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Raman, infrared, and x-ray evidence for new phases of nitrogen at high pressures and temperatures

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We report the existence and characterization of a distinct class of molecular phases of solid nitrogen at high pressures and temperatures by Raman scattering, infrared absorption, and powder synchrotron x-ray diffraction. The most remarkable is a phase (θ) which is characterized by strong intermolecular interactions and infrared vibron absorption. A second lower-pressure phase (ι) is diatomic with orientationally equivalent molecules. 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 results suggest a major revision of the phase relations of nitrogen at high pressures and temperatures.

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I. INTRODUCTION

The evolution of molecular solids under pressure constitutes an important problem in condensed-matter physics.[1] Under compression, delocalization of electronic shells and eventual molecular dissociation is expected, leading to the formation of a framework or close-packed structures. However, this process may not necessarily be simple and direct, because of 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[2] and until recently has been little studied over a wider range. For example, a theoretically proposed dissociation of nitrogen molecules under pressure[3] was recently confirmed experimentally.[4–6]

The phase diagram of nitrogen is shown in Fig. 1. On room-temperature compression, the supercritical fluid at 2 GPa solidifies to form the disordered (plastic) β phase.[7] The low P-T α and γ phases represent two ways of packing quadrupoles.[8] At higher pressures, another class of structures with nonquadrupolar-type ordering exists (δ, δ_{loc}, ϵ, ζ).[9–13] The δ phase is disordered with sphere- and disklike molecules orientationally distributed between corners and faces of a fcc unit cell.[12] With decreasing temperature and/or increasing pressure, the molecules partially order in a δ_{loc}-N_2 phase and then completely in ϵ-N_2. Theoretical calculations confirm the stability of the ϵ phase as the ordered phase in the 2–40-GPa range,[14] although some simulations[15] favor tetragonal structures (but this disagrees with available experimental data at these pressures). Further increase in pressure leads to a transformation to ζ-N_2. The transformation is quite pronounced at 21–25 GPa at low temperatures,[10] but at room temperature the changes (as measured by vibrational spectroscopy) are relatively subtle.[16,17] The available data suggest that the ζ phase is the only high-pressure phase prior to pressure-induced dissociation above 100 GPa.

The P-T region of the phases derived from δ-N_2 (δ_{loc}, ϵ, ζ) is observed to be quite wide (Fig. 1), apparently extending to the transition to nonmolecular phase η.[4,6] For comparison, γ-O_2,[8] a structural analog of δ-N_2 (Ref. 12) [see also β-F_2 and CO Refs. 8 and 13], is stable in a relatively narrow P-T range, beyond which structures with collinear molecules become energetically favorable (O_2, F_2) (Ref. 8) or chemical

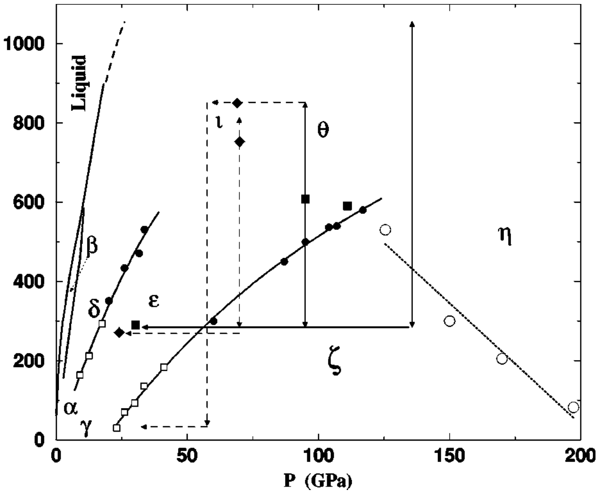

FIG. 1. Phase and reaction diagram of nitrogen at high pressures and temperatures. Solid thick lines are thermodynamical boundaries. Solid circles show the transitions between δ-ϵ and ϵ-ζ phases investigated in this work. Filled symbols (ι—diamonds, θ—squares) show the P-T points at which new phases were reached or back transformed to the known phases. The arrows show thermodynamic paths (schematic) used to reach θ (solid, thin lines) and ι (dashed, thin lines) phases and paths taken to investigate their stability. The transformations to nonmolecular η-nitrogen are shown by the open circles (Refs. 4–6) and thick dotted line which is only a guide to the eye. This region should be treated as a kinetic boundary. Phase boundaries at low P-T (open squares) are from Ref. 2 and the melting curve is from Ref. 7. The phase boundaries for the α, γ, and δ_{loc} phases are not shown.

