# Phase Transition in Fluid Nitrogen at High Densities and Temperatures

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Dynamic equation-of-state data are presented for liquid $N_2$ single- and double-shocked to pressures of 100 GPa (1 Mbar), compressions to fourfold over initial liquid density, and internal energies to 1 MJ/mole. Three double-shock points lie above the principal Hugoniot in pressure-volume space, the first such observation in condensed matter. The data are interpreted in terms of a continuous phase transition, identified as molecular dissociation by comparison of the shock compression curves of liquid $N_2$ and isoelectronic CO.

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Nitrogen is an ideal system for study of the insulator-to-metal transition. $N_2$ is a small, simple diatomic molecule. Extensive dynamic[1–3] and static[4] high-pressure equation-of-state data have been measured. An effective spherical intermolecular pair potential has been derived from the dynamic data.[5] The $N_2$-$N_2$ repulsive pair potential has been calculated *ab initio*.[6] The increase in the shock-wave compressibility at 30 GPa (300 kbar)[3] and 2.5-fold compression over initial liquid density has been attributed to molecular dissociation to the monatomic state.[5,7] Since nitrogen retains its diatomic molecular structure to 40 GPa at 300 K,[8] dissociation, if it occurs in the dynamic experiments, must be driven by the high shock temperatures which are calculated to be greater than 6000 K at 30 GPa.[9] Liquid $N_2$ can be shock compressed fourfold, which corresponds to a final density comparable to that at which monatomic metallic nitrogen may exist.[10] Thus, experimental and theoretical results suggest that $N_2$ undergoes a transition to the monatomic state at the densities and temperatures achieved in dynamic experiments at threefold to fourfold compressions.

By comparison, $H_2$ requires a greater compression of about fourteenfold to achieve the transition to the monatomic metallic state at 0 K.[11] The highest densities achieved in $D_2$ shock-wave experiments[12,13] are a factor of 2 smaller than that predicted[11] for the metallic transition and the dynamic data do not indicate dissociation of $H_2$.[14] Raman spectroscopic measurements show that $H_2$ retains its molecular nature to 60 GPa at 300 K.[15]

Nitrogen is believed to retain its diatomic molecular structure up to shock pressures of 30 GPa on the principal Hugoniot. This statement is a result of excellent agreement between Hugoniot data and the theoretical $P$-$V$ curve calculated with use of an intermolecular pair potential derived from an Ar potential by corresponding-states scaling.[5] Because the estimated shock temperature above 30 GPa is $\sim 1$ eV,[7] and approaching the dissociation energy of an isolated $N_2$ molecule, 9.8 eV,[16] the softening above 30 GPa has been attributed to molecular dissociation.[5,7] However, the amount of experimental data was insufficient to constrain a physical model because several other mechanisms could possibly account for the softening in the $P$-$V$ data—for example, electronic excitation as in Ar,[17] or a transition from hindered to free molecular rotation as the shock temperature becomes comparable to the large rotational anisotropy energy of the $N_2$ molecule.[6] Calculations have not accounted for the pressure softening either by electronic excitation[7,9] or by a transition to free molecular rotation.[7] Recent molecular dynamics calculations for dense, high-temperature nitrogen were concerned with the $N_2$ molecular phase, but one calculation indicated dissociation at conditions somewhat above the 30-GPa softening in the $P$-$V$ curve.[9]

In this Letter we report new single- and double-shock equation-of-state data for fluid nitrogen at shock pressures up to 100 GPa (1 Mbar), compressions up to fourfold over initial liquid density, and internal energies up to 1 MJ/mole of $N_2$. These data were obtained specifically to understand the mechanism for the increase in compressibility along the principal Hugoniot, that is, the single-shock pressure-volume ($P$-$V$) curve, above 30 GPa.[3]

Strong shock waves were generated by the impact of planar projectiles onto cryogenic specimen holders. Projectiles were accelerated to velocities of 5–8 km/s by means of a two-stage, light-gas gun.[18,19] The $N_2$ specimens were initially in the liquid state at 77 K and slightly above atmospheric pressure. The specimen holders were described previously.[3,20] Thermodynamic variables of shock pressure, density, and specific internal energy were derived from the measured impactor velocity, shock velocity, and initial liquid density by means of the Rankine-Hugoniot equations and the shock impedance-matching method.[3,20] The time resolution of the

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shock detection systems is $\lesssim 10^{-9}$ sec, which is much longer than the intermolecular collision time of $\sim 10^{-13}$ sec and the molecular vibration time of $\sim 10^{-14}$ sec. Hence, the data are representative of states in thermodynamic equilibrium. Five experiments were performed by first shocking specimens to states in the range of 20–40 GPa and then reshocking against a Cu anvil to higher pressures. One principal-Hugoniot experiment was performed to increase the maximum pressure of the single-shock data. In order to do this, our gun performance was enhanced to increase maximum impactor velocity from 7 to 8 km/s,[19] which required the dimensions of the specimen holder to be scaled down to 75% of our standard size. Experimental techniques for shocked liquids and the results for several representative fluids at high shock densities and temperatures have been reviewed recently.[21]

