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New phase in solid nitrogen at high pressures

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A Brillouin scattering study of nitrogen up to pressures of 21 GPa shows a phase transition with pronounced hysteresis at 16.5 GPa. This phase transition is consistent with recent Raman measurements of Buchsbaum, Mills, and Schiferl [J. Phys. Chem. **88**, 2522 (1984)] which could be interpreted as either a deformation of the lattice or the appearance of a new phase.

It has only recently become possible to perform Brillouin scattering studies in diamond anvil cells in a routine fashion. These studies[1-3] yield information on elastic properties which are in turn directly related to equations of state. In some cases the results may indicate the presence of phase transitions which have not been observed, or are difficult to observe, using other techniques.[4,5]

Because solid nitrogen is an excellent example of a molecular solid it has received considerable attention. Furthermore, the recent interest in the metalization of H_2 at high pressures, and the similarity of H_2 and N_2, has made a complete understanding of nitrogen an even more important undertaking. A good review of work done at low pressures ($\lesssim 1$ GPa) is given in Ref. 6. Recently, however, attention has been directed to the properties of nitrogen at high pressures, where the intermolecular repulsive forces become important. Raman investigations[7,8] up to 37.4 GPa found that the nitrogen stretching mode splits into a doublet at ~ 5.4 GPa and no anomalous behavior was observed above that pressure. This splitting of the Raman line was later explained using the results of x-ray investigations[9-11] as due to a phase transition from a low-pressure hexagonal phase (β-N_2) to a high-pressure cubic phase (δ-N_2). A more recent Raman study[12] up to 52 GPa finds that at pressures above ~ 20 GPa certain features appear in the spectra which are inconsistent with a cubic phase. Since these features appear gradually, however, it was not clear if they were due to a continuous deformation of the cubic lattice or to a new phase which had been formed.

A number of theoretical treatments of solid nitrogen have also been undertaken.[13-15] Using potentials to describe the interaction between N_2 molecules,[14] some of the Raman scattering results of Ref. 8 are explained on the basis of the low-temperature tetragonal phase of nitrogen (γ-N_2), a similar investigation[15] also predicts changes from tetragonal γ-N_2 to phases of lower symmetry, thus explaining the observed splitting of the Raman line.[7]

There has also been a recent report of a new phase of nitrogen[16] observed by shock-wave compression. This phase is attributed to dissociation of N_2 but since the effective temperatures in shock-wave experiments are high, it is not likely to be directly related to the observation reported in this article.

The Brillouin measurements to be reported here were performed on a 5+2 pass tandem Fabry-Perot interferometer using ~ 200 mW of 514.5-nm radiation from a single-moded Ar laser. The backscattering geometry was used and the diamond cell was loaded using the immersion technique.[9] The measured frequency shifts for pressures up to 15 GPa are shown in Fig. 1. The pressure was determined using the linear ruby-fluorescence scale. Since the frequency shift is directly related to the product of the sound velocity (v) times the refractive index (n) this is also given in Fig. 1. The dots are points obtained on increasing the pressure, the crosses are with decreasing pressure, and the squares are calculated frequency shifts using the data from Ref. 17. A number of points can be made from the results shown in Fig. 1.

(i) In the fluid region (below 2.4 GPa) the results in Fig. 1 are directly related to the bulk modulus (B) and longitudinal elastic constant (C) by

$$B = C = v^2\rho \quad , \tag{1}$$

where ρ is the density. Using

$$\ln\rho = \ln\rho_0 + \int_{P_0}^{P} \frac{dP}{B} \quad , \tag{2}$$

it would be possible to obtain values for $B(P)$ and $\rho(P)$ from the values of nv in Fig. 1, if the refractive index were known as a function of density or pressure.

