Molecular Dissociation and Shock-Induced Cooling in Fluid Nitrogen at High Densities and Temperatures

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Radiative temperatures and electrical conductivities were measured for fluid nitrogen compressed dynamically to pressures of 18–90 GPa (180–900 kbar), temperatures of 4000–14000 K, and densities of 2–3 g/cm^3. The data show a continuous phase transition above 30 GPa shock pressure and confirm that $(\partial P/\partial T)_v < 0$, as indicated previously by Hugoniot equation-of-state experiments. The first observation of shock-induced cooling is also reported. The data are interpreted in terms of molecular dissociation and the concentration of dissociated molecules is calculated as a function of density and temperature.

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Diatomic molecules such as nitrogen and hydrogen are ideal systems for the testing of our understanding of condensed matter at extreme pressures, densities, and temperatures. Questions of greatest interest are the conditions required to metallize the insulator phase and the role played by dissociation to the monatomic state. We recently observed a phase transition in equation-of-state data for fluid nitrogen above 30 GPa (300 kbar) shock pressure, 2 g/cm^3, and a calculated temperature of 6000 K.[1] By comparison of the shock-compression curves (principal Hugoniots) for liquid N_2 and isoelectronic CO, the data were interpreted in terms of a continuous dissociative transition to the monatomic state. This is physically reasonable because at 30 GPa N_2 is extremely dense, and the volume of monatomic nitrogen is much less than for the molecular state. The equation-of-state data included the first observation of double-shock points lying above the principal Hugoniot in pressure-volume space. These data showed that $(\partial P/\partial E)_v < 0$ and indicated that $(\partial P/\partial T)_v < 0$ in the phase transition region[1] since c_v is always positive; that is, that as pressure increases above the Hugoniot the temperature should decrease at specific volumes in the transition region.

In order to verify the observation of the phase transition and to verify that $(\partial P/\partial T)_v < 0$, we have measured both the single- and double-shock temperatures of liquid nitrogen. The data confirm that at fixed volume the double-shock temperatures are lower at pressures above the principal Hugoniot. In addition, we have observed an even more remarkable result: the first observation of shock-induced cooling. Irreversible shock energy normally heats a material. However, if liquid N_2 is first shock-compressed into the phase transition region, the specimen cools instantly (<10 nsec) on reshock against a transparent Al_2O_3 or LiF window. Shock temperatures of liquid nitrogen were measured previously, but only up to 20 GPa.[2] In order to investigate possible metallization, we have also measured the electrical conductivity of shocked liquid nitrogen, which becomes quite large, reaching 50 $(\Omega\ \mathrm{cm})^{-1}$ at 60 GPa and 12000 K. All these results are consistent with a continuous transition in which energy is absorbed in dissociation and ionization.

The observation of a phase transition in shocked 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.[3] Static high-pressure experiments at 300 K in diamond anvil cells to 130 GPa showed that solid N_2 retains its diatomic nature to the highest experimental pressures, although three transitions to new structures are observed.[4,5] The fact that N_2 dissociation occurs in the dynamic experiments and not in the static ones shows that the higher shock temperatures are responsible for driving this transition.

For comparison, H_2 retains its molecular form in the solid and the shock-compressed liquid to the highest pressures measured, which are, respectively, 150 GPa[6] at 300 K and 80 GPa at 7000 K.[7]

The possible existence of metallic nitrogen at megabar pressures and thousands of degrees is relevant to the recent observation of a relatively large magnetic field for Uranus.[8] If NH_3 in the central layer of Uranus were to decompose into metallic N, it could possibly contribute to the magnetic field. Of course, the same possibility applies to metallic hydrogen as well and with greater probability because of the great abundance of hydrogen in Uranus.