Our new nitrogen principal-Hugoniot point at 82 GPa is shown in Fig. 1, a plot of shock pressure versus relative volume, $V/V_0$, where $V$ and $V_0$ are the specific volume in the shock state and initial state, respectively. Also plotted in Fig. 1 are previous Hugoniot data for liquid $N_2$[1,3] and CO.[20] $N_2$ and CO are isoelectronic, they have very similar critical points, and in the shock experiments they had the same initial liquid densities, 0.81 g/cm$^3$. The curves through the data above 15 and 30 GPa for CO and $N_2$, respectively, were calculated from smooth interpolations through the data in shock-velocity, mass-velocity space. The low-pressure molecular Hugoniot was calculated by scaling an Ar potential by critical-point parameters and by including molecular rotation and vibration.[5] This theory predicts that both molecular $N_2$ and CO have the same shock compression curve, under the assumption of no molecular decomposition. Figure 1 shows that the $N_2$ and CO data follow the same theoretical curve up to 15 GPa, where the CO Hugoniot softens because of chemical decomposition.[20] The nitrogen data follow the molecular curve up to 30 GPa where softening also occurs. Since the double-shock data discussed below indicate a phase transition in this region of $P$-$V$ space, we interpret the softening in the $N_2$ curve to be caused by molecular decomposition as for isoelectronic CO. The $N_2$ reaction products are expected to be known phases of nitrogen, primarily $N_2$ and N, which identifies dissociation as the principal reaction mechanism. Other species like $N_3^-$ and/or as-yet unobserved larger complexes may possibly form as well. However, the calculated high temperatures, greater than 6000 K at 30 GPa, argue against the formation of extended, chemically bonded nitrogen species. The phases which are present might exist in solution or they may undergo phase separation into dispersed droplets. The Hugoniot curves in Fig. 1 for nitrogen and carbon monoxide once again merge above $\sim 70$ GPa where it appears that the fluids are so compressed that only the atom number density of the initial state determines the $P$-$V$ curve, and not the chemical arrangement.

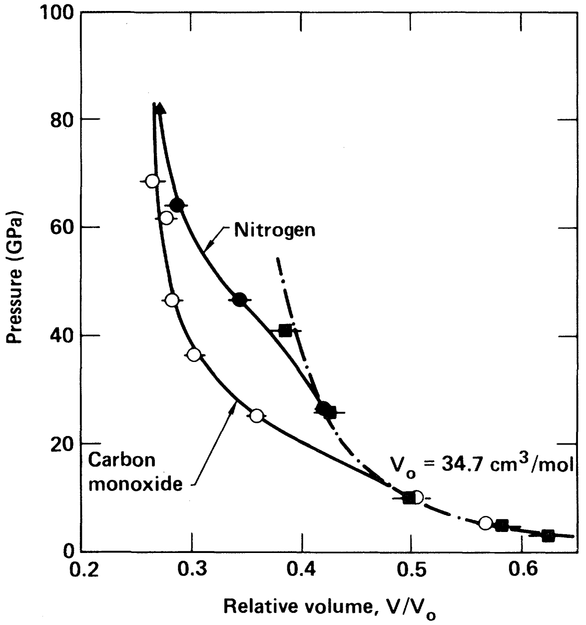

FIG. 1. Single-shock compression curves (Hugoniots) for liquid $N_2$ (triangle is this work, solid circles are from Ref. 3, squares are from Ref. 1) and CO (open circles are from Ref. 20). The solid curves were derived from smooth interpolations through the same data in shock-velocity, mass-velocity space. The dash-dotted curve is the theory of Ref. 5 for both molecular $N_2$ and CO (100 GPa = 1 Mbar).

Results for the double-shock nitrogen experiments plotted as pressure versus relative volume are shown in Fig. 2. The nitrogen principal Hugoniot of Fig. 1 is plotted in Fig. 2 without data points. The symbols on the principal Hugoniot in Fig. 2 indicate the first shock states from which specimens were double-shocked. The first-shock states were obtained by shock-impedance matching and were not measured directly. The symbol on each double-shock datum point matches the symbol on the principal Hugoniot from which the double shock was obtained. Two experiments were performed by double-shocking from 20 to 65 GPa. The results agree within experimental error. Three double-shock points starting at 20 and 25 GPa lie well above the principal Hugoniot. This is the first observation in condensed matter in which double-

