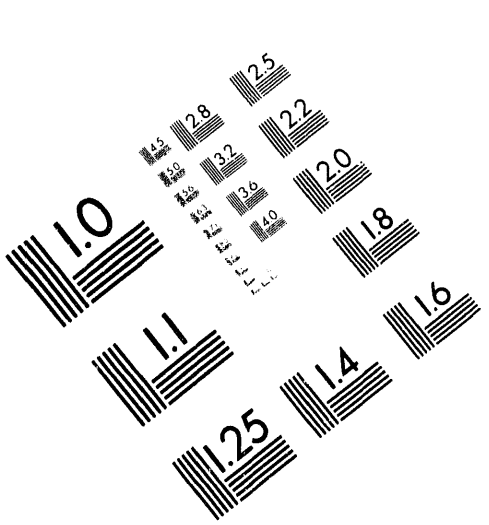

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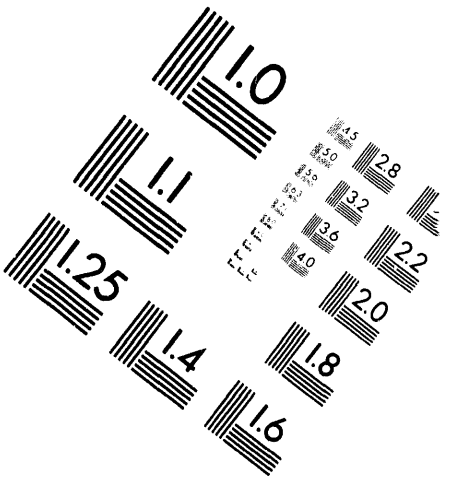

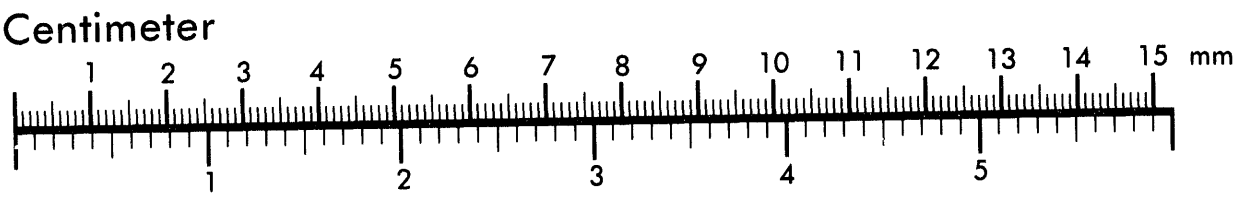

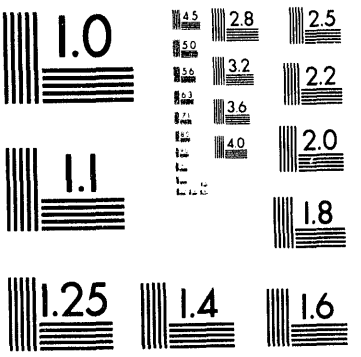

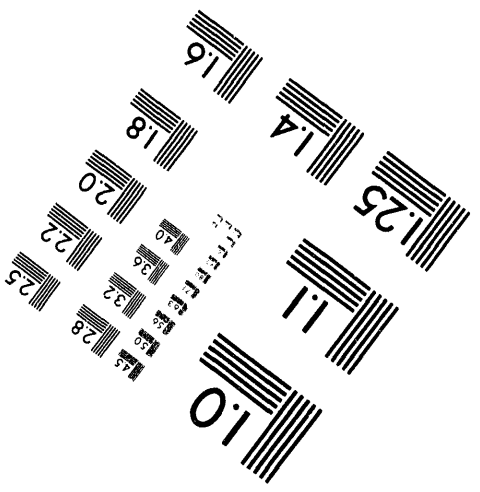

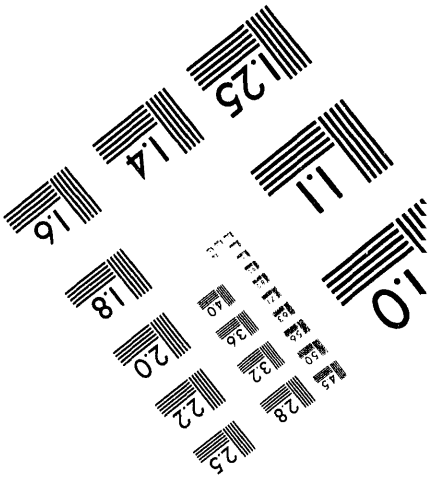

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Progress Towards the Synthesis of Polymeric Nitrogen

