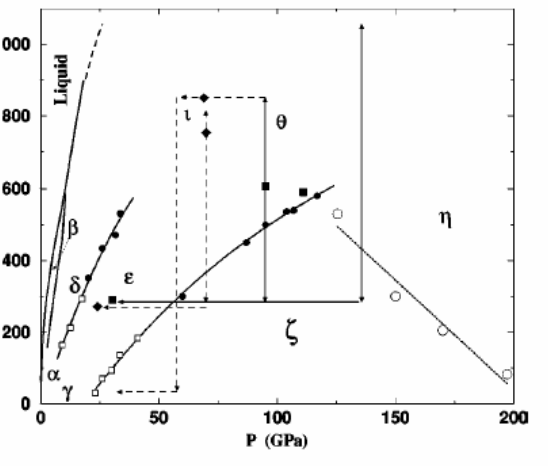

Fig. 1. Phase and reaction diagram of nitrogen at high pressures and temperatures (from Ref. [4]).

Results and Discussion.

We have obtained the ε-N_2 at high pressure and studied it above 43 GPa, the highest pressure of the previous study on ε-phase [6]. We have obtained diffraction data on this phase to higher pressures and observed the splitting of some diffraction reflections at around 64 GPa (Fig. 2). The phase observed above 64 GPa, named ζ, is indexed with a primitive orthorhombic cell containing 8 molecules in the unit cell. The continuous change of the volume at the ε - ζ transition (Fig. 3) implies a second-order character of this transition.

Above 115 GPa, the x-ray patterns shows two new peak-splittings, indicating a phase transition to a lower symmetry structure. The new phase, named here κ, is indexed on the basis of a monoclinic cell. For volume per molecule calculations, we assumed that the number of molecule per cell is such that there is no volume discontinuity.

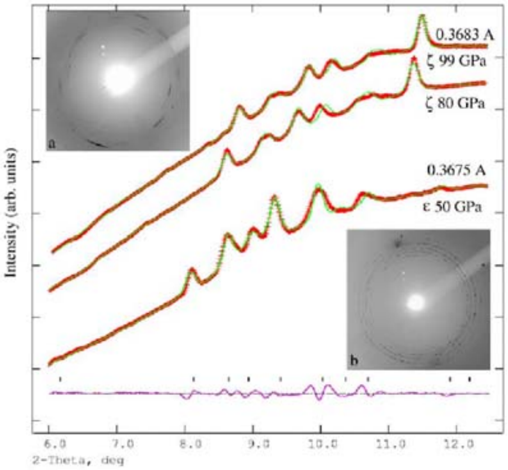

Fig. 2. GSAS Rietvield refinement of ε-N_2 at 50 GPa; LeBail fits of the integrated 2-D x-ray pattern of ζ-N_2 at 80 and 99 GPa and the corresponding CCD image of ζ–phase at 80 GPa (insert a). Compare with almost perfect powder pattern of ε-phase at 30 GPa (insert b). Lower curve: difference between data and fit for the Rietvield refinement of ε-N_2.

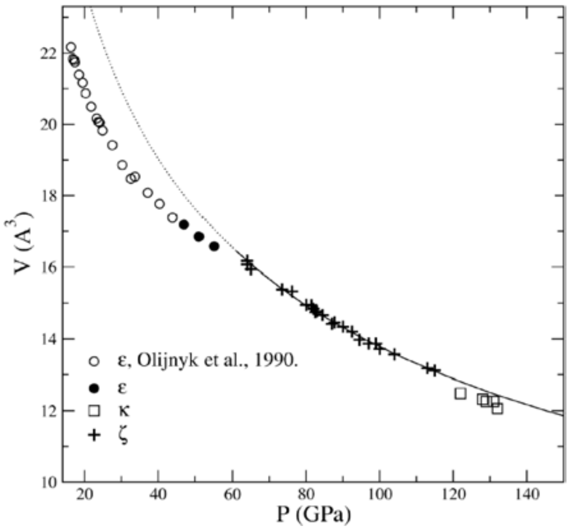

Fig. 3. Equation of state of nitrogen up to 130 GPa for the ε, ζ and κ phases, measured in present work. The data for ε phase from Olijnyk et al 1990 [6] are also shown.

Acknowledgments

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