Systematics of compression of hard materials

W J Nellis
Department of Physics, Harvard University,
Cambridge MA 02138, USA

E-mail: nellis@physics.harvard.edu

Abstract. Hard materials have the remarkable property that relatively little internal energy of shock compression is deposited as temperature and associated thermal pressure. As a result, the Hugoniot curve is nearly coincident with the 0-K isotherm. Since the isentrope is intermediate between isotherm and Hugoniot, all three curves of a given hard material are nearly coincident. Published data for diamond and Gd₃Ga₅O₁₂ (GGG) show this to be the case up to 600 GPa and 80 GPa, respectively. Above 100 GPa on the Hugoniot the incompressibilities, defined to be the derivative of pressure with respect to compression, of GGG, other oxides and even CaF₂ are significantly greater than that of diamond. In fact, above 100 GPa CaF₂ might well be the least compressible of any known material. Little EOS data of weakly compressible materials have been measured in a diamond anvil cell (DAC) above a few tens of GPa at 300 K because these materials often become amorphous, which means density in a DAC cannot be measured by X-ray diffraction. Amorphization suggests the onset of a sluggish phase transition. On the other hand, Hugoniot experiments readily measure density changes caused by compression and phase transitions independent of material structure. Hugoniots of weakly compressible materials suggest experiments to determine structures and compressibilities in laser-heated DACs at 100 GPa pressures, as has been done with TiO₂ and perovskite, and Hugoniot data might provide estimates of compressions of oxides representative of the deep interiors of rocky planets in other solar systems.

1. Introduction
Hard materials, also known as weakly compressible, incompressible, or strong materials, are interesting at high dynamic pressures because of phase transitions [1], to obtain estimates of densities of representative oxides in deep interiors of Earth and rocky exoplanets discovered recently [2], and for possible uses as anvils to achieve high static pressures. In dynamic high-pressure experiments hard materials are also useful as anvils between which a shock wave reverberates in a compressible liquid to achieve novel states of dense matter, such as metallic fluid hydrogen [3]. This quasi-isentropic compression process enables studies of the condensed matter physics of unusually dense states, mimics conditions in the deep interiors of giant fluid planets in this and in other solar systems, and is a possible synthesis route to metastable hydrogenous materials [3]. In order to measure properties of quasi-isentropically compressed fluids, anvils are needed whose equations of state are known on and off the Hugoniot, as well as anvils that remain optically transparent to measure temperature radiatively and remain electrically insulating to measure electrical conductivities of fluids by inserting electrodes through an anvil used in a shock reverberation experiment.
Many hard materials undergo phase transitions at shock pressures in the 100 GPa range. Many of these transitions are observed as relatively sharp and substantial increases in the incompressibility $\kappa$ defined as the derivative of pressure $P$ with respect to compression $\eta = \rho / \rho_0$ on the Hugoniot, $\kappa = (dP / d\eta)_H$, where $\rho$ and $\rho_0$ are the final and initial mass densities of compression. The structures of these virtually incompressible phases are not known from Hugoniot experiments. Because Hugoniot temperatures are normally significant, it is possible that these incompressible phases are a signature of melting to a highly coordinated fluid. On the other hand, shock-induced temperatures and associated thermal pressures are relatively low in incompressible materials. Thus, the sharp increases in incompressibility might be caused by collapse to solid phases with higher coordination. Since pressures and temperatures of these phases can be reached in a laser-heated DAC, structures above 100 GPa might be determined by X-ray diffraction in a DAC.

The purpose of this paper is to point out that Hugoniots of several incompressible materials above 100 GPa have already been measured, that their Hugoniots are nearly coincident with their isotherms, and that it would be useful to measure their optical and electrical properties and their off-Hugoniot equations of state (EOS) under dynamic compression. Hugoniots of hard materials also suggest experiments to be performed in a diamond anvil cell (DAC) because comparable pressures, densities, and temperatures in hard materials can be achieved by both static and shock compression.

2. General Considerations

The internal energies deposited at high pressures by adiabatic Hugoniot and isentropic compression and by isothermal compression at 0 K are given by:

$$E_H(V,T) - E_0 = \left(P_H(V,T) / 2\right)(V_0 - V)$$

(1)

$$E_S(V,T) - E_0 = - \frac{V}{V_0} \int_{V_0}^V P_S(V) dV$$

(2)

$$E(V,T = 0K) - E_0 = E_0(V) = - \int_{V_0}^V P_0(V) dV$$

(3)

where $E_H(V,T)$, $E_S(V,T)$, and $E_0(V)$ are the internal energies on the Hugoniot, isentrope, and 0-K isotherm, respectively, $E_0 = E_0(V_0)$ is the internal energy of the initial state, $P_H(V,T)$, $P_S(V,T)$, and $P_0(V)$ are the pressures on the Hugoniot, isentrope, and 0-K isotherm, respectively, $V = \rho^{-1}$ is the final specific volume and $V_0 = \rho_0^{-1}$ is the initial specific volume of each compression.