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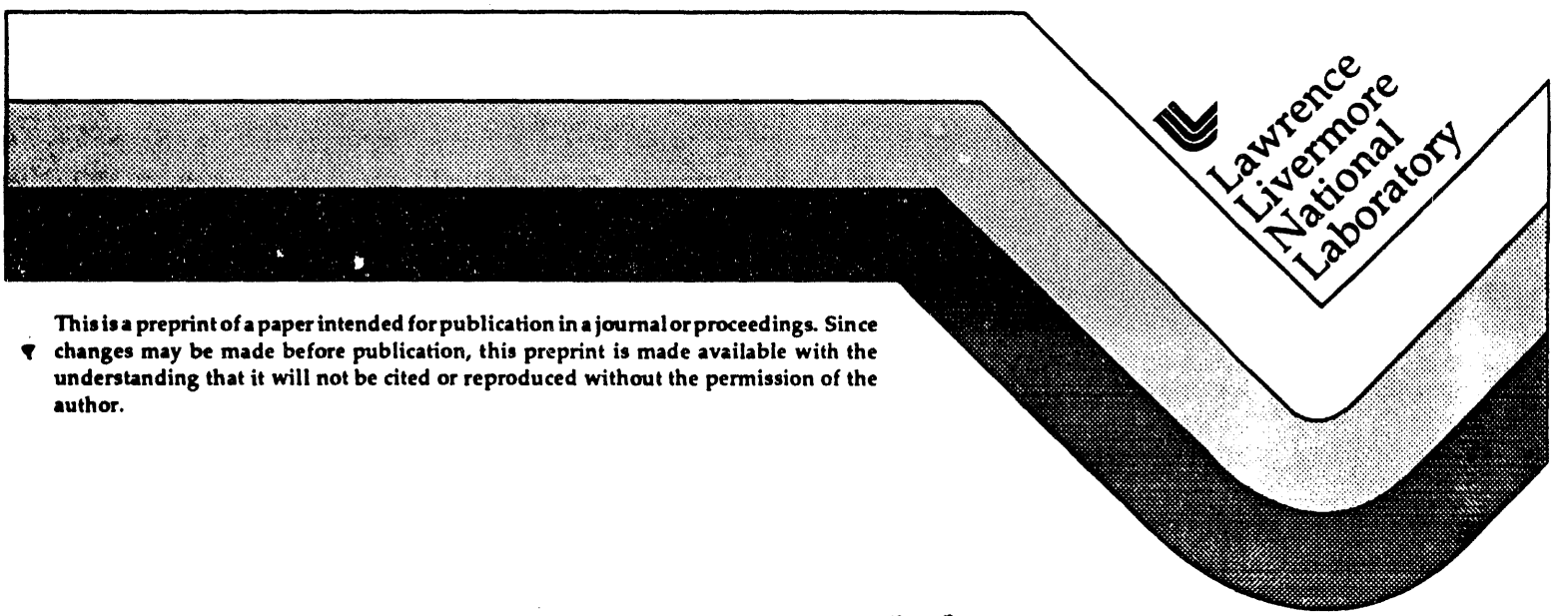

Progress Towards the Synthesis of Polymeric Nitrogen

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Introduction

Current conventional energetic compounds rely on strong covalent bonds within individual molecules for energy storage. A new class of energetic compounds has been recently proposed that entirely replaces weak van der Waals interactions with strong covalent bonds arranged in a continuous, uniform network, thus tremendously enhancing the energy per volume. In particular, recent theoretical calculations have suggested that a phosphorus-like or polymeric form of nitrogen may exist metastably at atmospheric pressure as a hard, insulating solid with an enhanced energy per unit volume.[1-3] It is predicted that the polymeric phase of nitrogen should be stable at high pressure, and therefore the megabar diamond anvil cell might provide the ideal vehicle for carrying out proof-of-existence experiments. Currently, we are bringing to bear technologies for achieving multimegabar pressures and temperatures of several thousand K.[4] These conditions are necessary to rearrange the bonds of strongly covalent systems into highly energetic configurations. There is no doubt that the transformations will show strong hysteresis making the initial synthesis difficult, but for these very same reasons, these new compounds potentially will be metastable at ambient conditions in their energetic state. We discuss our results and progress to date, indicating that we are well on our way to understanding the high pressure equation-of-state of solid N_2.