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dissociation takes place (case of CO). Although the above molecular crystals are different from the point of view of anisotropic intermolecular forces, one would expect that at high density the most effective packing of dumbbell molecules remains the dominant term in determining phase stability prior to dissociation.

High P-T phases of such materials only recently became accessible by *in situ* optical investigation due to the advances made in internal heating techniques[6,18] combined with the ability to generate pressures in excess of 100 GPa. Here we report the existence of two 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 distinct class of dense molecular nitrogen phases.

II. EXPERIMENTAL METHODS

This work is part of a broad effort to understand the high P-T transformations of nitrogen. We performed more than 20 experiments ranging from 15 to 1050 K and up to 150 GPa using *in situ* Raman spectroscopy and synchrotron infrared (IR) spectroscopy[19] and x-ray synchrotron diffraction on temperature-quenched samples. For Raman spectroscopy we used 514.5 and 487.9 nm and tunable red lines of a Ti-:sapphire laser as excitation sources. The pressures were generated by Mao-Bell high-temperature diamond-anvil cells equipped with two heaters and thermocouples.[18] The temperature was measured to within ± 1 K below 600 K and ± 5 K above 600 K. To determine the pressure, we used *in situ* fluorescence measurements of ruby and Sm:yttrium aluminum garnet chips loaded in the sample chamber. Energy dispersive x-ray diffraction was carried out at the beam line X17C of the National Synchrotron Light Source (NSLS), using a focused white beam.[20] To reduce possible texture problems, the sample was rocked in ω and χ over an angular range allowed by the diamond backing plates. The majority of the diffraction data, however, were collected at the 13-ID beam line of GeoSoilEnviroCARS (GSECARS) at the Advanced Photon Source (APS).[21] A focused, monochromatic beam at $\lambda = 0.4246$ Å (29.2 keV) was used, and the data were recorded on a MAR charge coupled device (calibrated with a CeO_2 standard). The sample was rocked in ω by $\pm 10°$ to average over as many crystallites as possible.

III. RESULTS AND DISCUSSION

When compressed at 300 K nitrogen transforms from the ϵ to ζ phase 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. 2 at lower temperatures. At 95 GPa when the temperature reaches ~ 600 K, the transition to θ nitrogen takes place. The transition can be observed visually since $\epsilon(\zeta)$-N_2 normally shows substantial grain boundaries, while 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-N_2 is heated at even lower pressures (e.g., 65–70 GPa), it transforms above 750 K to ι-N_2. It is also possible to access the ι phase from θ: we observed the transformation from the θ to ι phase on pressure release at ~ 850 K at 69 GPa (see below).

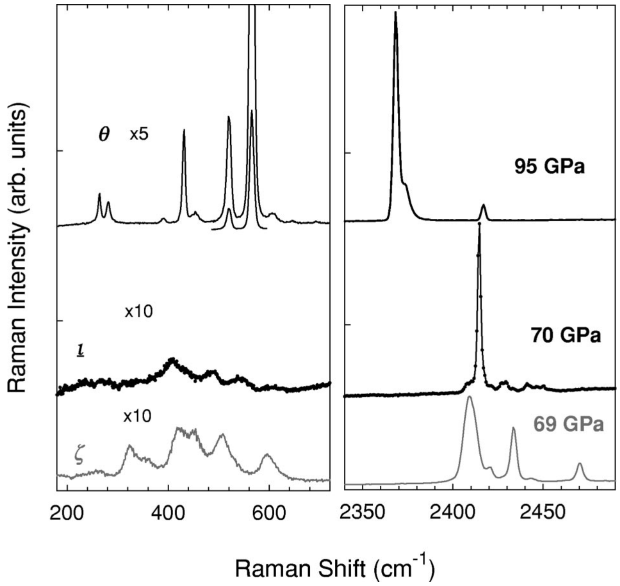

FIG. 2. Representative Raman spectra of θ and ι phases measured at 95 and 70 GPa and 297 K after quenching from high temperature. The spectra of the ζ phase used as a starting material are shown for comparison at the same temperature and at 69 GPa.

