Structure measurements of compressed liquid boron at megabar pressures

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Abstract. We report on the first measurements of the structure of compressed liquid boron, as it crosses the melt line in dynamic shock-compression experiments at a pressure of 100 GPa. Temporally, spectrally and angularly resolving x-ray scattering provides an independent and accurate measurement of the compression factor 1.5 and the electron density of $4 \times 10^{23} \text{ cm}^{-3}$ at moderate temperatures of 0.2–1 eV. At these conditions, the elastic scattering measurements provide the structure factor and indicate the liquid compressed phase with a coordination number of 8.3 in good agreement with predictions from first-principles molecular dynamic simulations.

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1. Introduction

Boron is suitable for many applications due to its unique physical properties. Examples are from igniters of airbags to semiconductor and electronic components. Crystalline boron is very hard \[1\] at normal temperature and becomes a superconductor at high pressure \[2\]. Recent studies have also shown that iron-doped \(\beta\)-boron is a p-type semiconductor with enhanced electrical conductivity and without significantly increased thermal conductivity. Also, because of its high neutron capture cross section, \(^{10}\)B is used to line walls of nuclear reactors and is attractive in medical applications such as boron capture therapy. In spite of its numerous applications the microscopic physical properties of boron remain largely unknown. While recent studies have made substantial progress investigating the stability of \(\alpha\)–\(\beta\)-boron at low temperatures and pressures, few experiments have investigated the high-pressure phase diagram of boron. Previous work on the phase diagram of boron have been carried out on synchrotrons using a diamond anvil cell to compress the sample using either x-ray diffraction \[3–8\] or x-ray Thomson scattering \[9\] to probe the boron. These studies are limited in the pressure–temperature phase space either to low temperature–high pressure or high temperature–low pressure due to the experimental difficulty of reaching this state. A high power laser can drive a strong shock reaching the high temperature–high pressure state.

In this paper, the first structure study of boron in the high pressure–high temperature parameter space is presented. We report on a dynamic shock compression experiment that shows a transition to liquid compressed from \(\beta\)-boron produced by a nanosecond-long energetic laser. This work is the first study of the boron Hugoniot using x-ray radiography combined with a study of the structure with x-ray Thomson scattering. The boron structure has been obtained from multi-angle x-ray Thomson scattering data. Hugoniot data were inferred from x-ray radiography data, and were compared to the molecular-dynamic (MD) calculations. Both the Hugoniot and structure data are in good agreement with MD calculations of the liquid compressed \(\beta\)-boron.

2. Experiment

We have probed the dynamically compressed state with short pulse laser-produced K-\(\alpha\) radiation using angularly, temporally and spectrally resolved x-ray Thomson scattering measurements \[10–13\]. The experiment was performed at the Titan laser facility at the Lawrence Livermore National Laboratory. The facility combines energetic long pulse lasers for shock compression with short pulse laser beams for probing with high brightness x-ray or particle beams. A high-energy beam with pulses of 5–10 ns duration with an intensity of 4–7 TW cm\(^{-2}\)
has been utilized to shock-compress solid density 170 \( \mu \)m thick boron. The beam delivered a total energy of 400 J at a laser wavelength of 527 nm that has been focused onto the target with a homogeneous intensity distribution over a diameter of 700 \( \mu \)m by means of a continuous phase plate. This configuration was employed to launch a planar shock front into the target.

Five to eight keV probing x-ray flashes were produced with a short pulse laser beam that has been configured to deliver 270 J in 80 ps at a wavelength of 1.053 \( \mu \)m. The beam was focused with an \( f/3 \) off-axis parabola on vanadium or copper foils. The interaction of a high-intensity laser, above \( 10^{16} \) W cm\(^{-2}\), produces hot electrons that produce inner-shell vacancies in cold atoms, leading to intense K-\( \alpha \) fluorescence x-rays. These serve as a high-energy x-ray probe which penetrates through dense shock-compressed matter. These K-\( \alpha \) x-rays are emitted in a short burst lasting approximately for the duration of the laser pulse, i.e. about 80 ps [14]. This capability allows probing the evolution of dynamically compressed state up to the moment when the shock has traversed the boron foil. Simulations indicate homogeneous high-density conditions shortly before the material begins to disassemble. The probe x-rays provided a point projection 18 times magnified radiograph of the compressed boron onto an imaging plate detector (Fuji BAS-MS2025), or were dispersed by a cylindrically bent 70 \( \times \) 25 mm large graphite highly oriented pyrolitic graphite crystal and focused and spectrally dispersed in a Van Hamos geometry onto an imaging plate detector.