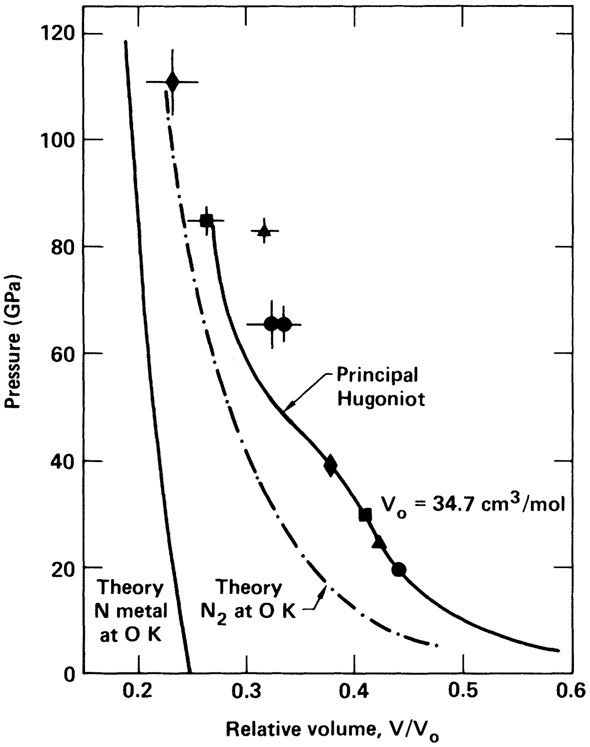

FIG. 2. Double-shock data with error bars for liquid $N_2$. Also shown is the nitrogen Hugoniot curve from Fig. 1. The symbols on the Hugoniot indicate the first shock states from which specimens were double-shocked. The symbol at each double-shock point matches the symbol on the Hugoniot from which it was reshocked. The theoretical curves are from Ref. 10 (100 GPa = 1 Mbar).

shock pressure is greater than Hugoniot pressure at a given volume, and implies that pressure increases with decreasing temperature at constant volume. The point double-shocked from 30 GPa lies on the principal Hugoniot. Thus, this effect can be observed only by double-shocking from a rather narrow range of volume on the principal Hugoniot in the molecular phase.

The specific internal energies of double-shock states are less than the energies on the Hugoniot at the same volume. Therefore, a double-shock state has a smaller temperature $T$ than the state on the Hugoniot at the same volume, since heat capacity is positive. Because double-shock states are colder than single-shock states at the same volume, thermal pressure and total pressure are smaller for double-shock states, provided the material is not changing phase in the region of interest. Thermal pressure is characterized by the Grüneisen parameter $\gamma = V(\Delta P/\Delta E)_V$, where $P$ is pressure, $E$ is specific internal energy, and the differences are taken between values for double-shock data points and values on the single-shock Hugoniot at the same volumes. In the absence of a phase transition, the usual case, $\gamma$ is positive, and double-shock points lie below the principal Hugoniot. Remarkably, for our three double-shock points at $V/V_0 \gtrsim 0.3$, $(\Delta P/\Delta E)_V$, $\gamma(-1.8$ at $V/V_0 = 0.32)$, and $(\Delta P/\Delta T)_V$ are *negative,* which indicates strongly that $N_2$ is undergoing a phase transition.

In Fig. 2 the 0-K isotherms[10] for molecular and metallic nitrogen are also plotted. The curve for nitrogen metal was calculated for the fcc structure. More recent calculations show that the bcc phase is more stable and that the 0-K isotherm for the bcc phase is shifted to about 10% lower volumes,[22] which does not affect this discussion. In Fig. 2 our data near $V/V_0 \simeq 0.25$ are in a density range in which theory suggests that monatomic metallic nitrogen may be metastable at 0 K. The high temperatures achieved in our dynamic experiments could be expected to drive the dissociation of $N_2$ at lower pressures and densities than required at 0 K.

The challenge of these data is that a model is required which simultaneously explains both the curvature in the Hugoniot, and the observation that $(\Delta P/\Delta E)_V < 0$ for $V/V_0 \simeq 0.3$. At present no such theory exists and we can only postulate phenomenological models based on what is known for nitrogen. By analogy with isoelectronic CO, the curvature in the nitrogen Hugoniot above 30 GPa is caused by molecular dissociation. At constant volume near $V/V_0 \simeq 0.32$, the concentration of $N_2$ molecules increases with increasing pressure above the Hugoniot because the temperature decreases in this direction. In the two-phase region a detailed theory is needed to determine whether the energy balance between dissociation energy, repulsive potential energies between the various interacting particles, and molecular vibration and rotation are sufficient to explain the data quantitatively, or whether additional phenomena, like electronic excitation and the large anisotropy of the $N_2$ repulsive potential, must be taken into account. The anisotropy in the *ab initio* $N_2$-$N_2$ repulsive potential varies by a factor of 100, depending on the angle at which two $N_2$ molecules approach each other,[6] and is about an order of magnitude larger than for $H_2$.[23] This large anisotropy could possibly inhibit a close-packed structure at high densities. Since the repulsive potential for nitrogen atoms is spherically symmetric, the fluid would be able to compress to a more closely packed phase as more molecules dissociate. In this case the softening of the Hugoniot could possibly be caused by both the absorption of dissociation energy, which is then not available for thermal pressure, and the higher compressibility of spherical nitrogen atoms relative to anisotropic $N_2$ molecules.

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