Figure 2 shows the Raman spectra of the ι and θ quenched to room temperature. In order to have spectra of all phases discussed here at similar conditions we present them at room temperature. The high-temperature spectra of ι and θ are very similar to ones measured upon quenching the sample to 300 K. Also, at the present it is technically not possible to collect IR spectra at elevated temperatures and as result all IR measurements were performed at 300 K. The Raman and IR spectra of the ζ phase (obtained by compression at 300 K) from which these phases were formed are shown for comparison at 69 GPa (Fig. 2) and 97 GPa (Fig. 3).

Raman spectra of both θ and ι exhibit vibron excitations (Fig. 2, right panel), although their number and frequencies differ from those of all other known molecular phases. The changes in the low-energy region of the spectra (Fig. 2, left panel) for θ phase are very pronounced. The lattice modes of θ nitrogen are very sharp and high in intensity compared to either ι or ζ (also ϵ). This is a clear indication that molecular ordering in θ is essentially complete, whereas other molecular phases may still possess some degree of static or dynamic orientational disorder. The lattice modes of ι-N_2 are also different from those in ζ and ϵ: they are extremely weak and broad, suggesting that this phase is not completely orientationally ordered.

Figure 3 shows infrared-absorption spectra of new phases together with the ζ phase used as initial material. Again, the

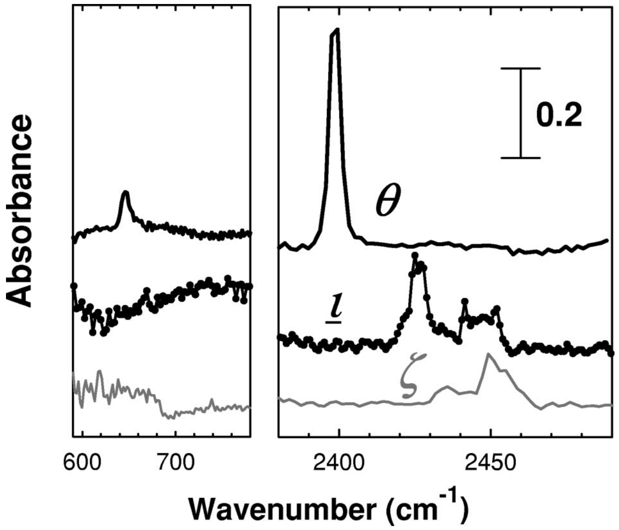

FIG. 3. Infrared modes of θ and ι phases measured at 95 and 70 GPa and 297 K after quenching from high temperature. The spectra of the ζ phase used as a starting material were measured at 97 GPa and are shown for comparison at the same temperature.

number, frequencies, and intensities of vibron excitations (Fig. 3, right panel) are different from other known phases. In the case of ι-N$_2$ the spectrum differs mainly in positions of the absorption bands while the IR vibron mode of the θ phase has a much larger oscillator strength compared to other N$_2$ phases [cf. H$_2$ in phase III (Ref. 22) and ϵ-O$_2$ (Ref. 23)]. There is a more pronounced Raman and IR softening of the vibron bands of θ nitrogen compared to the other modifications (ι, ζ, and ϵ). This observation together with the presence of a strong IR vibron is consistent with the existence of charge transfer (e.g., see Refs. 22–24) related to the formation of lattice-induced dipole moments or association of molecules.$^{23-25}$

