Deriving equations of state from non-hydrostatic data

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Abstract. Modeling of non-hydrostatic strains allows extraction of a reliable (quasi-hydrostatic) equation of state from diamond-cell x-ray measurements at high pressures, as illustrated by new data on Os collected to 60 GPa at room temperature: axial- and radial-diffraction measurements are in good agreement with data collected using Ar and He pressure media, as well as with first-principles calculations, in confirming that osmium is the densest but not the most incompressible element. Dynamic-loading methods can generate much higher pressures than static compression, however, shock compression leads to high temperatures there is much interest in compression using ramp waves. This can be accomplished with graded-density mechanical impacts, or with laser-driven pressure waves; other means of maintaining low temperatures include pre-compression and cooling of the sample before it is dynamically compressed by ramp- or multiple-shock waves. Reduced temperatures lead to enhanced strength, which makes it necessary to model both temperature and strength effects in order to extract the equation of state. A unified approach combining analysis of static and dynamic compression measurements offers a means of determining pressure–density equations of state to high compressions.

1. Introduction

Static high-pressure experiments use pressure-transmitting media in order to reduce non-hydrostatic (shear) stresses that can have deleterious effects on calibrations and measurements (e.g., of the equation of state) [1-3]. In shock-compression experiments, non-hydrostatic effects exist below the Hugoniot elastic limit [4]. More generally, the degree of non-hydrostaticity depends on a combination of stress, strain rate and temperature [4-5].

Our objective is to identify practical strategies for addressing non-hydrostatic stresses in both static and dynamic high-pressure experiments. These stresses can affect nearly all experiments at pressures above few tens of GPa, a pressure range important for characterizing changes in crystal structures, chemical bonding and a wide range of other properties [6]. The positive aspect of non-hydrostaticity is that it allows determination of practical properties, such as material strength [7]; it can also reduce...
kinetic barriers that would otherwise hinder phase transitions. However, shear stresses can significantly affect quantitative measurements of material properties, and the resulting state is not well described by equilibrium thermodynamics (e.g., because of the formation of dislocations, surfaces and other non-equilibrium structures).

We illustrate quantification of non-hydrostatic effects through two examples, static compression of osmium [8] and dynamic compression of diamond [5, 9]: respectively, the stiffest metallic and non-metallic elements known. Although we can vary the state of stress in static experiments, the problem is that we do not yet have reliable means of quantifying the full stress tensor as a function of position across the sample. In contrast, though the large stress gradients and elevated temperatures achieved in dynamic experiments greatly reduce strength effects, it is difficult to disentangle the thermal from shear effects influencing measurements.

2. Quasi-Hydrostatic Experiments on Osmium

Osmium powder (99.8 % purity, 10 µm particle size) was loaded with an argon pressure medium in a 125 µm diameter sample chamber in a Re gasket that had been indented to a final thickness of 60-70 µm [10]. The sample was mounted in a symmetric diamond-anvil cell having 300 µm culets, and probed with an x-ray beam approximately 10 µm wide (beamline 12.2.2 for the Advanced Light Source, ALS). Powder X-ray diffraction patterns were collected in angle-dispersive geometry at room temperature using monochromatic radiation (l = 0.48594 ± 0.00004 Å and 0.61990 ± 0.00004 Å) and a MAR345 image-plate detector [11]. The pressure, determined by ruby fluorescence [12], was taken as an average of several measurements across the sample. The software package FIT2D [13] was used for beam-position and sample-to-detector distance calibrations, and for collapsing the two-dimensional diffraction images to one-dimensional patterns. We minimized non-hydrostatic conditions by thermally annealing the sample at each pressure, with pressurized air being used to heat the entire cell to temperatures of ~40-60˚ C for 2-5 minutes. We observed significant decreases in pressure variations across the sample after heating, indicating diminishment of shear stresses.

![ADXRD Patterns of Os](a)

We found Osmium to remain in its ambient hexagonal close-packed structure to the highest pressures of our experiments, 64 GPa (figures 1 (a-b)) and also under non-hydrostatic conditions (figure 4), consistent with results of prior studies. We performed full-spectrum fits of the diffraction profiles with Le Bail and Rietveld methods [14], and were also able to use single-peak fits (PeakFIT V4.06) to
determine the lattice parameters and unit-cell volumes based on 9 diffraction peaks up to 30 GPa and 4 peaks beyond this pressure. The pressure at a given volume was determined before and after collecting diffraction patterns, and the pressure–volume ($P–V$) equation of state we find under compression and decompression is in good agreement with prior experimental data, including measurements with a He pressure medium (figure 2) [15-17] and with results of first principles relativistic electronic structure calculations [8].

