it is furthermore crucial to note that a distinct part of the nucleation driving force given by the change in Gibbs energy is already released by stable cluster formation (SOM section 2.6, fig. S14, and Fig. 2).

Prenucleation-stage cluster formation on the basis of equilibrium thermodynamics can be qualitatively shown also for the biominerals calcium phosphate and calcium oxalate (SOM section 2.7 and fig. S15) and suggests a similar nucleation mechanism for these minerals. The cluster-formation mechanism on the basis of equilibrium thermodynamics can be speculatively explained by entropic solvent effects. The probable release of water molecules from the hydration layer of ions caused by cluster formation may result in an increased number of degrees of freedom of the system. In classical nucleation theories, only enthalpic effects (interaction potentials) are taken into account, and entropic solvent effects are neglected. In the end, a pH-dependent change of ionic hydration layers may explain the pH dependency of cluster-formation thermodynamics.

References and Notes

Shock-Wave Exploration of the High-Pressure Phases of Carbon

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The high–energy density behavior of carbon, particularly in the vicinity of the melt boundary, is of broad scientific interest and of particular interest to those studying planetary astrophysics and inertial confinement fusion. Previous experimental data in the several hundred gigapascal pressure range, particularly near the melt boundary, have only been able to provide data with accuracy capable of qualitative comparison with theory. Here we present shock-wave experiments on carbon (using a magnetically driven flyer-plate technique with an order of magnitude improvement in accuracy) that enable quantitative comparison with theory. This work provides evidence for the existence of a diamond-bc8-liquid triple point on the melt boundary.

Consequently, understanding the melt properties of diamond at high pressures and densities achievable through compression by large-amplitude shock waves is paramount for designing capsules and drive-pressure pulse shapes that minimize the possibility of microstructural effects during the implosion phase of the capsule. Such effects could lead to heterogeneities that would seed instabilities capable of quenching the implosion (4).

Previous models for carbon based on the chemical picture framework have shown great variation in the diamond melt boundary (5–8). The melt boundary of diamond has also been explored within the framework of quantum calculations by Grumbach and Martin (9, 10) and Wang et al. (11). Both groups predicted a maximum in the melt curve for diamond near 500 GPa and ~8000 to 9000 K. More recently, Correa et al. (12) used ab initio molecular dynamics (AIMD) simulations to explore the phase diagram, considering both the diamond and bc8 solid phases. They also predicted a maximum in the diamond melt curve, in reasonable agreement with Grumbach and Martin (9). Furthermore, as can be seen in Fig. 1, Correa et al. (12) predicted the existence of a diamond-bc8-liquid triple point at ~850 GPa. Romero and Mattson (13) used AIMD methods to determine the Hugoniot of carbon, the locus of end states achievable through compression by large-amplitude shock waves (14), in the pure solid (diamond) and liquid phases, suggesting that the Hugoniot would enter the pure liquid phase at a pressure above the triple point.

Concurrently, the melt properties of diamond have been explored experimentally with the use of large laser facilities. Using the Omega laser, Bradley et al. (15) observed a rapid increase of reflectivity with shock velocity that reached saturation at ~1000 GPa. This saturation was interpreted as evidence for the completion of melt along the principal Hugoniot. More recently, groups from Japan (16), using the Gekko laser, and France (17), using the Laboratoire pour l’Utilisation des Lasers Intenses (ULLI) laser, obtained Hugoniots measurements in the pressure ranges of 500 to 2000 GPa and 600 to 1500 GPa, respectively.

The results from these studies largely agree within experimental uncertainty. However, to reach the required energy densities, the laser spot size was a few hundred microns, resulting in a restriction in the sample thickness of
~20 \mu m to ensure one-dimensional loading, which then resulted in experimental durations of <1 ns and uncertainty of the inferred pressure and density on the Hugoniot of ~5 to 10%. As illustrated in Fig. 2A, this accuracy is not adequate to provide quantitative comparison with theory. Whereas the experimental results obtained at LULI (17) suggest a substantial density increase upon melt (and thus a negative slope in the melt curve), its value is not well constrained because of the large experimental uncertainty. Thus, there is still a lack of understanding of the shock response of diamond in the vicinity of the melt boundary.

We present the results of magnetically accelerated flyer-plate experiments on diamond performed at the Sandia Z machine (18) over the pressure range of 550 to 1400 GPa. The relatively large lateral area of the flyer plates permitted simultaneous shock loading of multiple samples of several hundred micron thickness, comparable with those typical of gas-gun studies (19). Furthermore, the ability to precisely measure an impact velocity in such experiments placed substantial constraints on the particle velocity and thus on the inferred pressure and density. These aspects enabled roughly an order-of-magnitude improvement in accuracy as compared with previous work in this pressure range (16, 17), as illustrated in Fig. 2. Coupled with the reflectivity results of Bradley et al. (15) and a detailed AIMD study of the Hugoniot response of diamond, these experiments indicate the existence of a diamond-bc8-liquid triple point on the principal Hugoniot of diamond at ~875 GPa and ~6.6 g/cm$^3$ density.