For strong materials such as diamond and sapphire, $u_s = C + Su_p$, where $u_s$ is shock velocity, $u_p$ is particle velocity, $C = 10 km / s$ and $S = 1$. Thus, $P_H = (\rho_0 C)^2 (V_0 - V)$ up to ~100 GPa plus small nonlinear contributions caused by higher order terms in $(V_0 - V)$. If pressure is linear in $(V_0 - V)$, then $P_H = P_S = P_0$ [3]. This is true because thermal pressures are so small in dynamically compressed hard materials. As an example, the compression of diamond measured by Pavlovskii under shock compression up to 600 GPa [4], measured by Occelli et al under static compression up to 140 GPa at 300 K [5], and the calculated 0-K isotherm of Kunc et al [6] are illustrated in figure 1.

The Hugoniot of diamond suggests that diamond does not undergo a first-order phase transition up to a shock pressure of 600 GPa. The value of its slope $S = 1$ is anomalously small. Most materials have values of $S$ in the range 1.1 to 1.8. Most oxides are relatively incompressible at lower shock pressures, as indicated by their large velocity of sound at ambient and a large Hugoniot Elastic Limit.
Figure 1. Measured Hugoniot (solid curve [4]) and 300-K isotherm (open circles [5]) and calculated 0-K isotherm (dotted curve [6]) of diamond. The isentrope (not shown) is intermediate between Hugoniot and isotherm. Cold compression dominates equation of state of diamond along its Hugoniot up to 600 GPa.

(HEL). Gd$_3$Ga$_5$O$_{12}$ (GGG), for example, has an HEL of $\sigma_{HEL} = 30$ GPa. Between 65 and 120 GPa, $S = 0.66$, which suggests a sluggish phase transition in this range of shock pressures. This sluggish phase transition is probably one to an amorphous phase, as observed in DAC measurements between 74 and 84 GPa [7]. In this regime, shock pressures are only a few percent greater than static ones. That is, the Hugoniot and isotherm of GGG are nearly coincident up to the highest pressure at which both have been measured. Above 120 GPa $S = 2.1$, which indicates completion of the transition and collapse to an essentially incompressible phase in the range 120 to 260 GPa [1].

In GGG $S = 2.1$ above 120 GPa, and $\kappa$ is much larger than that of diamond with $S = 1$. It takes significantly more pressure to compress GGG a given amount than is required to compress diamond the same amount. For GGG at 250 GPa $\kappa = 2.4$ TPa, while for diamond $\kappa = 0.89$ TPa [1]. However, Hugoniot data provide no information on structure.

Sapphire, single-crystal Al$_2$O$_3$, has slope $S = 0.96$ up to 340 GPa [8] and diffusive phase transitions near ~1500 K and 150 GPa [9]. The small slope of GGG in the region of its sluggish phase transition suggests that the small slopes of sapphire and diamond are also caused by continuous transitions toward increasing disorder with increasing shock pressure. The 300-K isotherm of ruby up to ~100 GPa [10] agrees with the Hugoniot of sapphire within the error bars. Ruby is Al$_2$O$_3$, doped with ~0.5 %Cr. Thus, thermal pressures in shock-compressed sapphire are small.

The observation of an incompressible phase of GGG at high pressures prompted a search of the literature to see if other incompressible phases have been observed previously. Hugoniot data of Al$_2$O$_3$ [8,11], CaTiO$_3$ perovskite [12], GGG [1], and CaF$_2$ [13] are shown in figure 2. Shock pressure of sapphire is nearly linear with compression up to 340 GPa. In contrast CaTiO$_3$ perovskite and cubic Gd$_3$Ga$_5$O$_{12}$ undergo sluggish phase transitions near 100 GPa. At higher pressures both oxides collapse to a virtually incompressible phase.