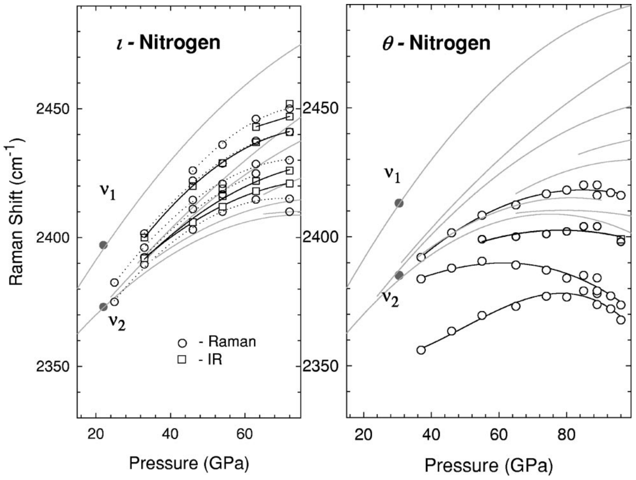

FIG. 4. Left: Raman (open circles) and infrared (open squares) frequencies of vibron modes as a function of pressure for ι phase. Right: Raman (open circles) and infrared (open square) frequencies of θ phase. All measurements were done on the pressure release at 300 K. Filled circles correspond to the vibron frequencies after the transformation to the ϵ phase from θ and ι phases. Gray lines are data for the ϵ and ζ phases from Ref. 17.

The pressure dependence of the Raman-active vibron modes [Figs. 4(a) and 4(b)] was studied on unloading at 300 K in new phases. ι-N$_2$ exhibits typical behavior for such molecular crystals: branching of vibrational modes and increasing of separation between them with pressure due to increasing intermolecular interactions. All of the vibrational modes originate from the same center, which is close to the frequency of the ν_2 disklike molecules in ϵ-N$_2$. Thus, the structure of the ι phase is characterized by the presence of just one type of site symmetry for the molecules and the large number of vibrational modes arises from a unit cell having a minimum of eight molecules. For the θ phase, two different site symmetries are present. The higher frequency $\nu_{1\theta}$ gives rise to three Raman bands and one in the IR, while the lower frequency of $\nu_{2\theta}$ correlates with only one Raman band. Figures 4(a) and 4(b) also show that the spectra have several cases of frequency coincidence of Raman and IR vibron modes, which excludes an inversion center for both structures.

Surprisingly, we find that the θ and ι phases have a very large domain of pressure and temperature metastability. The pressure dependence of the Raman spectra (Fig. 4) was studied in a wide pressure range at 300 K in both phases. Because of technical reasons, most data were taken on pressure release, although experiments carried out on different conditions did not reveal that any measurable differences in frequencies of the θ and ι phases depended on the sample history.

Performing x-ray analyses on low-Z materials in the 100 GPa pressure range and high temperatures is difficult due to the low scattering efficiency and small openings in the diamond backing plates, leading to low signal/noise ratios. Nevertheless, we performed preliminary synchrotron x-ray diffraction to confirm the existence of two new structures (Fig. 5). First, we found good agreement with previously reported results for the low-pressure phases.^{27,28} Only a few reflections could be observed above 50 GPa because of strong sample texture. The highly textured nature of the sample could result in substantial changes in intensities of diffraction peaks from an ideal powder and even prevent observation of some of them. For the θ-phase results presented here, we combined the energy- and angle-dispersive measurements for three samples with presumably different preferred orientations of crystallites. 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. 29). 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.^{16,26} In contrast, the x-ray-diffraction patterns of the samples after $\epsilon \rightarrow \theta$ and $\epsilon \rightarrow \iota$ transformations differ substantially from those of the ϵ and ζ phases, and from each other (Fig. 5).

Tentative indexing of the peaks of θ nitrogen gives an orthorhombic unit cell [e.g., with lattice parameters $a = 6.797(4)$, $b = 7.756(5)$, and $c = 3.761(1)$ at 95 GPa]. The systematic absences, lack of inversion center and presence of high-symmetry sites (see above) are consistent with space