AIMD calculations for carbon were performed using the Vienna ab initio simulation program, a plane-wave density functional theory code developed at the Technical University of Vienna (20–22). Initial calculations performed to determine the thermodynamic stability regions for the liquid, diamond, and bc8 phases were largely consistent with those reported by Correa et al. (12), as shown in Fig. 1 (23). This work focused primarily on the determination of the principal Hugoniot, in particular along the melt boundary.

The Rankine-Hugoniot jump conditions (14), which are derived by considering conservation of mass, momentum, and energy across a steady propagating shock wave, provide a set of equations relating the initial energy $E$, volume $V$, and pressure $P$, with steady-state, post-shock values

\[
(E - E_0) = P/2(V_0 - V)
\]

\[
P = \rho_0 U_s u_p
\]

\[
\rho = \rho_0 [U_s/(U_s - u_p)]
\]

where $\rho$, $U_s$, and $u_p$ denote the density, shock velocity, and particle velocity, respectively, and the subscript 0 denotes initial values ($P_0$ is taken to be zero) (24). The first of these equations, derived from the conservation of energy, provides a prescription for the calculation of the Hugoniot. For a given $P$, an initial estimate is made for the temperature ($T$), or $\rho$ that would satisfy Eq. 1. On the basis of the resulting AIMD calculation, corrections are made to $T$ or $\rho$, and the process is repeated. The resulting iteration converges rapidly and provides very accurate Hugoniot states within the framework of the AIMD.

The results of the Hugoniot calculations are shown in Fig. 1. The solid (diamond) Hugoniot is predicted to intersect the melt boundary at ~680 GPa, along the diamond-liquid coexistence curve. In contrast, the liquid Hugoniot is predicted to intersect the melt boundary at ~1040 GPa, along the bc8-liquid coexistence curve. For intermediate pressures, the Hugoniot is predicted to be on the melt boundary, inclusive of the proposed diamond-bc8-liquid triple point. This prediction of the triple point lying within the coexistence region of the Hugoniot raises an interesting question: Is there an experimental observable that could indicate the presence of the triple point along the principal Hugoniot? The answer lies in the compressibility and is directly related to the predicted anomalous diamond-liquid and normal bc8-liquid melt lines, respectively.

Calculations performed within the coexistence region, and in particular around the predicted triple point, are shown in Fig. 3, which illustrates the diamond-liquid and bc8-liquid coexistence regions in the vicinity of the triple point in $P$-$\rho$-$T$ space, along with projections in the $P$-$T$ and $P$-$\rho$ planes. The predicted Hugoniot is also plotted in this figure. Approaching the triple point from lower pressure, the Hugoniot lies along the diamond-liquid coexistence curve. An increase in pressure corresponds to an increase in the volume fraction of the liquid in the diamond-liquid composition. Because the diamond-liquid melt boundary is predicted to be anomalous in this region, the liquid has a higher $\rho$ than does the diamond-phase solid. This results in a more rapid increase in $\rho$ with $P$, as illustrated in Figs. 2 and 3. At a pressure just beyond the triple point, the composition of the Hugoniot state changes abruptly to a mixture of

Fig. 1. Phase diagram for high-energy density carbon. Solid gray line, phase boundaries from Correa et al. (12); dot-dashed gray line, diamond-liquid melt curve from Grumbach and Martin (9); dashed gray line, diamond-liquid melt curve from Wang et al. (11); solid blue line, predicted adiabat for Neptune (Uranus similar) (28); solid black line, AIMD Hugoniot from this work.

Fig. 2. Diamond $P$-$\rho$ Hugoniot: (A) previous data and (B) this work. Solid line, AIMD Hugoniot from this work; dashed line, AIMD metastable solid (diamond) and liquid Hugoniots from this work; yellow circles, Gekko laser (16); green triangles, LULI laser (17); blue square, Pavlovskii (29); red diamonds, this work.