3. Results

Figure 1 compares the Hugoniot curves calculated from MD simulations and two experimental points where the x-ray radiography data have been taken.
Figure 2. X-ray Thomson scattering for various scattering angles at pressures of 105 GPa. The data correspond to scattering vectors $k = 1.3, 2.0, 2.6$ and $2.8 \, \text{Å}^{-1}$, from smallest to largest scattering angle. The strong increase in elastic (Rayleigh) scattering at zero x-ray energy compared to the inelastic scattering at $-40 \, \text{eV}$ is clearly visible in the shock-compressed boron.

In our work, we emphasized the region between the solid and the liquid Hugoniot, where the phase transition is expected to happen. The x-ray radiography data [15–17] provide a spatially and temporally resolved measurement of the density of the compressed boron and hence the trajectory of the shock front. From the density and shock velocity obtained, shock pressure was inferred through the Rankine–Hugoniot equations. The main source of error of this measurement is the exact knowledge of the entire spectrum of the backlighter. Indeed, energies between 6.4 and 20 keV contribute significantly to the total contrast of the image. To constrain the spectrum, we used silver step filters on the side of the detector as well as a CCD working in the single hit regime, resulting in an error of $\pm 20\%$ of the mass density. The shock front position is known to better accuracy limited only by the spatial resolution and temporal blurring of the K-\(\alpha\), leading to an error bar of $\pm 10\%$ for the pressure. The principal Hugoniot for compressed liquid boron was calculated with MD simulations within the generalized gradient approximation of density functional theory and the Born–Oppenheimer approximation. The simulations were performed with the planewave based code Qbox, with an energy cutoff at 475 eV and a Toullier–Martins pseudopotential. The initial condition of the simulation of uncompressed boron is the ideal $\beta$-boron structure [18] with 105 atoms per unit cell at 300 K. In addition we started simulations for liquid boron at higher densities and temperatures and compared with solid boron. The resulting internal energy and pressure were used to determine points at which the Rankine–Hugoniot conditions were fulfilled.

Figure 2 shows the scattering spectra for shocked boron at various scattering angles. The data have been measured at laser drives of $4 \, \text{TW cm}^2$ at $\rho = 3.4 \, \text{g cm}^{-3}$, 120 GPa. Shocked boron shows remarkably different scattering amplitudes when compared to boron at ambient conditions indicating that the material has undergone structural changes. Although in this study we are mainly concerned with the absolute intensities of the elastic scattering signal, we note
that the inelastic energy shift of 40 eV at $\theta = 31^\circ$ indicates an electron density of $4 \times 10^{23} \text{cm}^{-3}$ ($\pm 10\%$) from the dispersion relation for electron plasma waves, i.e. plasmons [11]. With an ionization state of 2.3, we find a mass density of $3.2 \pm 0.35 \text{g cm}^{-3}$ consistent with the results from radiography [15]. In the x-ray scattering process, distinct elastic and inelastic scattering features are resolved [11]. For interactions with free or delocalized electrons the incident x-ray photon with frequency $\omega$ is large enough to give a significant Compton shift to the frequency of the scattered radiation. During the scattering process, the incident photons transfer the momentum $p = \hbar k / 2\pi$, and the energy $E = (\hbar k / 2\pi)^2 / 2m_e$, to the electrons. Momentum and energy is primarily transferred to the free and delocalized electrons whose binding energy is less than the energy $(\hbar k / 2\pi)^2 / 2m_e$.

The elastic scattering signal primarily arises from scattering off bound electrons with ionization energies larger than $(\hbar k / 2\pi)^2 / 2m_e$. These are states deep in the Fermi sphere that cannot be excited, and energy is not transferred during the scattering process [11]. The total scattering spectrum is described by the dynamic structure factor:

$$S(k, \omega) = \left| f(k) + q(k) \right|^2 S_{ii}(k) \delta(\omega) + Z_l S_{\text{ee}}(k, \omega) + Z_C \int S_{\text{CE}}(k, \omega - \omega') S_S(k, \omega') d\omega'.$$  

The first term in equation (1) accounts for the density correlations of electrons that dynamically follow the ion motion. This includes both the bound electrons, represented by the ion form factor $f(k)$, and the screening cloud of free and (valence) electrons that surround the ion, represented by $q(k)$. $S_{ii}(k)$ is the ion–ion density correlation function. The second term in equation (1) gives the contribution in the scattering from the free electrons that do not follow the ion motion. Here, $S_{\text{ee}}(k)$ is the high frequency part of the electron–electron correlation function and it reduces to the usual electron feature in the case of an optical probe. Inelastic scattering
Figure 4. The ion–ion structure factor $S_{ii}(k)$ from MD: (a) boron at initial density and room temperature, (b) boron in liquid phase at initial density, (c) compressed boron at $3.4 \text{ g cm}^{-3}$ in liquid phase and (d) compressed boron in solid phase at $3.4 \text{ g cm}^{-3}$.

by bound electrons is included in the last term of equation (1), which arises from bound–free transitions to the continuum of core electrons within an ion, $S_{ce}(k)$, modulated by the self-motion of the ions, represented by $S_s(k)$.