Background

The low pressure phases of N_2 have been characterized amply and are believed to be well-understood from theoretical considerations.[3, 5-12] At pressures greater than a few 10's of GPa, knowledge of the structures of N_2 becomes much more sketchy. Tentative structural identifications have been proposed based on low temperature Raman data to 52 GPa (Fig. 1).[10] Since many N_2 phases are stable only at low temperature, the phase diagram at room temperature is markedly different.[9] A transition from a cubic disordered (δ) to a rhombohedral ordered (ε) phase occurs at 18 GPa. Identification is based on Raman as well as X-ray diffraction data. At the slightly higher pressure of 22 GPa, a new phase (η) has been reported based on Raman vibrational (vibron) modes.[10] X-ray diffraction patterns do not demonstrate a transition at this pressure.[12] X-ray and Raman vibron and lattice (phonon) measurements suggest no transitions up to 44 and 54 GPa respectively.[9, 12] Based only on Raman vibron determinations extending to 110 GPa, transitions at 66 GPa ($\eta \rightarrow \theta$) and at 100 GPa ($\theta \rightarrow \iota$) have been reported.[7] These high pressure crystalline structures have not been established experimentally. Theoretically, various high-pressure molecular phases have

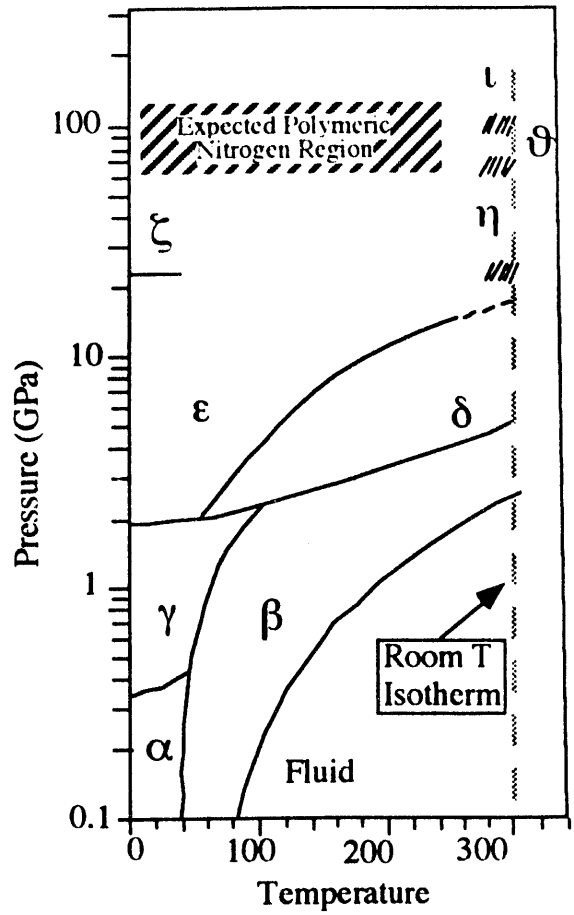

Fig. 1 Phase diagram of nitrogen. (Adapted from Ref. 9)

been studied with the ε phase found to be the preferred form above 2 GPa at low temperature in agreement with experiment.[13] Recently calculations suggest that at about 65 GPa, nitrogen will undergo a molecular to polymeric transition. This phase is predicted to be insulating.[1-3]

Results

We report new Raman vibron and phonon results that, while consistent with previously published data, demonstrate new phenomena and subtleties in the high-pressure behavior of N_2. Specifically, our Raman data do not support the previously identified transitions at 66 GPa and 100 GPa.[7] On the other hand, extremely low-intensity vibron peaks about two orders of magnitude less than the fundamental demonstrate that a completely new and unexpected transition occurs in N_2 at about 70 GPa. This newly measured phase probably involves a minor crystallographic rearrangement of the molecules.

Raman scattering has proven to be an indispensable probe for high-pressure research. N_2 exhibits two manifolds of Raman active modes, internal (vibrons at ~2400 cm^{-1}) and lattice (phonons at ~100 cm^{-1}) vibrational modes. Both sets of modes have

been used to identify phase transitions in molecular solids including N_2. The power of characterizing both the phonons and vibrons can exemplified by the $\delta \rightarrow \varepsilon$ and the $\varepsilon \rightarrow \eta$ transitions in N_2 where *one* of the sets of modes exhibit changes but *not* the other. First-principles theoretical calculation of both sets of modes can also provide additional insight constraining structural identification.[14]

Our primary goal for these experiments was to characterize the nature of the high-pressure phase transitions in N_2. Consequently, we have reproduced previous measurements, and though we obtain very similar data, there are enough differences that we arrive at very different conclusions. According to X-ray diffraction measurements, an $R\bar{3}c$-like structure is stable with increasing pressure up to 44 GPa.[12] The $R\bar{3}c$ structure allows three distinct Raman-active vibron modes, although it is usually assumed that the two modes arising from counterparts of the δ-phase disk sites are essentially degenerate, an assumption which is not borne out in recent theoretical calculations.[14] Nevertheless, a third vibron peak (a shoulder on the low frequency vibron peak) at 22 GPa has been interpreted as indicating the onset of the $\varepsilon \rightarrow \eta$ phase transition.[10] The crystalline structure of the η phase is unknown but clearly is a close relative of the $R\bar{3}c$ structure. The phonons show no measurable change across this pressure range implying no major symmetry change, consistent with x-ray measurements.

