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METASTABLE POLYMERIC NITROGEN FROM N₂/H₂ ALLOYS

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ABSTRACT

Studies of high-density binary mixtures of simple molecular solids have uncovered a new aspect of high-pressure chemistry. In contrast to the many previous studies on relatively inert mixtures, here we show that high pressures can lead to unexpected behavior in reactive compounds. Raman studies were performed on nitrogen and hydrogen binary alloys at room temperature to 83 GPa. To pressures of 30 GPa, large vibron deviations from those of the pure materials suggest complex phase behavior. An unusual phase separation is observed near 35 GPa, which results in two distinct solid phases, one rich in both nitrogen and hydrogen and the other relatively amorphous. Spectroscopic signatures that can be attributed to N-N stretching were observed at high pressures.

1. INTRODUCTION

Extended phases of molecular solids represent a new paradigm of covalently bonded polymeric materials synthesized under extreme conditions with advanced optical, mechanical, and energetic properties. The existence of extended solids has been demonstrated using high-pressure/high-temperature synthesis methods in several systems such as nitrogen [Eremets et al., 2004; Eremets et al., 2007; Lipp et al., 2007], carbon monoxide [Lipp, et al., 2005], carbon dioxide [Iota et al., 2007] and oxygen [Militzer and Hemley, 2006] and rich phase diagrams have been derived for each. However, the recovery of the materials to ambient conditions has, with the exception of carbon monoxide [Lipp et al., 2005] posed considerable difficulty, precluding implication or performance testing of these materials in beneficial systems.

With the unexpected discovery that binary mixtures of simple gases, such as nitrogen and oxygen, may lead to the stabilization of ordered extended molecular solid phases [Vos et al., 1992; Loubeyre et al., 1993; Somayazulu et al., 1996; Loubeyre et al., 1994], some

focus has shifted to this entirely new class of materials strongly influenced by weak van der Waals forces at lower pressures. Since the discovery of the first van der Waals compound He(N₂)₁₁ [Olijnyk and Jephcoat, 1997], several binary mixtures have been investigated [Vos et al., 1992; Loubeyre et al., 1993; Somayazulu, et al., 1996; Loubeyre et al., 1994; Olijnyk and Jephcoat, 1997; Loubeyre and LeToullec, 1995; Sihachakr and Loubeyre, 2004; Sihachakr and Loubeyre, 2006; Galtsov et al., 2006] and while these earlier studies primarily focused on mixtures with one noble gas component, recently the field has expanded to include purely diatomic mixtures. Structural determinations of the various solid phases observed have often accompanied the binary reaction phase diagrams, such as for O₂/H₂ [Loubeyre and LeToullec, 1995] and O₂/N₂ [Sihachakr and Loubeyre, 2004]. In many of these materials, both components of the mixture become fully incorporated into the crystalline structure and form distinctive compounds with different physiochemical properties than those observed in the parent molecules. In the case of N₂/O₂ mixtures, a photo-induced neutral-ionic transformation of the mixture occurred near 5 GPa and Raman spectroscopic and x-ray characterization showed the O₂ molecules became trapped in a nitrosonium nitrate cage, forming a clathrate-like structure [Sihachakr and Loubeyre, 2006]. Mixtures of O₂/H₂ were found to be stable at pressures near 7.6 GPa, despite their explosive nature under ambient conditions and three explosion boundaries, which separate the regions of fast and slow reactions, were observed during the determination of the reaction diagram of the O₂/H₂ mixture [Loubeyre and LeToullec, 1995].