Fig. 3. Coexistence regions and Hugoniot in $P$-$\rho$-$T$ space. The Hugoniot (black line) enters the diamond-liquid coexistence region (orange band) at ~680 GPa (6.02 g/cm$^3$), reaches the diamond-bc8-liquid triple point at ~850 GPa, and exits the bc8-liquid coexistence region (pink band) at ~1040 GPa (7.04 g/cm$^3$). The Hugoniot has two solutions at the proposed triple point: (i) a mixture of diamond and liquid (6.52 g/cm$^3$) and (ii) a mixture of bc8 and liquid (6.62 g/cm$^3$).
liquid and the bc8 phase of the solid. Again, an increase in $P$ corresponds to an increase in the volume fraction of the liquid. However, in this region the melt boundary is predicted to be normal, and thus the $P$ of the liquid is lower than that of the bc8 solid. As a result, $P$ increases less rapidly with $P$, and the Hugoniot increases in stiffness compared with the segment along the diamond-liquid coexistence, as illustrated in Figs. 2A and 3. In addition, a discontinuity is predicted in the Hugoniot at the triple point due to the fact that two solutions to Eq. 1 exist at the triple point: (i) a mixture of diamond and liquid and (ii) a mixture of bc8 and liquid.

Thus, the presence of the triple point within the coexistence region is manifest by the Hugoniot being broken into four distinct segments, each having a different compressibility. In contrast, the absence of the triple point would result in the Hugoniot being broken into three segments. As can be seen in Fig. 2A, the compressibility differences predicted by AIMD for the various segments of the diamond Hugoniot are substantial; the difference in $P$ between the metastable extensions of the solid and liquid over this pressure range is $>5\%$ on average. However, quantitative comparison with this prediction requires experimental Hugoniot data with greatly improved precision, with respect to previous work in this pressure range (16, 17).

A series of experiments on polycrystalline diamond were performed on the Z machine at Sandia National Laboratories, a pulsed power accelerator capable of producing extremely large current ($\sim20$ MA) and magnetic field densities ($\sim10$ MG) within a short-circuit, coaxial load geometry. These current and magnetic field densities result in substantial magnetic pressures (in excess of 400 GPa) produced over time scales of a few hundred nanoseconds. The resulting impulse is capable of propelling the outer anode plates of the coaxial load outward at high velocity. With proper shaping of the current pulse and design of the coaxial load geometry, macroscopic metal plates (several square centimeters in lateral area and several hundred microns in thickness) can be launched as flyer plates, to velocities approaching 35 km/s. Moreover, these plates are capable of being used in high-precision equation of state measurements at several hundred gigapascal pressures (23, 25).

A 17–40-mm copper flyer plate was magnetically accelerated to peak velocities between 13 and 24 km/s. The relatively large area of the flyer plate was exploited by impacting multiple diamond samples, as shown in Fig. 4A. Each experiment consisted of two quartz or sapphire windows bracketing three polycrystalline diamond samples, each of which were backed by quartz or sapphire windows. In all cases, at least two of the samples were microcrystalline diamonds, which were largely transparent; in some cases, the third sample was nanocrystalline diamond, which was completely opaque. The diamond samples, fabricated using chemical vapor deposition techniques, were nominally 6 mm square in lateral dimensions and 520, 750, and 950 µm in thickness. Actual thickness at the center of each sample was determined to within $\sim1$ to 2 µm from multiple measurements across the surface of the sample with the use of a through-the-lens laser auto focus instrument.

We used a velocity interferometer (26) to optically measure velocity via the Doppler shift of light reflecting from a moving surface. A total of 16 diagnostic channels were available for each experiment, enabling multiple, redundant diagnostic channels to be fielded at each sample location. The transparency of the microcrystalline diamond samples allowed for laser light to initially reflect from the copper flyer plate. In these cases, each data record consisted of the velocity of the copper flyer plate over its entire trajectory, enabling the velocity at impact to be determined with $\sim0.5\%$ (23). Also, on the same data record were clear fiducials of the flyer-plate impact with the diamond sample and subsequent transmission of the induced shock wave from the diamond sample into the quartz or sapphire window. This provided a highly accurate transit time through the sample, unaffected by any nonplanarity of impact. Transit times were on the order of 20 to 45 ns, with $\sim0.4$-ns resolution, enabling $U_s$ for each sample to be determined in the range of $\sim1$ to $2\%$ (23). In the case of the nanocrystalline samples, the impact time was interpolated from the observed impact time of the transparent samples on either side. This reliance on laterally displaced measurements to infer the transit time resulted in somewhat greater uncertainty in $U_s$ of $\sim2$ to $4\%$. Because each of the three diamond samples on a given panel was nearly identically loaded, weighted averaging (27) could be used to reduce the overall uncertainty in the measured $U_s$ to $\sim1\%$ or less for most experiments.