The CaF$_2$ Hugoniot data of Altshuler et al [13] obey $u_s = C + S u_p$, and are quite remarkable. Below 100 GPa $S = 1.00$ and above 100 GPa $S = 2.23$. At lower shock pressures fluorite undergoes a sluggish continuous transition in a relatively compressible phase. Once the phase transition completes at 100 GPa, CaF$_2$ is essentially incompressible at higher pressures. Under compression in a DAC at 300 K, CaF$_2$ transforms at 9.5 GPa with an ~11% volume change to an orthorhombic PbCl$_2$-type structure, which is 9-coordinated [14]. Thus, shock-compressed CaF$_2$ is expected to be relatively compressible in a disordered PbCl$_2$-type phase in the range 10 to 100 GPa. Above a shock pressure of 100 GPa, CaF$_2$ is essentially incompressible, which suggests the high-pressure phase has a coordination of 11 or 12. It is remarkable that above 100 GPa CaF$_2$, which is relatively weak at ambient and contains no C or O might be the most incompressible material known, including...
Figure 2. Shock pressure versus compression: \( \text{Al}_2\text{O}_3 \) (solid triangles [8], open triangles [11]), GGG (xs [1]), \( \text{CaTiO}_3 \) (dots [12]), and \( \text{CaF}_2 \) (open circles [13]).

Figure 3. Measured Hugoniots and isotherm of \( \text{TiO}_2 \) plotted as pressure versus compression. Uppermost curve is [15], middle curve is [13] dotted curve is 300-K isotherm after pulsed heating at arrow [16].

Measured Hugoniots of \( \text{TiO}_2 \) [13,15] are plotted in figure 3. In the range of shock compressions from 1.2 to 1.5 \( \text{TiO}_2 \) undergoes a sluggish continuous phase transition similar to that in \( \text{Gd}_3\text{Ga}_5\text{O}_{12} \). Above a shock pressure of ∼100 GPa, \( S = 2.21 \) and \( \text{TiO}_2 \) is virtually incompressible. \( \text{TiO}_2 \) has also been compressed in a DAC up to 80 GPa. The sluggish phase transition in a DAC is observed as continuous amorphization until \( \text{TiO}_2 \) eventually becomes too amorphous to determine volume with X-ray diffraction, as for \( \text{Gd}_3\text{Ga}_5\text{O}_{12} \) [7]. At this point Dubrovinsky et al laser-heated amorphous \( \text{TiO}_2 \) above 1100 K and thermally quenched it under pressure to a \( \text{PbCl}_2 \)-type orthorhombic structure that is 9-coordinated [16]. As for \( \text{CaF}_2 \), \( \text{TiO}_2 \) might also transform to a 11 or 12 coordinated phase above 100 GPa, as suggested by its virtually incompressible Hugoniot above 100 GPa [13].

Static laser heating at high pressures in a DAC has been used to demonstrate the existence of an equilibrium phase at extreme conditions. Perhaps, the prototypical examples are demonstrations that (Mg,Fe)\( \text{SiO}_3 \) perovskite is stable up to 130 GPa and 2000 by Knittle and Jeanloz [17], up to several 10 GPa at high temperatures by Tsuchida and Yagi [18], and up to 100 GPa and 3000 K by Serghiou et al [18]. These results show (Mg,Fe)\( \text{SiO}_3 \) perovskite is probably the major constituent of Earth.

3. Conclusions
Several conclusions can be drawn from these general considerations: (i) The Hugoniot and 0-K isotherm of a hard material are nearly coincident. (ii) Hugoniot data of diamond and sapphire do not have limiting compressions under static and shock pressures below 600 GPa and 340 GPa, respectively. That is, the observed increase in compression with pressure depends weakly on
pressure. (iii) In contrast Gd$_3$Ga$_5$O$_{12}$, TiO$_2$, CaTiO$_3$ perovskite, and CaF$_2$ have limiting shock compressions of about 1.8-fold of initial density at measured pressures in the range 100 to 300 GPa. At substantially higher shock pressures and temperatures, thermal excitation of electrons will eventually cause compression to increase above 1.8-fold, eventually approaching 4-fold at ~100 TPa shock pressures. (iv) The exoplanet discovered recently has a mass of about 7 earth masses. Assuming its density depends weakly on volume, this planet would have about twice the radius and twice the effective interior pressure of Earth. The pressure at the Earth’s core-mantle boundary (CMB) is estimated to be 130 GPa. Based on published Hugoniot data up to ~300 GPa, the density of rock in this exoplanet is probably no more than at the CMB, about twice crystal density at the surface of the planet, independent of structure and composition. (v) A large number of hard crystals exist with a range of densities and compressibilities, which means pressure, density, and temperature of fluid metallic hydrogen, and other compressible fluids, can be tuned over a wide range using a reverberating shock wave between hard crystals of materials other than sapphire.

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5. References
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