In contrast to the numerous experimental studies of other binary mixtures, there has been comparatively little attention devoted to mixtures of N₂ and H₂. Recent powder diffraction studies have shown the structures of quenched condensed *n*H₂-N₂ alloys deposited on copper substrates depend strongly on the rate of condensation at ambient pressure [Galtsov et al., 2007]. Near the 13.8 K triple point of hydrogen, the hydrogen component dissolves in the nitrogen matrix, which suppresses the

rotational quantum properties normally observed in free hydrogen. It was noted the hydrogen incorporation into the nitrogen unit cell generated a rather subtle distortion of the nitrogen lattice [Galtsov et al., 2007], which, upon temperature increase reverts to the conventional nitrogen lattice as the hydrogen molecules escape the sample. This attests to the metastability of this phase and that its appearance is due to the strong nonequilibrium conditions that exist. It is not clear if this phenomenon occurs only at specific concentrations or under other temperature/pressure regimes [Galtsov et al., 2007]. Theoretical simulations of binary mixtures of nitrogen and hydrogen within high-pressure/high-temperature regimes suggest that the addition of hydrogen to nitrogen may influence the metastability of nitrogen polymorphs typically only stable under extreme conditions [Mattson, 2003]. Of particular interest is the cubic-gauche form of nitrogen, which has been proposed to have an enormous energy capacity [Olijnyk and Jephcoat, 1997], but has yet to be recovered to ambient conditions [Eremets et al., 2004; Eremets et al., 2007; Lipp et al., 2007; Mattson, 2003]. When introduced in a 2:1 ratio ($N_2:H_2$), these simulations have shown that the hydrogen binds, through either covalent bonding or ionic interactions, to the unstable terminal ends of the polymeric chain. The passivation of the terminal ends induces metastability in the nitrogen polymer and prevents back transformation to molecular nitrogen upon return to ambient conditions [Mattson, 2003]. It is expected that under high-pressure conditions, the material will crystallize, resulting in pronounced modifications to the x-ray diffraction as well as the optical spectra, allowing for structural determination. Our Raman spectroscopic studies of a 2:1 N_2/H_2 mixture to pressures near 85 GPa show evidence for complex phase behavior, which differs significantly from the pure components as well as the existence of an incomplete phase transition to a singly-bonded nitrogen material as low as 35 GPa.

2. EXPERIMENTAL

Ultrahigh purity nitrogen (99.99 %) and hydrogen gas (99.99%) were mixed in the molar ratio of 2:1 determined using the virial coefficients. The N_2/H_2 mixture was permitted to equilibrate over the course of several days. The resulting sample was loaded into the diamond anvil cell using a specialized high-pressure gas system described elsewhere [Mao et al., 1986]. Raman spectra were obtained from an Ar^+ ion laser operating at 514.5 nm with an optical system described previously [Goncharov et al. 1998]. The pressure was determined from the wavelength shift in the R_1 fluorescence band [Zha et al. 2000]. The UV-vis absorption spectra were recorded between 200 and 800 nm employing a deuterium lamp focused on the sample with a spot size of ~ 80 microns in diameter.

3. RESULTS AND DISCUSSION

Photomicrographs of the N_2/H_2 alloy obtained during the course of the room-temperature compression measurements are shown in Figure 1. To 6.2 GPa, the sample remained a transparent fluid and slightly above this pressure solidification into several large translucent grains was observed. With slow increases in pressure, preservation of the large grains was possible to slightly above 17 GPa. As is shown in Figure 1, a second Raman feature ca. 2390 cm^{-1} appears on the high frequency side of the strong band near 2370 cm^{-1} near 18 GPa. Although these vibrational features are comparable with the $\delta \rightarrow \epsilon$ phase transition of pure N_2 [Schneider et al., 1992], Figure 2 shows the pressure dependence of the Raman modes of the alloy are substantially higher than those for pure nitrogen, presumably due to the structural perturbation caused by the presence of hydrogen.