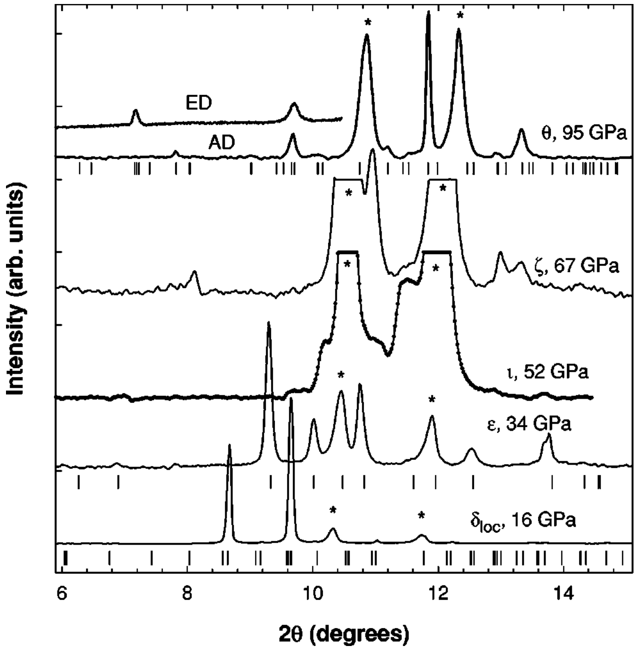

FIG. 5. X-ray diffraction patterns of nitrogen phases measured at different pressures and 297 K. Asterisks denote diffraction from the Re gasket. AD and ED refer to angle- and energy-dispersive techniques. For the ED pattern, the 2θ was calculated using $\lambda = 0.4246$ Å. Ticks show the calculated positions of the x-ray reflections proposed structure of these phases (see text). Despite the use of sample rocking, intensities of some diffraction lines are affected by sample texture (e.g., θ phase).

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. Extrapolation of the equation of state of ϵ-N_2 measured to 40 GPa (Ref. 27) shows that volume for this phase is about 14 Å^3/molecule at 95 GPa, which gives an upper bound assuming a pressure-induced (density-driven) transition. Comparison with the experimentally determined unit-cell volume (198 Å^3) suggests 16 molecules in the unit cell, giving 12.4 Å^3/molecule in the θ phase and an 11% volume collapse at the ϵ-θ transition. The number of molecules is in agreement with vibrational spectroscopy data, although it is possible to describe the vibrational spectra with a smaller number (up to 8).

In order to better understand the P-T provenance of new phases and their relation with other polymorphs of nitrogen (Fig. 1), we pursued extensive observations in different parts of the phase diagram. The new phases are found to persist over a wide P-T range. As noted above, both phases could be quenched to room temperature. On subsequent heating, the θ phase remained stable when heated above 1000 K between 95 and 135 GPa and does not transform to the nonmolecular η phase (shown by arrow in Fig. 1). But on pressure release it transforms to ι-N_2 at 69 GPa at 850 K. 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-ι equilibrium line (see Fig. 1). At room temperature, θ-nitrogen remains metastable as low as 30 GPa on unloading. Similarly, ι-nitrogen remains metastable to 23 GPa; at these pressures both phases transform to ϵ-N_2 on unloading. ι-N_2 was found to be stable at low temperatures (down to 10 K) at pressures as low as 30 GPa. We note that η nitrogen so far has been accessed only from ζ-N_2 (see Fig. 1). The apparent kinetic boundary (open circles in Fig. 1) that separates these phases can be treated as a line of instability of ζ-N_2. Likewise, the ι and θ phases have been reached only from the ϵ phase, though they probably can be formed from δ as well. We observed that on further increase of pressure and temperature, the θ phase does not transform to the nonmolecular η phase (to at least 135 GPa and 1050 K). We suggest that it might instead transform to a (perhaps different) nonmolecular crystalline phase on compression. This nonmolecular phase may not be easily reached by compression at 300 K because of a kinetic barrier separating it from ζ-N_2.

IV. CONCLUSIONS

The above results provide important insights into the behavior of solid nitrogen at high pressures and temperatures. The ι-phase appears to represent a different kind of lattice consisting of disklike molecules, presumably packed more efficiently compared to the mixed disk- and spherelike δ-family structures. The θ phase is more complex. Its striking vibrational properties indicate that it is characterized by strong intermolecular interactions, perhaps with some analogy to H_2-phase III,[24] ϵ-O_2,[23] or CO_2-II.[30] If the interactions are strong enough, the phase may be related to theoretically predicted polyatomic species,[31] but this requires further investigation. Our data show that the new phases are thermodynamically stable high-pressure phases since they are formed irrespective of thermodynamic path. Indeed, our data indicate that ζ-N_2 may be metastable in much of the P-T range over which it is observed, since it is typically obtained only as a result of compression at $T < 500$ K of the ϵ-N_2 (see also Refs. 6 and 26). 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 due the presence of substantial transformation barriers between different classes of structures. These structures include the well-known phases based on weakly interacting N_2 molecules,[8] the recently observed nonmolecular phase,[4,6] and the strongly interacting molecular phases documented here.

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