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NITROGEN AT VERY HIGH PRESSURE

W. J. NELLIS
Lawrence Livermore National Laboratory
University of California
Livermore, CA 94550

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W. J. NELLIS

Lawrence Livermore National Laboratory, P. O. Box 808,
Livermore, California 94550, USA

Abstract

High-pressure results for nitrogen are reviewed and discussed in terms of phenomena that occur at extreme conditions.

1. Introduction

Nitrogen is one of the most thoroughly investigated materials at high pressure because of its importance to condensed matter physics, planetary science, and chemical explosives. Because it is a relatively simple and stable diatomic molecule, nitrogen has been studied over a wide range of pressures, densities, and temperatures in both fluid and solid molecular phases. At sufficiently high dynamic^{1,2} and static^{3,4} pressures nitrogen undergoes phase transitions, including a dissociative fluid-fluid transition above 30 GPa (300 kbar) and 7000 K.² From a planetary viewpoint, nitrogen is cosmologically abundant and expected to be a major constituent of Uranus and Neptune⁵ in the form of NH_3 or, at the high pressures and temperatures of the deep interior, as pure nitrogen or in compounds with H, O, and C. For Uranus and Neptune the conditions in the "ice" layer, which is actually in the fluid phase, range up to a few 100 GPa and several 1000 K.⁵ These conditions can be achieved in the laboratory by the shock compression of liquids. Thus, the properties of nitrogen at high shock pressure provide insight into the nature of materials inside Uranus, an important issue because of the unusual magnetic field observed for that planet by the Voyager II spacecraft.⁶ Also, nitrogen is a major detonation product of reacted explosives.⁷ Hence, the properties of dense, fluid nitrogen at detonation, reshock, and release pressures up to several 10 GPa are important for developing mixture models for reacted explosives.⁸

2. Shocked Molecular Phase

Equation-of-state data have been measured in the molecular fluid phase by the shock compression of liquid nitrogen.⁹⁻¹² The molecular range extends

up to about 30 GPa on the principal Hugoniot shown in Fig. 1. These pressure-volume data and data for other small molecules were successfully explained by a theory which scales the spherically-symmetric exponential-six pair potential of Ar by critical-point parameters, assumes rotational degrees of freedom are fully excited, and assumes that molecular vibrational levels are equally spaced in energy, as in the gas phase, and populated according to a Maxwell-Boltzmann distribution.¹³ This theory calculates a pressure-volume (P-V) curve in excellent agreement with the shock data up to about 30 GPa and 7000 K¹³ and provides evidence that the N₂ molecule persists to these extreme conditions. The excellent agreement also means that molecular vibrational equilibrium is achieved in a time of ~ 1 ns, the time resolution of the shock velocity measurement of the equation-of-state experiments. If

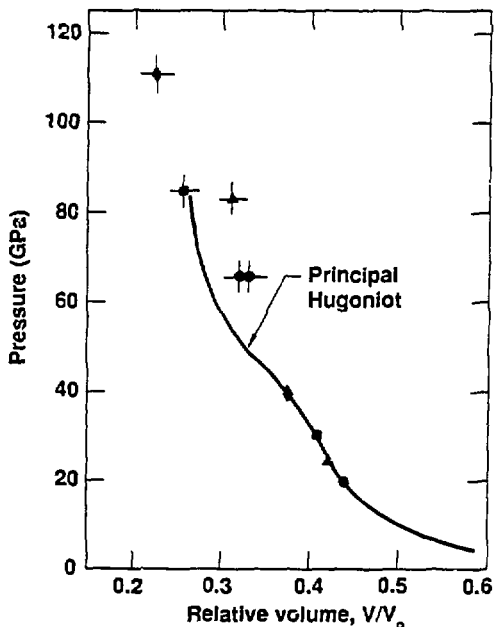


Fig. 1. Principal Hugoniot (solid curve) and double-shock points for liquid nitrogen initially at 77 K. Symbols without error bars are first-shock states and corresponding symbols with error bars are second-shock states (Reference 1).