The most notable transition in the N_2/H_2 alloy occurs near 35 GPa with the emergence of two clearly distinct phase regions. The translucent Phase A is rich in both nitrogen and hydrogen as evidenced by the Raman spectral profiles shown in Figure 1. The appearance of four nitrogen mode frequencies centered at 2372 cm^{-1} , 2420 cm^{-1} , 2425 cm^{-1} , and 2452 cm^{-1} suggest the nitrogen component is arranged in a lattice similar to that of ϵ - N_2 [Olijnyk and Jephcoat, 1997; Bini et al., 2000]. Within the pressure range of 35 – 75 GPa, the frequencies of these modes gradually increase, whereas between 75 GPa and 83 GPa, the frequencies begin to soften. This transition point towards mode softening in the N_2/H_2 alloy is substantially lower than that of pure nitrogen (~ 100 GPa) [Goncharov et al., 2000; Olijnyk and Jephcoat, 1999], indicating the significant differences in the physiochemical behaviors of the alloy relative to the parent molecules.

In addition to the two modes assigned to the nitrogen vibrons, three broad Raman features are observed starting near 35 GPa, which can be tentatively assigned to the lattice modes of Phase A (300 cm^{-1}), N-N bending (590 cm^{-1}), and N-N stretching (900 cm^{-1}). At 35 GPa, these features are very weak which leads us to believe the phase transition is rather sluggish and incomplete at this pressure. With subsequent pressure increases, the vibrational maxima become clearly resolvable and in fact, the 590 cm^{-1} and 900 cm^{-1} N-N features are very similar in frequency to those of singly-bonded cubic gauche nitrogen as is shown in Figure 2 [Eremets et al., 2004; Lipp et al., 2007]. It is apparent that although the concentration of the singly bonded N_2/H_2 alloy increases as the pressure increases, even at the maximum pressure studied of 84 GPa, the phase transition is still incomplete since the nitrogen vibrons are still rather strong. This suggests that the transition