![Figure 2. Comparison of quasi-hydrostatic compression measurements on Os, with the solid line being a Birch-Murnaghan fit to the present experimental data.](image)

Using the measured zero-pressure volume of $V_0 = 27.977 (± 0.023)$ Å$^3$, a third-order Birch–Murnaghan [18] fit to the data yields a zero-pressure bulk modulus $K_{0T} = 389 (± 9)$ GPa and pressure derivative $K_{0T}' = 5.0 (± 0.5)$ (figure 2); here, subscripts 0 and T indicate zero pressure and isothermal conditions, respectively. Our values are obtained by a weighted least-squares fit of normalized pressure ($F = P[3f(1+2f)^{5/2}]^{-1}$) as a function of Eulerian strain ($f = 0.5[(V/V_0)^{2/3} – 1]$).

The $c/a$ lattice-parameter ratio is also in accord with available experimental values (figure 3) [15-17], though we find no reproducible evidence of subtle shifts that have previously been claimed for $c/a$ as a function of pressure [17].
Figure 3. Variation in c/a ratio of Os with pressure under quasi-hydrostatic conditions (solid line is a guide to the eye).

3. Non-Hydrostatic Experiments on Osmium
A modified Mao-Bell type diamond-anvil cell with large openings on two sides [19-20] was used in radial diffraction geometry to collect non-hydrostatic compression data on Os powder (99.8 % purity, 10 µm particle size) with no pressure medium at beamline 12.2.2 of the ALS. A small platinum flake was embedded in the osmium as an internal pressure standard [21], and a kapton/boron gasket was used to contain the sample. Monochromatic x-rays of 0.49594 ± 0.00004 Å wavelength, and focused to a spot size of 20 x 20 µm, were used to collect diffraction patterns over a 2θ range from 0° to 38° (Mar345 image plate detector placed 287 mm away from the sample). The diffraction images were integrated from 0° to 360° azimuth over 10° sectors for analysis with the MAUD software (figure 4) [22-23].

Figure 4 (a). Diffraction pattern at 5 GPa.
Figure 4. X-ray diffraction patterns of non-hydrostatically compressed Os calculated from MAUD refinements (left), with the 2D experimental patterns (right) showing the development of texture at 5 GPa. Osmium remains in the hcp structure under these conditions.

With $\sigma_1$ and $\sigma_3$ being the radial and axial components of stress in the sample, $\sigma_P$ the mean normal stress (defining the hydrostatic pressure), and $t = (\sigma_3 - \sigma_1)$ the deviatoric (uniaxial) stress, the observed $d$-spacings depend on the angle $\eta$ between the diffracting plane normal and the load axis:

$$d_m(hkl) = d_p(hkl)\left[1 + \left(1 - 3\cos^2\eta\right)Q(hkl)\right]$$

based on anisotropic linear elasticity theory [24]. Here $d_p(hkl)$ is the $d$ spacing under hydrostatic pressure $\sigma_P$ and $Q(hkl)$ is given by

$$Q(hkl) = \left(\frac{1}{3}\right)[\alpha(2G_R(hkl))]^{-1} + (1 - \alpha)(2G_v)^{-1}$$

$G_R(hkl)$ is the shear modulus under iso-stress (Reuss) conditions, $G_V$ is the shear modulus under iso-strain (Voigt) conditions, and both $G_R(hkl)$ and $G_V$ are functions of the elastic moduli; $\alpha$ (fraction between 0 and 1) gives the relative weight of iso-stress and iso-strain conditions.

The $d$-spacing varies linearly with $(1 - 3\cos^2\eta)$ and, within the context of the linear-elastic model [24], the intercept gives hydrostatic-pressure values of $d$-spacings, $d_p$ (corresponding to the “magic-angle” $\eta = 54.7^\circ$). We used the MAUD-refined values of $d_{100}, d_{002}, d_{101}, d_{102}, d_{110}, d_{200}$, and $d_{112}$ for several $\eta$ in (1) to obtain hydrostatic values and the resulting lattice parameters (‘$a$’ and ‘$c$’) for different pressures. Similarly, $d_{111}, d_{200}, d_{220}, d_{311}, d_{222}$ MAUD-refined values for Pt were used in (1) to obtain hydrostatic values of lattice parameter and hence pressure.