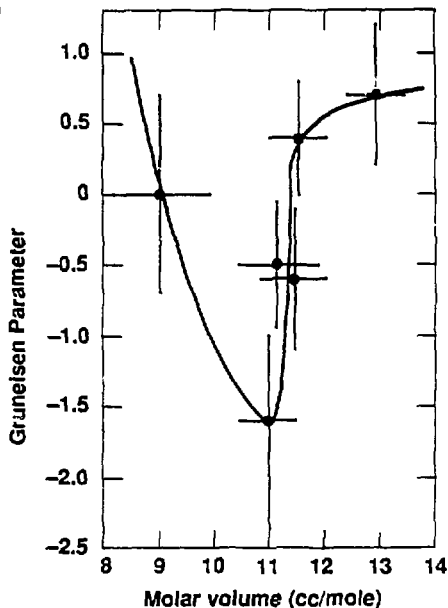


Fig. 2. Average Grüneisen parameters for nitrogen calculated from Hugoniot of Reference 1 and double-shock data of Reference 1 (solid circles) and Reference 12 (solid squares) vs molar volume ($V_0 = 35$ cc/mole).

vibrational equilibrium were not achieved on an ns time scale, then relatively more internal shock-compression energy would be distributed into thermal energy, the measured shock velocity would be larger, and the measured shock-compression P-V curve would be stiffer than observed.¹³ The relaxation time for energy transfer from translational to vibrational degrees of freedom was calculated recently to be ~ 0.5 ns for fluid N_2 at conditions comparable to 30 GPa shock pressure,¹⁴ in agreement with considerations of the shock-compression P-V data discussed above. The scaled theory¹³ also calculates shock temperatures in good agreement with experimental data.^{2,15}

Recent pulsed coherent anti-stokes Raman scattering (CARS) spectra for liquid N_2 single-shocked up to 16 GPa and double-shocked up to 34 GPa show that the spacings between vibrational levels of N_2 are constant within the uncertainties of the experimental data and consistent with gas phase values and that excited vibrational states are populated in ≤ 50 ns, an upper bound equal to the duration of the laser pulse used for the Raman scattering experiments.¹⁶ These experimental results are in good agreement with the N_2 gas-phase vibrational spectrum assumed previously by theory¹³ and provide an upper-bound on the vibrational equilibration time consistent with the ns ones discussed above.

Anisotropic N_2-N_2 potentials have been derived and effective spherical potentials can be found which yield thermodynamic data in good agreement with experiment.¹⁷

3. Shock-Induced Dissociation

Nitrogen undergoes a continuous, dissociative phase transition in the fluid state above 30 GPa, 2 g/cm^3 , and 7000 K, based on several experimental observations. The comparison of the shock-compression curves for liquid N_2 , isoelectronic CO, and theory for the molecular fluid phase of each suggested dissociation as the mechanism causing deviations from the molecular-phase Hugoniot of N_2 above 30 GPa.¹ Dissociation is a logical phenomena by which dense molecular nitrogen could respond to high density and temperature. By taking the radial positions of the zeros in the repulsive pair potentials for the N_2-N_2 ¹³ and $N-N$ ¹³ interactions as an estimate of the effective hard-sphere diameters in the dense fluid, a significant

volume decrease is obtained for two N atoms relative one N_2 molecule. High shock temperatures could thus drive dissociation as a mechanism to accommodate high densities. The densities at which the phase transition is observed are close to where theory suggests that monatomic solid nitrogen might be metastable at 0 K.¹⁹ Again high temperatures can drive this transition to the monatomic state in the shock experiments.

