Different Mechanisms of Phase Transformation for Boron in Equilibrium and Under Shock Indicated by Equation-of-State Comparisons

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Boron is a prototype for low-*Z* and superhard materials and a candidate for making ablators for high-energy-density and inertial confinement fusion experiments. Clarifying the structure, stability relation, and melting of the various boron polymorphs at high pressure has long been a subject of interest in materials sciences. Density functional theory (DFT) calculations and diamond-anvil cell (DAC) experiments[1–3] were performed at pressures up to ~200 GPa. Based on these, equilibrium phase diagrams of boron were constructed, which showed high melting temperatures (>4500 K) and a nonicosahedral, metallic α-Ga phase at above 80 to 90 GPa. Dynamic compression experiments were conducted on boron up to 5608 GPa, which measured the pressure–density equation of state (EOS),[4,5] diffraction and electrical conductivity,[6,7] or liquid structure factor[8] along the shock Hugoniot.

In this work, we use first-principles molecular dynamics (MD) to calculate the EOS and shock Hugoniot of various boron phases (α-B_{12}, β, γ-B_{28}, α-Ga, and liquid using different cell shapes), following similar procedures as in Ref. 5. We use a 2000-eV plane-wave basis cutoff, Γ point for Brillouin zone sampling, and simulation cells with 96 to 144 atoms, and generate canonical (*NVT*) ensembles that consist of 5000 to 10,000 snapshots in each MD simulation.

Our results show that if phase transitions occur in shock-compressed boron at the same pressure–temperature conditions as those expected based on the equilibrium phase diagram, the Hugoniot would have two major discontinuities at 15 and 80 GPa, respectively (Fig. 1). Moreover, melting along the Hugoniot occurs at 1500 to 3500 K and 150 to 250 GPa unless some unknown structure stabilizes over α-Ga at 100 GPa and 2000 K. Discontinuities in Hugoniot density are also expected but are clearly not observed according to the experimental data. Instead, the experimental data appear smooth and follow the trend of our predicted Hugoniot for the α-B_{12} and β-B_{106} phases at up to 80 GPa and follow that of α-B_{12} as well as γ-B_{28} and probably also β-B_{106}, but definitely not α-Ga, at 80 to 112 GPa. These indicate that, instead of transforming into the γ-B_{28} phase, boron under shock compression may remain in the same β or α-B_{12} phase as its initial state up to at least 80 GPa.

In addition, our simulations show that γ-B_{28} melts when temperature increases from 1400 to 1500 K. Therefore, the transformation to γ-B_{28}, if occurring above 80 GPa, would be associated with a jump in temperature and immediately followed by melting or transformation into some other solid structures. Moreover, our DFT-MD simulations show that β-B_{106} remains stable at ~115 GPa and 600 K, and large atomistic displacement or structural instability occurs when temperature exceeds 800 to 1000 K or pressure exceeds 130 GPa. We also find that α-B_{12} remains stable at ~133 GPa and instability occurs at above 150 GPa, for 1000 K or lower temperatures. These data set the upper bounds for β-B_{106} or α-B_{12} samples to remain stable when boron is shocked to above 80 GPa. With stronger shocks above 200 GPa and 3500 K, liquid boron is obtained. Temperatures along the shock Hugoniot are increasingly higher than cold compression along an ambient-temperature isotherm. The transformation kinetics is therefore expected to be slower in room-temperature, static-compression experiments.

Our findings on the phase transitions in shocked boron based on the EOS point of view are supported remarkably well by DAC[9] and explosive-shock[7] experiments with diffraction, which found that β-boron was the stable structure up to ~100 GPa, at which amorphization occurred. It is interesting to note that the Hugoniot temperature of β-B_{106} at 90 GPa is ~600 K according

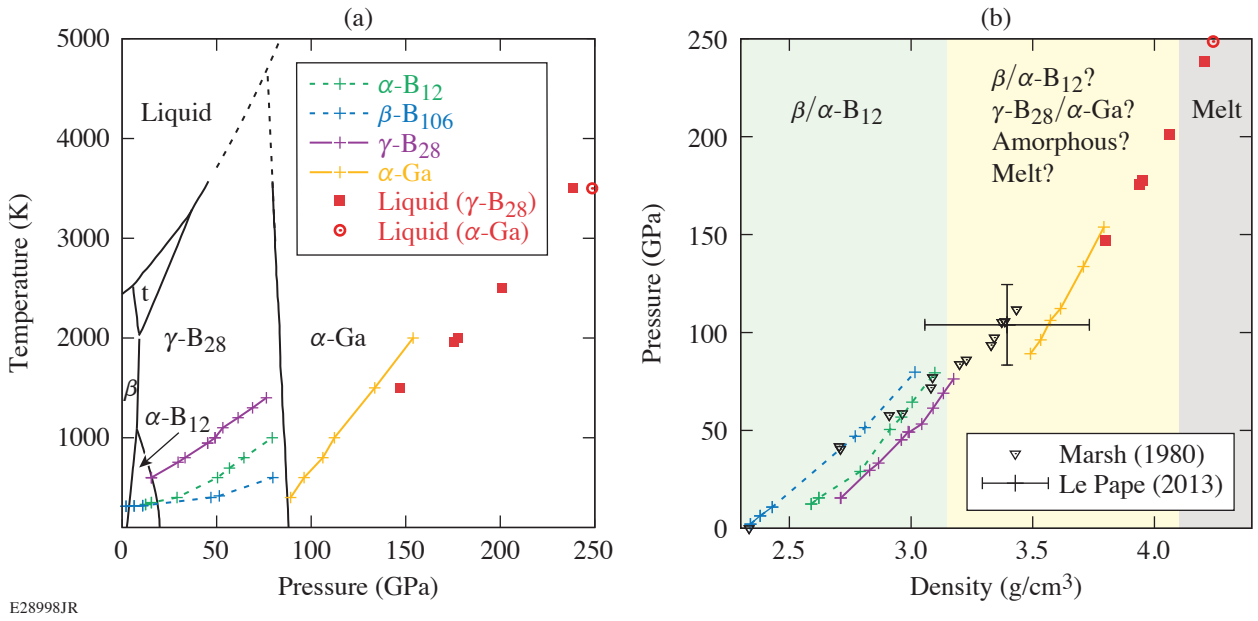

Figure 1
Our first-principles Hugoniots of various boron phases plotted in (a) an equilibrium phase diagram[1,2] and (b) a pressure–density plot in comparison with experimental data.[4,8] The dashed colored curves are expected Hugoniot profiles of β and α-B_{12} phases if the sample is shocked to the corresponding pressures but does not transform to other phases. The lines are guides to the eyes. We approximately divide the Hugoniot into three sections: structure at below ~90 GPa is likely α-B_{12} or β, above ~200 GPa is melt, and between 90 and 200 GPa is uncertain.

to our calculations. The absence of γ-B_{28} or α-Ga phases in the shock experiments, together with findings in laser-heated DAC experiments[10] that heating to ~2000 K is required to make γ-B_{28} or α-Ga phases out of β boron, suggests an energy barrier of 0.05 to 0.17 eV between β and γ/α-Ga phases. The observed amorphization in experiments[7,9] is likely a joint product of the energy barrier that slows down the process of phase transformation and the decreased stability of β boron at megabar pressures.

Our results strongly indicate differences in the mechanisms of phase transitions in equilibrium and under shock and raise questions about kinetics or nonequilibrium processes that materials may undergo during the time scale of the pressure loading.

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