Strong shock waves were generated by the impact of planar Al and Ta projectiles into cryogenic specimen holders. The projectiles were accelerated to velocities of 5–8 km/sec by means of a two-stage light-gas gun. Pressures, densities, and internal energies were obtained by measurement of impact velocity and use of the shock impedance-match method with the known equations of state for Al, Ta, nitrogen, and Al_2O_3. The N_2 specimens were initially in the liquid state at 77 K and slightly above atmospheric pressure. The specimen holders used the cryogenic design described previously.[9]

For the shock-temperature experiments the technique consists of measurements of the spectral radiance of light emitted from a shock-heated sample, as described previously for H_2O.[10] A planar impactor strikes an Al wall containing the front side of a liquid N_2 sample, with a transparent Al_2O_3 window in the rear side of the sample cavity. For single-shock experiments optical luminosity from the moving shock front can escape through the transparent unshocked portion of the specimen and through the unshocked Al_2O_3 window. When the shock wave arrives at the window, a shock of larger amplitude is reflected back into the specimen and transmitted into the window. Shocked Al_2O_3 is transparent up to 100 GPa and partially transmitting at higher pressures.[11] The emission intensity from shocked Al_2O_3 is negligible because the calculated shock temperature of Al_2O_3 at 100 GPa is only 1000 K.[12] Light emitted from shocked nitrogen was directed out of the target chamber by a turning mirror to an emission spectrometer, consisting of photomultipliers, which record time-resolved intensities in six narrow wavelength bands, and a 1024-channel, linear, intensified, diode array which records the complete spectrum from 200 to 800 nm, integrated over a 50-ns time interval. The time resolution of the photomultiplier system is ~10 ns. The data were converted to absolute intensity by comparison with calibrated tungsten ribbon lamps. Intensity versus wavelength data were least-squares fitted by a Planck gray-body function to obtain the temperature T and the emissivity ε.[10] For our fits ε is generally in the range 0.8–1.0. A constant emissivity was sufficient to obtain fits which agreed with measured spectral intensities to within experimental uncertainties.

For the electrical conductivity experiments, two electrodes were inserted into the specimen cavity, as for H_2O experiments.[13] The resistivity of each cell was calibrated for conductivity in separate experiments by use of electrolytes of known electrical conductivity.

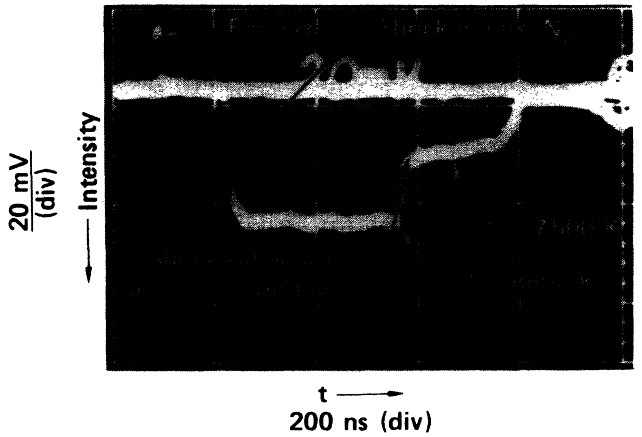

FIG. 1. Oscillogram from the 546-nm channel of our optical pyrometer. The temperature rises in $t \sim 10$ ns when the shock breaks out in the nitrogen. The signal remains constant as the shock wave traverses the sample indicating a steady shock wave, then decreases sharply when the nitrogen is double-shocked against the Al_2O_3 window. This decrease in temperature after the double shock is the first observation of shock-induced cooling.

In Fig. 1, we show a representative oscillogram from one of the photomultipliers for a temperature experiment (voltage, optical luminosity, and temperature increase downwards). For materials studied previously,[10,14] the sample was first shocked to a pressure of P_1 and at the sample-window interface was double-shocked to $P_2 > P_1$ with a corresponding increase in temperature. An increase in shock pressure results in additional work on the system and so the temperature usually increases. In Fig. 1, nitrogen is single-shocked to 36 GPa and then double-shocked against Al_2O_3 to 84 GPa with a 1300-K *decrease* in temperature. An experiment using LiF as the transparent anvil showed the same shock-cooling behavior.

In Fig. 2, we show the data of single-shock temperature versus volume for fluid nitrogen. The temperature ranges from 4000 to 14000 K at pressures from 17.5 to 80 GPa, corresponding to relative volumes of 0.44–0.27. We see a marked softening of the temperature between 30–60 GPa, as for the pressure-volume data in the same regime.[1]