Double-shock equation-of-state data lie above the principal Hugoniot¹ and show that $(\partial E/\partial P)_V < 0$ in the phase transition region. These data are shown as the symbols with error bars in Fig 1. The average Grüneisen parameter $\gamma = V(\partial P/\partial E)_V$, calculated using the principal Hugoniot and the double-shock equation-of-state data, is plotted vs molar volume in Fig. 2. The specific internal energies of the double-shock points above the Hugoniot are 'lower than for the states on the Hugoniot at the same volumes. The resulting negative γ 's are indicative of a phase transition, which occurs in a relatively narrow range of volume near $11 \text{ cm}^3/\text{mol}$ ($V_0 = 35 \text{ cm}^3/\text{mol}$). Figure 2 illustrates how the N_2 molecule becomes unstable above a compression of 2.7 over initial liquid density and 7000 K.

The fact that $(\partial E/\partial P)_V < 0$ predicted that $(\partial T/\partial P)_V < 0$,¹ since heat capacity is positive. Double-shock temperature experiments verified this prediction, provided evidence for crossing isotherms, and most remarkably showed shock-induced cooling, as illustrated in Fig. 3.² Shock-induced cooling indicates that so much internal energy is absorbed in the phase transition at the higher pressure and density of the double-shock state that the temperature of the double-shock state is actually lower than that of the first-shock state. The variation of shock temperature with shock pressure or volume shows a softening at $\sim 30 \text{ GPa}$, the same pressure as in Fig. 1.²

The electrical conductivity, plotted in Fig. 4, rises rapidly with pressure between 19 and 27 GPa (4000-7000 K) and increases more slowly between 34 and 61 GPa (8000-12000 K).² The change in behavior occurs near 30 GPa, as for the pressure-volume¹ and the temperature-pressure data. Electrons are probably the dominant carriers by virtue of their high mobility relative to ions. The high densities and temperatures suggest that electron scattering probably occurs with a mean-free path of the order of a molecular diameter over the entire range of the data. The increase in conductivity would then be dominated by the increase in carrier concentration. Above 30 GPa, where substantial amounts of dissociation occurs, electrons are probably ionized

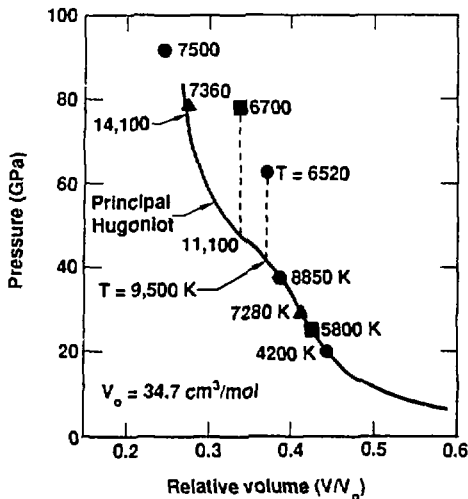


Fig. 3. Principal Hugoniot is solid curve. Each pair of identical symbols corresponds to single- and double-shock temperatures measured in same experiment. This figure shows $(\partial T/\partial P)_V < 0$ in phase transition region, shock-induced cooling (hexagons), and crossing isotherms at 80 GPa.

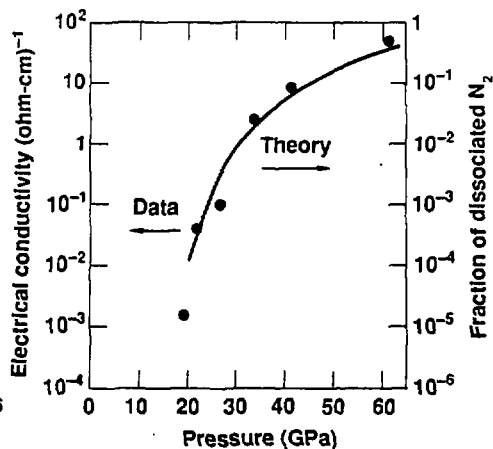


Fig. 4. Electrical conductivity and calculated dissociated fraction of N_2 vs shock pressure (Reference 2).

primarily from N atoms. The excited electronic states of the N atom are at significantly lower energies than for the N_2 molecule. At the high densities achieved, these levels would be expected to broaden into bands with the monatomic states lower than the diatomic ones.