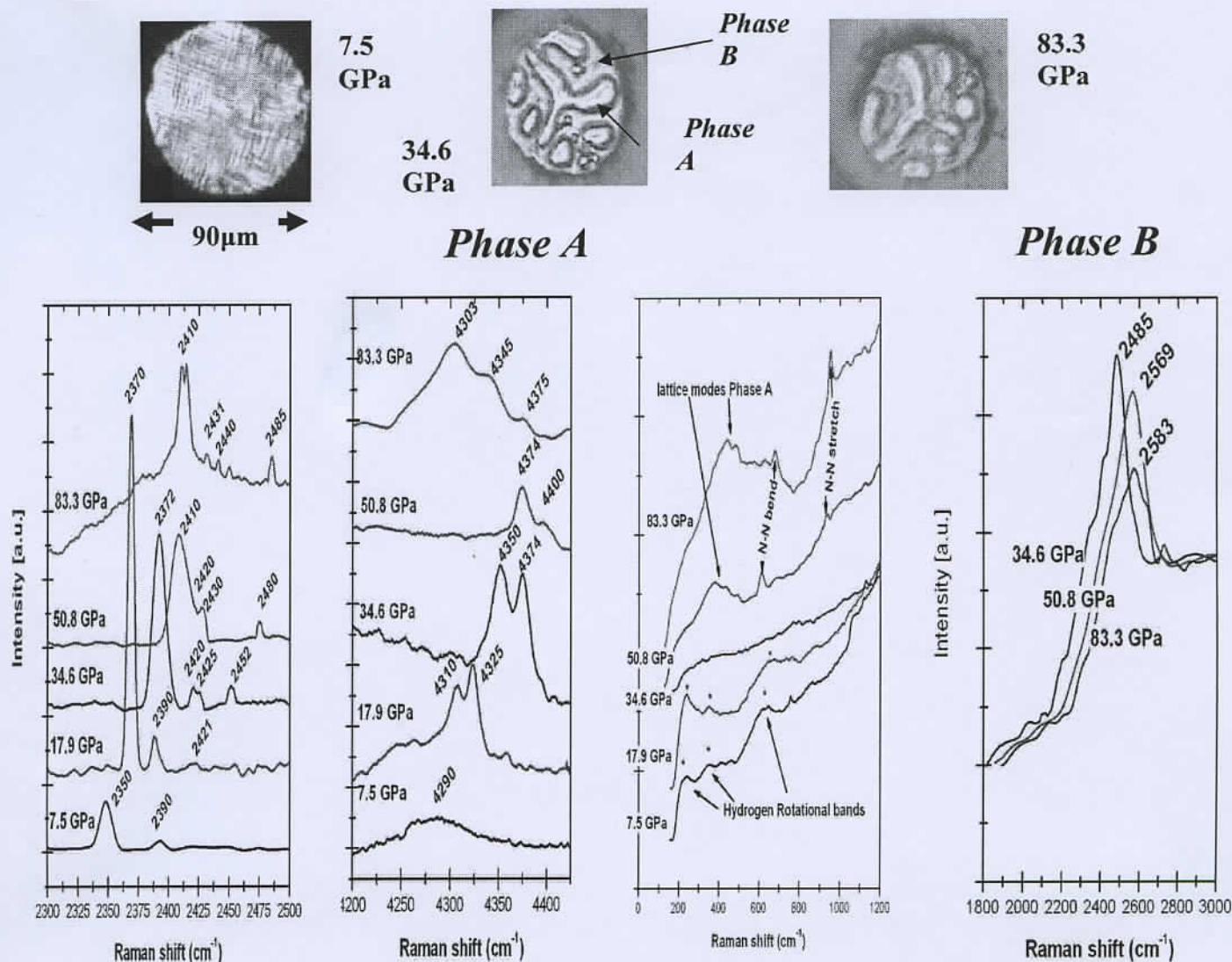


Figure 1. Representative Raman spectra and photomicrographs of the N_2/H_2 alloy as a function of pressure. Spectral regions of interest are correlated to specific sample regions.

may be strongly affected by kinetics and heating may be required for a complete conversion.

The vibrational features of the hydrogen component of the alloy bears little resemblance to many known hydrogen-containing mixtures over the entire pressure range studied. Between 8 GPa and 18 GPa, the bandwidth of the hydrogen mode decreases and the intensity increases due to solidification and ordering of the structure. Rather abruptly near 18 GPa, the mode splits into two well-defined maxima, which we assign to the repositioning of the hydrogen molecules into two inequivalent site symmetries in the lattice, much like δ - N_2 [Schneider et al., 1992]. When compared to pure hydrogen [Mao and Hemley, 1994] and hydrogen enclosed in a neon matrix [Loubeyre et al., 1992], Figure 2 shows that the behavior of the hydrogen component of the alloy more closely resembles pure hydrogen than

hydrogen in a frozen matrix. This result is remarkable in that it seemingly suggests the hydrogen is trapped in a nitrogen cage, much like the N_2/O_2 complex [Sihachakr and Loubeyre, 2006]. The onset of vibrational softening in the alloy (40 GPa), is nearly 15 GPa lower than the infrared turnover of pure hydrogen is even more interesting and implies that the hydrogen component of the alloy is subjected to much more vibrational coupling and has a weaker intramolecular bond than pure hydrogen.

In addition to the rather interesting vibrational observations of Phase A over the pressure range studied, we observed several unusual characteristics of Phase B. At 35 GPa, the material is yellowish which with subsequent pressure increases deepens to a dark red. The strong red color characterize it as being different from amorphous η - N_2 [Gregoryanz et al., 2001] and possibly