With increasing pressure, we find that vibron peaks split in a continuous fashion possibly starting as low as ~25 GPa.[9] Since the X-ray data show no phase transformation in this pressure range and since the splitting appears continuous rather than abrupt, we interpret this splitting as resulting from growing crystal field interactions and implying no sudden symmetry change. In fact, we infer *no phase transitions* until ~ 70 GPa, since there are no discontinuous splittings or intensity changes in the vibrational modes, in contrast to previous reports (Fig. 2).[7] Our phonon measurements support our conclusions, as the modes show no obvious discontinuity in intensity or frequency.

At about 70 GPa, we observe very low intensity structure in the vibrational spectrum that appear discontinuously. These new peaks are emphasized in Fig. 3. The peak marked by an asterisk is the N_{14}-N_{15} vibrational mode, the N_{15} atom occurring at a 0.37% abundance. This structure is being interpreted as evidence for a new phase transition, though because the major vibron and phonon branches do not show obvious changes, we interpret the transition as involving a minor crystallographic rearrangement. One possibility is the doubling of the previous unit cell, which would permit previously forbidden modes to become Raman active. X-ray scattering results support our conclusion that a phase transition occurs in this pressure range.[11] We measure no changes in the phonon spectra across this pressure range.

Lastly, we observe no discontinuous changes in intensity or frequency in both the vibron and phonon modes up to 130 GPa. Previous identifications of a transition occurring at 100 GPa reported discontinuous behavior in intensities (the disappearance of a peak) in the vibron spectra. We observe no evidence for a phase transition occurring at 100 GPa.