The calculated fraction of dissociated N_2 molecules^{2,20} is also plotted vs pressure in Fig. 4 and shows that the electrical conductivity is approximately proportional to the concentration of N atoms, which is consistent with the picture that the conductivity is dominated by electrons ionized from dissociated N atoms.

Effective dissociation energies and rates in dense fluid N_2 have recently been estimated.²⁰⁻²² These results show that the effective dissociation energy decreases with increasing pressure and density and that

the order of magnitude of the reaction time for dissociation decreases with pressure, approaching the time resolution of the shock experiments and reaching a few percent at the pressures where the effects of dissociation are observed in the experimental data.

4. N_2 at High Static Pressure

The observation of a phase transition above 30 GPa in shocked liquid nitrogen led to a theoretical prediction that at 0 K solid N_2 might transform to a monatomic phase at pressures possibly below 100 GPa.²³ Static high-pressure Raman-scattering experiments at 300 K in a diamond anvil cell up to 130 GPa showed that solid N_2 retains its diatomic nature up to this pressure, although three transitions to new structures are observed.^{3,4} The Raman scattering data to 130 GPa³ are shown in Fig. 5. The fact that N_2 dissociation occurs in the dynamic experiments and not in the static ones shows that higher shock temperatures drive this transition.

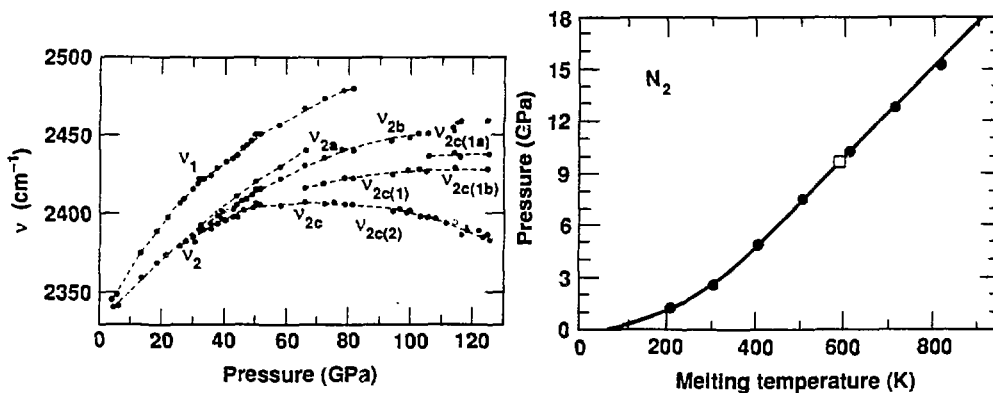


Fig. 5. Pressure dependence of Raman-active N_2 vibrons up to 125 GPa in diamond anvil cell (Reference 3).

Fig. 6. Pressure vs melting temperature for N_2 measured in diamond anvil cell. Solid curve is smoothed experimental data. Open square is beta-delta-fluid triple point. Circles are theory (Reference 24).

The melting curve of N_2 has been measured to 18 GPa and 900 K in a diamond anvil cell²⁴ and is shown in Fig. 6. The theoretical analysis of the experimental data shows that melting of N_2 is influenced strongly by librational motions in the dense solid.²⁴ The lowest shock temperature measurement of 2000 K at 10.6 GPa¹⁵ is well above the melting temperature of 600 K at this pressure, showing that the shock compression data for liquid nitrogen are well into the fluid phase.

The room-temperature static-compression P-V curve of solid N_2 has been measured from 5 to 10 GPa. These data show that a structure with the Pm3n space group is retained throughout this pressure range.²⁵ The phase diagram of solid N_2 has been mapped up to 52 GPa by Raman²⁶ scattering.

5. Conclusion

Nitrogen is one of the most studied materials at high pressure and shows a richness of physical phenomena.

Acknowledgements

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