At the high densities and temperatures of these experiments, fluid nitrogen is expected to be in thermal equilibrium. The constant light intensity for the first shock in the oscillogram of Fig. 1 shows a steady shock wave traversing the specimen. The double-shock temperature is observed to equilibrate in a time less than the resolution of the diagnostic system (10^{-8} s). The slight decay in the double-shock luminosity is most probably caused by shock-induced optical absorption in the Al_2O_3 window. Computationally, thermal equilibrium was shown to be established in shocked Ar, a simple fluid, in $\sim 5\times10^{-13}$ s at only 1.2 GPa and 500 K.[15] The relaxation time for energy transfer from the translational to vibrational degrees of freedom was calculated recently to be 5×10^{-10} sec for fluid N_2 at conditions comparable to 30-GPa shock pressure.[16] At 7000 K the time between

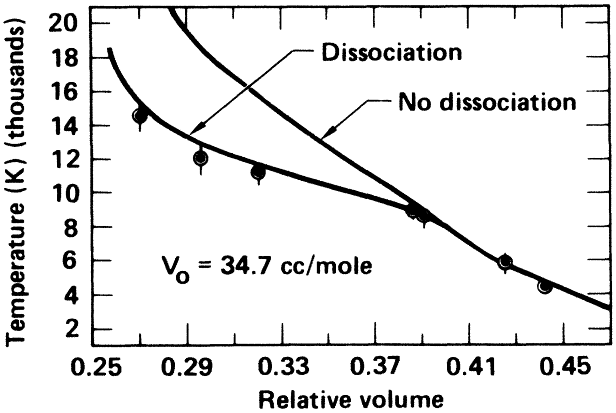

FIG. 2. Shock temperature vs volume for fluid nitrogen. The solid lines are theoretical curves calculated both with and without dissociation. The experimental data show a marked softening relative to the temperatures calculated without dissociation.

molecular collisions is $\sim 4\times 10^{-14}$ s. The N_2 molecular vibration time is also $\sim 10^{-14}$ s. These times are much less than the time resolution of the temperature and conductivity measurements and less than the time resolution of the equation-of-state experiments. Thus, nonequilibrium effects are expected to be small in all the experiments.

In Fig. 3, measured temperatures are shown at representative points on the fit to the P-V shock-compression curve. Also shown are the measured double-shock temperatures at the corresponding pressures and volumes. Clearly, Fig. 3 shows that temperature decreases with increasing pressure above the Hugoniot at constant volume in the phase transition region; that is, $(\partial P/\partial T)_v < 0$, as predicted.[1] We also observe crossing isotherms near $\sim$80 GPa, where nitrogen was single- and double-shocked to the same P and V, but to temperatures which differ by a factor of 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). The change in behavior occurs near 30 GPa, as for the pressure-volume[1] and the temperature-pressure data. Electrons are probably the dominant carriers by virtue of their high mobility relative to ions. The high densities (1.8–2.7 g/cm^3) and high temperatures (4000–12000 K) 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. Below 30 GPa, where a purely molecular model explains the N_2 equation-of-state data,[17] electrons are ionized primarily from N_2 molecules. At higher pressures and temperatures, where substantial amounts of dissociation occurs, electrons are probably ionized 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. A simple estimate based on the Drude model shows that our conductivity data correspond to about 1 conduction electron per 100 original N_2 molecules. The conductivity of 50 $(\Omega\text{-cm})^{-1}$ is a factor of 10^{-3} smaller than that of a transition metal at room temperature, but infinitely greater than that of a liquid N_2 at 77 K which has no measurable electrical conductivity.