(ii) At the fluid-to-solid phase transition Brillouin peaks

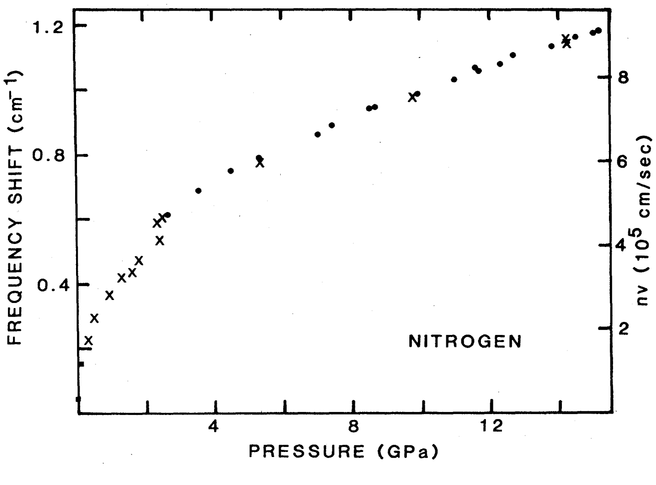

FIG. 1. Brillouin frequency shift from nitrogen vs pressure in the range 0–15 GPa. Dots and crosses are for increasing and decreasing pressures, respectively. Squares are calculated from data in the literature.

from both fluid and solid were observed simultaneously indicating that, as expected, both phases coexist at that pressure.

(iii) In the region between 2.5 GPa and 15 GPa the measured frequency shifts are the same from run to run. This could be explained with the assumption that this phase always forms in the same orientation. However, this explanation is unlikely since the solid can be obtained by going from fluid to solid or by decreasing the pressure from the high-pressure phase (not shown in Fig. 1). A more likely interpretation is that this phase is almost elastically isotropic.

(iv) The results in Fig. 1 show no evidence for a phase transition at ~5 GPa as indicated by the Raman[7,12] and x-ray[9-11] results. Although this in itself does not represent a contradiction, in our experiments it appeared that the sample remained birefringent above 5 GPa, a fact which is inconsistent with the existence of a cubic phase[9-11] in that pressure range. Further x-ray and optical experiments are necessary to clarify this point.

In Fig. 2 the measured frequency shifts in the region 14–21 GPa are shown. Each of the different symbols represents different runs; full and open symbols indicate increasing and decreasing pressure, respectively. The phase transition which is evidenced in Fig. 2 is also observable visually; below the transition the sample is "water clear" while above, although still transparent and colorless, it shows signs of containing many "grain boundaries." The appearance and disappearance of these visual effects coincide with the limits of the hysteresis shown in Fig. 2. The scatter in the points above the transition is consistent with different preferential orientations of the sample being formed in different runs, each being characterized by different elastic properties.

The Brillouin results provide no information on the structural nature of the new phase. It is clear, however, from the Raman results[7,12] that show that the stretching mode is observable up to 52 GPa, that we are dealing with a molecular solid. The magnitude of the velocity changes and of the hysteresis tend to imply a substantial rearrangement of the molecules at the transition.

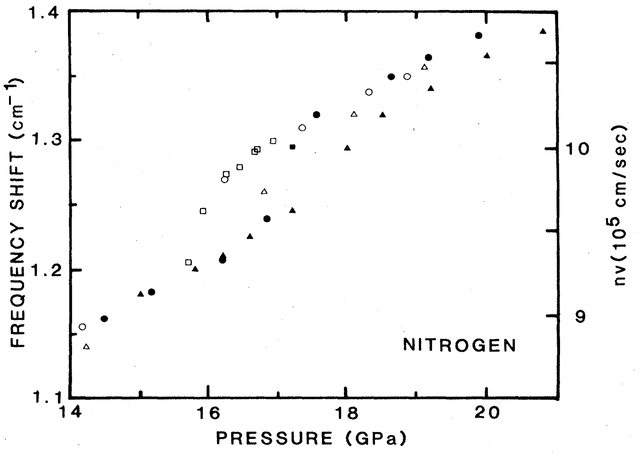

FIG. 2. Brillouin frequency shift from nitrogen vs pressure in the range 14–21 GPa. Full and open symbols are for increasing and decreasing pressures, respectively. Different symbols correspond to different runs.

The results presented here may also prove useful as a pressure calibration when N_2 is used as an inert pressure medium, as has been suggested in Ref. 7.

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