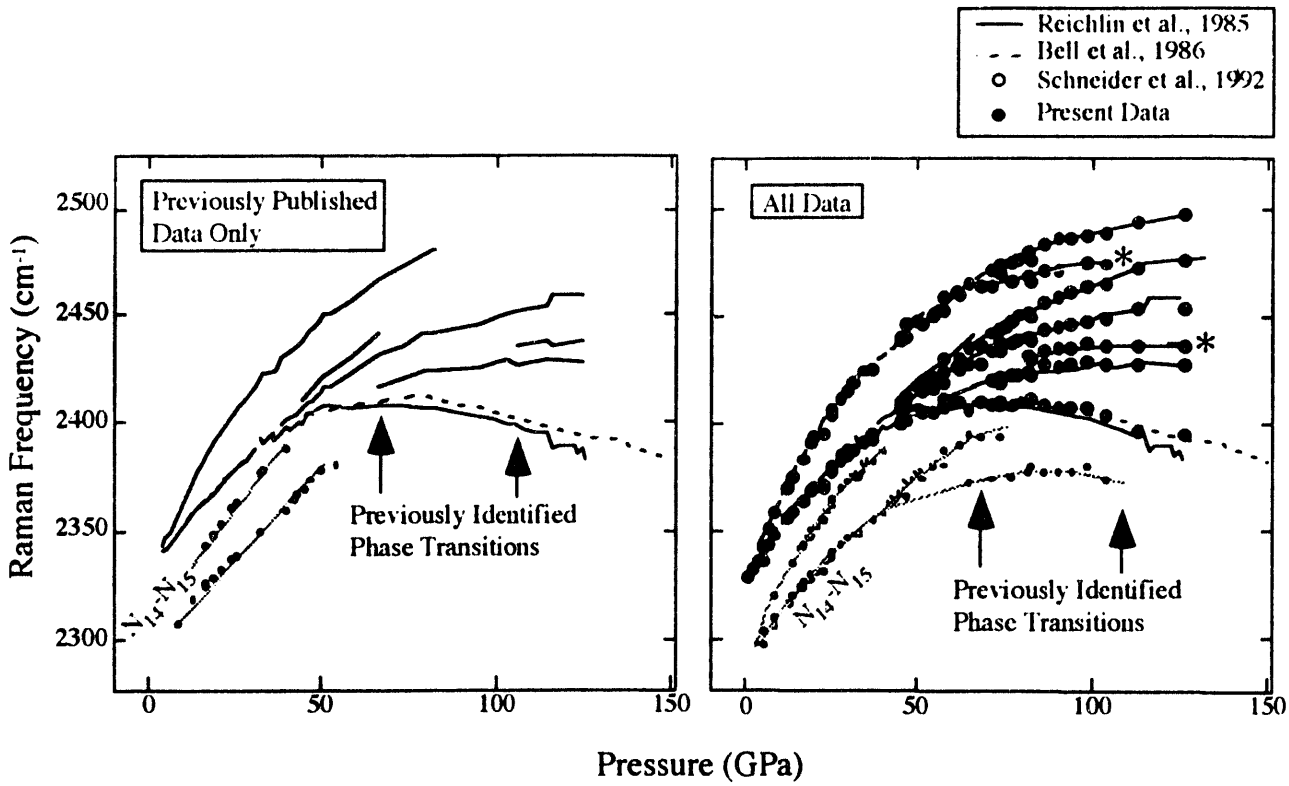

Fig. 2 Vibron mode frequencies versus pressure. We observe continuity in intensity and frequency of major peaks across 66 GPa and 100 GPa implying no major phase transition occurs. We see new peaks (branches noted by asterisks) appearing at about 70 GPa suggesting a minor phase transition occurs.

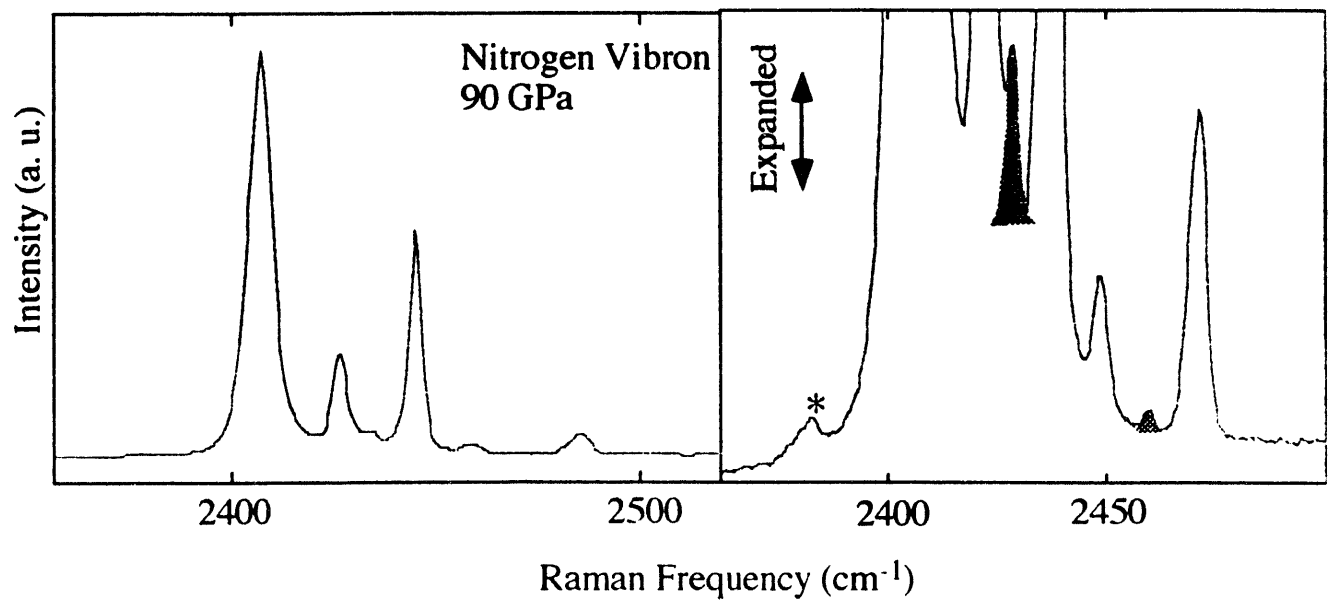

Fig. 3 Vibron spectra. The new peaks are shaded in as a guide to the eye. The peak marked by the asterisk is the signal from the N_{15}-N_{14} isotopic impurities.

Summary

We have significantly revised the phase diagram of N_2 at high pressures and identified a new phase transition. The one transition at ~70 GPa would appear to involve a minor crystallographic distortion. Starting at about 120 GPa, N_2 gradually transforms with increasing pressure to a coffee-brown color, though we point out the system remains molecular. This observation is interesting for two reasons: (1) because the bandgap in N_2 is showing indications that it is closing and possibly *en route* to becoming metallic and (2) because metallic behavior is expected on general grounds to weaken the molecular bond. We are now in the regime where the molecular character is measurably weakening, perhaps presaging a dissociation transition to the polymeric phase.

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