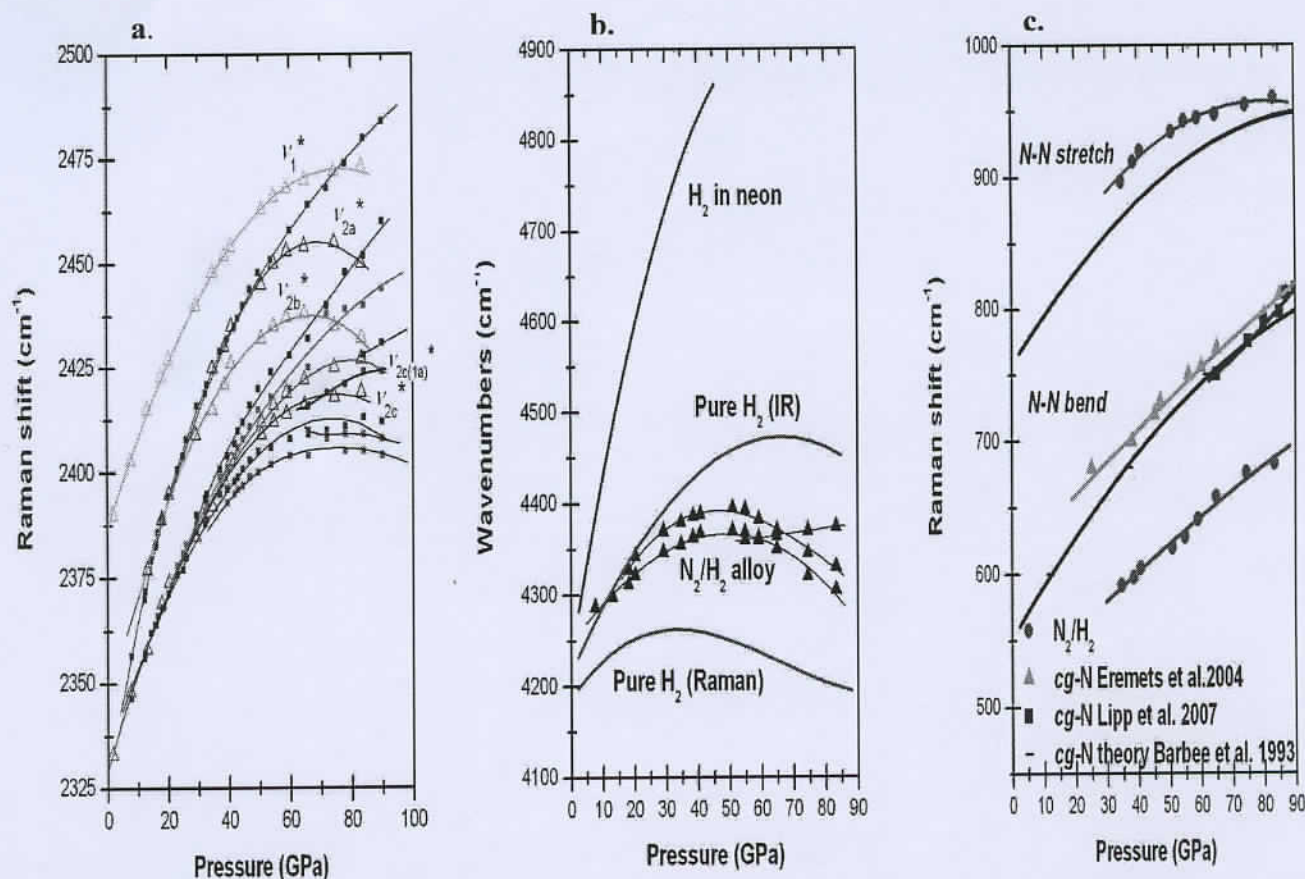


Figure 2. The Raman mode frequencies of the (a) nitrogen component, (b) hydrogen component, and (c) single bonded nitrogen phase of the N_2/H_2 alloy compared with those of pure materials and cubic-gauche nitrogen. The shifts of the nitrogen component of the N_2/H_2 complex (open triangles) are labeled according to Olijnyk and Jephcoat (1997) and analogous data for pure N_2 [Olijnyk and Jephcoat, 1997] are also shown for comparison. Hydrogen vibron shifts of the N_2/H_2 complex (solid triangles) are compared to the Raman and infrared vibrons of pure hydrogen [Mao and Hemley, 1994] and those of hydrogen in a neon matrix [Loubeyre et al., 1992].

similar to the previously observed $cg-N$ [Lipp et al., 2007] which is thought to be a viable precursor to $cg-N$. Phase B of the alloy is relatively amorphous over the entire pressure range, as the Raman spectra obtained are virtually featureless except for a rather unusual feature centered near 2485 cm^{-1} . This vibrational peak has not been reported in any other high-pressure nitrogen compounds and further characterization is necessary to determine the origin of this feature.