Although with larger error bars and scatter, the compression determined from our non-hydrostatic experiments agrees well with the results obtained from quasi-hydrostatic measurements (figure 5). In the case of Os, therefore, it appears that a reliable $P$–$V$ equation of state is obtained from non-hydrostatic data. We cannot claim that this is a general result based on the present study alone, but the agreement is notable given the stiffness of our sample. Still, we do observe variations in $c/a$ ratio that correlate with development of lattice-preferred orientation (figure 4), not electronic structure changes [8].
Figure 5. Quasi-hydrostatic equation of state derived from non-hydrostatic measurements on Os. The solid line shows the Birch-Murnaghan fit to the present data, yielding $K_{0T} = 395$ (± 20) GPa and $K'_{0T} = 5$ (± 1), which compares well with the quasi-hydrostatic results (figure 2) as well as with the ultrasonic value $K_{0T} = 406$ (±5) GPa for polycrystalline osmium [25].

4. Non-Hydrostatic Effects in Dynamic Experiments

Static compression is limited to peak pressures of about 3-5 Mbar, whereas dynamic experiments provide access to the tens of Mbar pressures relevant to the deep interiors of Saturn and Jupiter (~ 30-70 Mbar peak pressures), and of super-Earth and super-giant exoplanets. Ramp compression [26] provides more gradual loading than shock waves [27], and is therefore expected to produce less heating. Ramp compression is thus well suited for reproducing planet-interior conditions, which are largely characterized by isentropic temperature profiles, and also to achieving the highest compressions in samples.

Diamond, formed from the fourth most abundant cosmochemical element, is important both as a constituent of “icy” planets such as Uranus and Neptune and because of its singular properties (e.g., high bulk modulus, thermal conductivity, transparency across a broad spectrum of electromagnetic wavelengths). Thus, it is used as a pressure chamber for dynamic (pre-compression) as well as static high-pressure experiments (e.g., [28]). Diamond exhibits a nearly constant melting temperature at 9-20 Mbar [29-30], and an exceptionally large dynamic strength [5, 9].

Both strength and temperature result in an offset (higher magnitude of stress at a given compression) for the dynamic-compression measurements relative to a fluid response. Therefore, in order to disentangle the combined effects of strength and temperature on dynamic (shock- and ramp-)
compression data, we analyze the derivative of the stress–strain relation that is measured. For an elastic–perfectly plastic material, the shear stress remains constant above the yield stress and the strength-induced offset in stress (relative to the fluid Hugoniot at given strain) remains constant.

Assuming a linear \( U_s u_p \) relation for the Hugoniot \( (U_s = c + s u_p) \) for shock velocity \( U_s \) and particle velocity \( u_p \), a Mie-Grüneisen analysis [28] shows that the Hugoniot and isentrope slopes at a given density \( (\rho = 1/V) \) are related by

\[
\frac{\partial P_H}{\partial \rho} - \frac{\partial P_s}{\partial \rho} = \frac{\gamma^3}{c^2} \left[ 1 - \frac{\rho_0}{\rho} \right] \left[ 1 - s \left( 1 - \frac{\rho_0}{\rho} \right) \right]^3
\]

where \( \gamma \) is the Grüneisen parameter (assumed to depend on density alone). Therefore, if the Hugoniot \( (c \text{ and } s) \) is known, the \( P-\rho \) slope of ramp-compression measurements can be compared against slopes of both Hugoniot and isentrope as a function of density in order to determine the entropy associated with ramp loading. Once dynamic-compression measurements are related to the Hugoniot and isentrope, and reduced to either with this approach, they can be analyzed jointly with the results of isothermal-compression and wave-velocity (e.g., ultrasonic or Brillouin scattering) experiments through a finite-strain approach involving the normalized pressure as a function of strain, \( F(\phi) \) [31].

Analysis of multi-Mbar data for diamond [5] using (3) suggests that both strength and entropy effects can be important under ramp loading. Our knowledge of material behavior under ramp compression is limited, and we do not have a good microscopic understanding of how samples behave under such conditions: defect production as well as heating may both contribute. Alternative loading paths, including multiple (multi-step) shocks need to be explored in order to better tune and understand strength and entropy effects. Also, experiments achieving much higher compressions by ramp loading at MJ-laser facilities such as NIF can provide testing grounds for microscopic theories of dynamic material response over a wide range of strains and strain rates.

5. Conclusions

Real progress is being made in accounting for the effects of non-hydrostaticity in high-pressure measurements, under both static and dynamic conditions. In the case of static measurements, it is important to (i) collect data on decompression as well as compression; (ii) quantify the effects of different states of stress by making measurements with different pressure media and with thermal annealing (modest external heating or more intense laser heating); and (iii) using radial diffraction to complement axial-diffraction measurements. In the case of dynamic loading, ramp, multi-shock and pre-compression experiments are beginning to provide the information needed to distinguish entropy (thermal and defect) from strength effects. Ramp compression may follow a stress–strain path quite distinct from that of an isentrope.

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