The elastic scattering intensity is sensitive to $f(k)$, which denotes the atomic form factor for scattering from tightly bound electrons. The screening function $q(k)$ represents the screening cloud of free and valence electrons that shield the ionic potential in the Debye sphere [19]. Important for comparisons with MD simulations, the x-ray scattering spectra allow us to determine the scattering amplitudes in absolute units. The center of gravity of the inelastic (plasmon) resonance, exactly known via the f-sum rule

$$Z_f \int d\omega \omega S_{ee}(k, \omega) = \left(-\frac{\hbar k}{2\pi}\right)^2/2m_e$$

has been exploited to calibrate the Thomson scattering spectrum.

By fitting the plasmon feature, the absolute intensity of the Rayleigh scattering feature $W_R(k) = [f(k) + q(k)]^2 S_{ii}(k)$ follows directly from the measured integrated scattering amplitude of the elastic peak. This term has been further analyzed; in our conditions only the
$k$-shell electrons contribute to the form factor $f(k)$. It has been calculated with hydrogenic wave functions and appropriate screening parameters [20], in our conditions $f(k)$ is the dominating term. The screening cloud $q(k)$ has been calculated using equation (41) in [21], which expresses $q(k)$ in general terms of the electron response function for the interacting electron gas. We use a theoretical approximation for $q(k)$ that is based on local field corrections, the latter being known via the plasmon dispersion measurement [22]. This results in a total error of $q(k)$ of 10%, resulting in a total error of 20% for $S_{ii}$.

Figure 3 shows the experimentally inferred ion–ion structure as a function of $k$ for a range of scattering vectors of $k = 1.3 \, \text{Å}^{-1}$ till $4.3 \, \text{Å}^{-1}$. The form factor function $f(k)$ (black curve), which is theoretically well known is the dominant term and remains almost flat over the range of $k$ studied in this experiment. The screening cloud function $q(k)$ (red curve) is theoretically most uncertain but its contribution decreases sharply as a function of $k$, having a lower impact, for longer $k$ only, on the error of the ion–ion structure determination.

4. Discussion and conclusion

Figure 4 shows the calculated structure factor from first principles MD simulations in four different states of boron: solid boron, compressed solid boron, liquid and compressed liquid boron. Experimental points of $S_{ii}$ at 105 GPa and a density of $3.4 \, \text{g cm}^{-3}$ are overlaid, in figure 4(c). Experimental data and MD simulations are in excellent agreement, as the pressure versus density point on the Hugoniot curve lies at the boundary of the solid/liquid phase (see figure 1). The ion structure factor confirms that the compressed boron is indeed in a liquid phase. So when the density increases from 2.4 to $3.4 \, \text{g cm}^{-3}$, the main peak shifts to higher $k$ due to a shortening of the bound length under pressure [7]. Going from solid to liquid (figure 4(a)–(d)) by increasing the temperature from 300 to 2500 K results in a smoothing of the structure factor due to the gradual loss of bounding and randomization of the position of boron atoms in the liquid phase. Structure factors obtained by Price et al [9] in the liquid state at ambient density...
have revealed the presence of two peaks. The first peak is typical of glasses semi-conductor or liquid. As the density of the liquid boron increases both peaks are shifting to higher value of $k$.

From the the MD pair correlation function, the ion structure factor, is calculated through the usual Fourier transform, shown in figure 5. The average coordination number is calculated by integrating the area under the first peak of the pair correlation function. Previous studies of liquid boron [9] at 2400 K and 2.4 g cm$^{-3}$ resulted in a coordination number of 6.0. As the density increases from 2.4 to 3.4 g cm$^{-3}$, the coordination number increases from 6.0 to 8.3, indicating a coalescence of the second shell of atoms into the first one as the density increases. Similar behavior was observed in solid compressed boron [3], a continuous phase transition to a metallic phase, with an increase of the coordination number from 6 to 12.

In conclusion, our new measurements have given us insight into the behavior of compressed boron in the liquid phase. The data shown carry information on the evolution of the crystal lattice through a phase transition and compression. We have observed an increase in coordination number with density. Our work provides a missing point in the picture of compressed boron, at high temperature and pressure. The properties of the liquid compressed phase of boron seem to follow the properties of solid compressed boron, a continous increase in the coordination number with density due to the flexibility of the icosahedra structure. In addition, this work provides an excellent benchmark for MD first-principles calculations of compressed boron. The initial state of boron can be described by a $\beta$-boron phase. Being aware of the long-lasting controversy on the initial state of boron this is by itself a precious information. Secondly, the Hugoniot curves independently calculated are in good agreement (figure 1) with the density-pressure point obtained from the x-ray radiography. Finally the ion–ion structure factor in the liquid phase and its agreement to the experimental points suggest that this technique is a powerful one to diagnose phase transitions in shock compressed matter.

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