Equations 1 to 3 could then be used to determine $P$ and $U_s$ of the diamond in the shocked state, as shown graphically in Fig. 4B. A linear $U_s-U_p$ response for copper, obtained from experimental data, provides a quadratic relation for the $P-u_p$ response of copper (23). Given Eq. 2, $P$ in the shocked state of the diamond is constrained to lie along a chord with slope given by $\rho_dU_d$. The intersection of these two curves provides $P$ and $u_p$ in the shocked state. In this way, $u_p$ was determined to better than $1\%$ in all cases. Given $U_s$ and $u_p$ for diamond, $P$ could then be inferred through the use of Eq. 3. Propagation of uncertainties in $U_s$ and $u_p$ resulted in uncer-
We again employed a two-step fitting process to determine the most probable breakpoint locations and segment slopes while enforcing continuity of \( U \) (23). The AIMD calculations suggest a discontinuity in \( U'\) at the triple point (Fig. 5), with an abrupt drop in \( U \). However, the magnitude of this drop is <1%. It is not clear that the present data exhibit the necessary accuracy to warrant this level of sophistication. Furthermore, because of the anomalous and normal diamond-liquid and bcc-liquid melt boundary regions, respectively, the discontinuity in \( U'\) must be negative; treating the triple point as continuous avoids any unphysical results for the four-segment fit in which a positive discontinuity in \( U'\) occurs.

The resulting four-segment piecewise-linear fit is shown as a red line in Fig. 5B. As can be seen in the figure, substantial slope changes still occur at pressures near ~700 and ~875 GPa. In particular, the inclusion of a fourth segment only influences the fit above ~875 GPa through an additional subtle slope change at a pressure of ~1060 GPa, but otherwise it is quite similar to the three-segment fit. However, this scenario provides a way to reconcile the present results with those of Bradley et al. (15). The four-segment fit and the Bradley results would suggest the onset and completion of melt at ~700 and ~1060 GPa, respectively. Furthermore, the present results would indicate a substantial slope change within the coexistence region at ~875 GPa, commensurate with the presence of a triple point. Because of the discontinuity in \( U'\) at the triple point, the present data can only constrain the location of the proposed triple point between ~850 to 880 GPa; this corresponds to the pressure range between data points that encompasses the location of the second breakpoint.

Thus, the following picture emerges. The first slope change (at \( P \) and \( \rho \) of 699 GPa and 6.08 g/cm^3, respectively) corresponds to the onset of melt from the diamond phase. The second slope change (at \( P \) and \( \rho \) between ~850 to 880 GPa and ~6.53 to 6.67 g/cm^3, respectively) corresponds to a triple point along the solid-melt boundary. The third slope change (at \( P \) and \( \rho \) of 1064 GPa and 7.01 g/cm^3, respectively), coincident with the saturation of reflectivity observed by Bradley et al. (15), corresponds to the completion of melt from a solid phase other than diamond.

These values correlate well with the predicted AIMD values for the triple point at \( P \) and \( \rho \) of 850 GPa and 6.52 to 6.62 g/cm^3, respectively, and are also in quite good agreement with the AIMD predictions of the onset and completion of melt at ~680 GPa and ~1040 GPa, respectively. Also, the magnitudes of the slopes of the four-segment fit are in quite good agreement with those obtained from the AIMD calculations, as illustrated in Fig. 5A. This level of agreement provides a high-fidelity experimental validation of AIMD methods in prediction of the carbon response at these high-energy density conditions, and it also provides evidence for a diamond-bcc-liquid triple point.

References and Notes
10. M. P. Grumbach and R. M. Martin also discussed the bcc melt line. However, the temperature and \( dT/dP \) were estimated from the Lindemann melt criterion and observations regarding the pressure change observed for the melting of the simple cubic structure, respectively. Ab initio methods were not used in the bcc melt line determination.
23. Materials and methods are available as supporting material on Science Online.
24. Longitudinal stress, \( \sigma_{L} \), should be used for shock states that remain in the solid phase, as it is possible that the solid state can support shear stresses such that \( P > \sigma_{L} \), however, the majority of the data presented here is either in the coexistence region or the pure fluid, in which case the shocked state is expected to be hydrostatic.
30. We would like to acknowledge the crew of the Sandia Z facility for their contributions in the design, fabrication, and assembly of the experiments, as well as the fielding of diagnostics. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy’s National Nuclear Security Administration under contract no. DE-AC04-94AL85000.

Supporting Online Material
www.sciencemag.org/cgi/content/full/322/5909/1822/DC1
Materials and Methods
Figs. 51 to 56
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25 March 2008; accepted 17 November 2008
10.1126/science.1156278

www.sciencemag.org SCIENCE VOL 322 19 DECEMBER 2008 1825

Downloaded from http://science.sciencemag.org/ on July 21, 2017
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Science 322 (5909), 1822-1825.
DOI: 10.1126/science.1165278