The distinctive color transition from yellow at lower pressures to red at higher pressures has been speculated to be due to a partial conversion of $N\equiv N$ to conjugated $N-N=N-N$ type bonds [Lipp et al., 2007]. As is shown in Figure 3, at pressures below 30 GPa, the UV-vis absorption spectra is dominated by a strong band which can be assigned to the transition between the valence band and antibonding band of the nitrogen

component. Following the phase transition, a second band appears towards higher energy. This new band shifts towards higher energy and increases in intensity. The appearance of these bands near 35 GPa provides strong evidence for a change in conjugation. The intensity increase as well as the color change over the compression sequence can be correlated to an increase in concentration of the conjugated material [Herzberg, 1966]. Coupling the appearance of $N-N$ vibrational features near 35 GPa and the decrease in the intensities of the nitrogen vibrons to the UV-vis results provide a conclusive link between the formation of a singly bonded network structure and the conjugated red colored phase. As previously proposed, the most likely mechanism for the transformation of the amorphous red phase to a singly bonded nitrogen polymer is a stepwise opening of the nitrogen-nitrogen triple bond [Lipp et al., 2007].

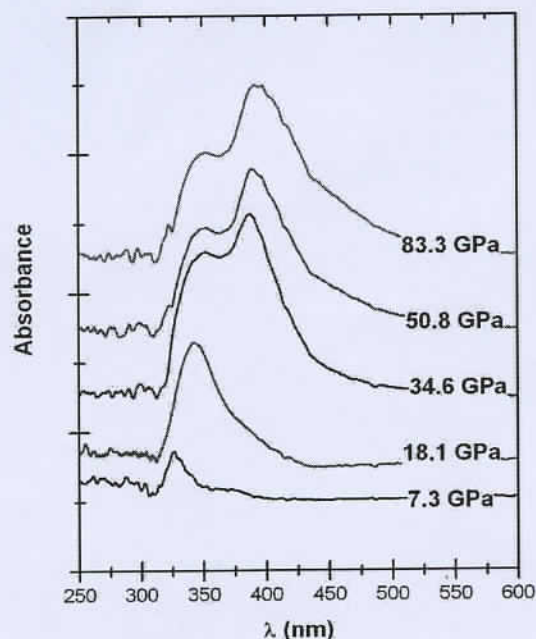


Figure 3. UV-vis spectra of Phase B measured at ambient temperature during the compression cycle.

4. CONCLUSION

In summary, we have performed Raman and UV-vis optical measurements of a N_2/H_2 alloy to 84 GPa. Above 35 GPa, two unique phases appear. Our results provide evidence that a singly bonded nitrogen phase is formed from the alloy slightly above 35 GPa. Although the phase transformation remained incomplete over the entire pressure range studied, Raman signatures of N-N bending and stretching are observed and show small increases in intensity, suggesting the concentration of the material increases over the pressure range. Phase B showed unusual Raman spectra, characterized by a single Raman peak centered near 2500 cm^{-1} ; over the compression sequence the intensity of this feature decreased. Visibly, the phases changes from yellow to red in color over the pressure range studied, indicating a change in electronic structure and possibly a change in conjugation. The appearance of a second feature in the UV-vis spectra confirmed this. The formation of this conjugated phase suggests it is a precursor to nonmolecular forms of nitrogen, as earlier proposed [Lipp et al., 2007]. The two phases observed in this study remain stable over a wide pressure range from 84 GPa (the maximum pressure applied in the previous study) down to 6 GPa where they transform back to a fluid. Further studies are underway to understand and control the metastability of both phases as well as understand the relationship and interaction mechanisms of the phases.

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