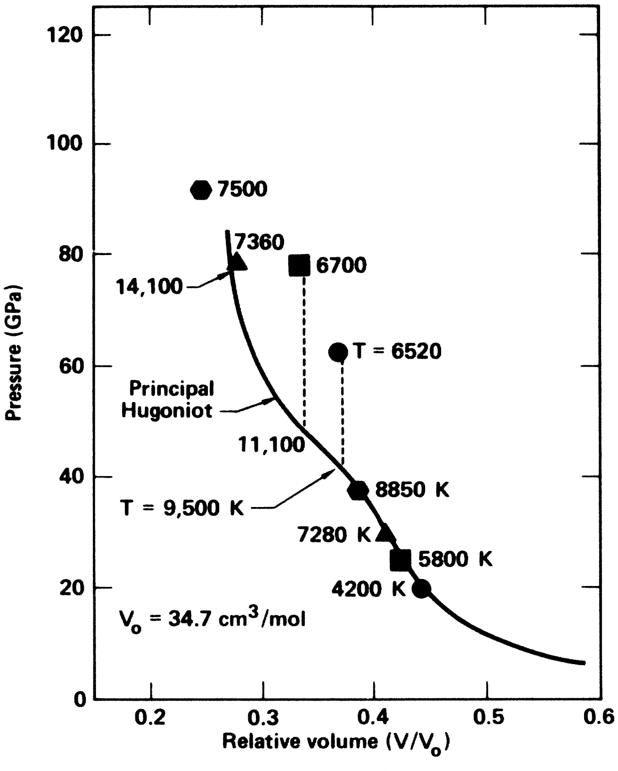

FIG. 3. Pressure-volume curve (principal Hugoniot) is shown as the solid black line. Each pair of identical symbols corresponds to single- and double-shock points in the same experiment. The figure illustrates the fact that $(\partial P/\partial T)_v < 0$ in the phase transition region, as well as shock-induced cooling as one goes from the two points indicated by the hexagons.

The model used for the Hugoniot calculations shown in Figs. 2 and 3 is a version of one described at length in a previous study of molecular nitrogen,[17] but modified here to include dissociation into atoms. The model correctly predicts the pressures and temperatures along the principal Hugoniot. Agreement between theory and experiment for the double-shock pressures shown in Fig. 2 is very good for the two highest reflected points, but not for the lower two. The theory also accounts, qualitatively, for the observed occurrence of shock cooling on a reflected Hugoniot.

The novel feature of this model is the introduction of a

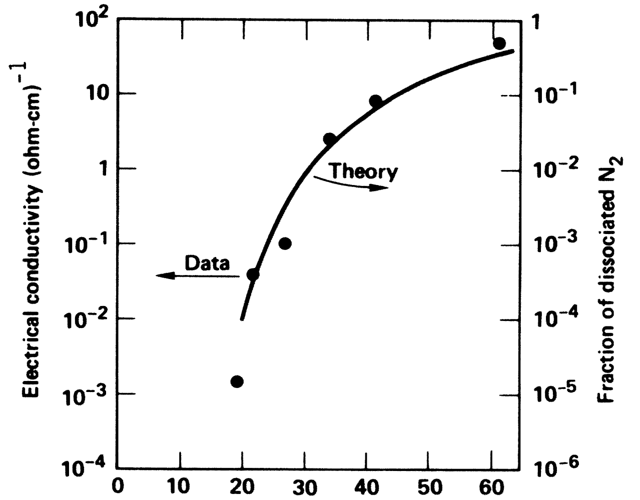

FIG. 4. Electrical conductivity and calculated dissociated fraction of N_2 molecules vs pressure.

density-dependent dissociation energy. In the gas phase, 9.76 eV are required to break the molecular bonds. It is important to recognize that in the fluid, shocked to three times normal density, recombination into a condensed phase will return a portion of this value as cohesive energy. This leads to a dissociation energy which is less than 9.76 eV, and which depends strongly on the density of the fluid. This model will be described in detail in a separate paper.[18]

The calculated fraction of dissociated N_2 molecules is plotted versus pressure in Fig. 4. Figure 4 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. Thus, the phase transition is accompanied by an electronic transition, as observed recently at the gas-vapor critical point of Cs.[19,20] The calculation also indicates that about 50% of the N_2 molecules are dissociated at highest pressures and temperatures.

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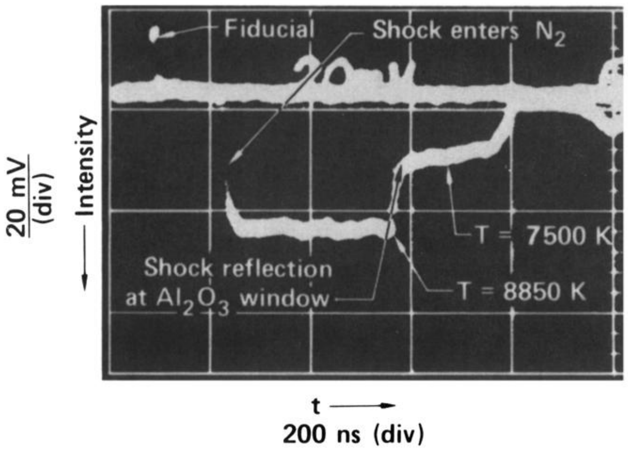

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