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CONDENSED MATTER PHYSICS | RESEARCH ARTICLE

High-pressure structural parameters and equation of state of osmium to 207 GPa

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Abstract: The most incompressible transition metal osmium (Os) has been studied under high pressure. There is significant interest in Os because of the structural anomalies attributed to topological transitions in the Fermi surface for valence electrons in the hexagonal close-packed phase. We report on measurements of structural parameters and equation of state on Os metal to a pressure of 207 GPa at ambient temperature using platinum as a pressure standard. We obtained angle-dispersive X-ray diffraction data at a synchrotron source with closely spaced pressure intervals to observe any discontinuities or anomalies in the axial c/a ratio at high pressures. Rietveld refinements of X-ray diffraction data show a slowly varying axial ratio (c/a) with a broad minimum at 75 GPa. Our data do not provide any evidence of anomalous behavior in the c/a ratio in Os at 25 or 150 GPa as have been reported in previous studies. Our experimental results are in agreement with theoretical calculations that do not predict any anomalous behavior in c/a ratio in Os under extreme conditions. We present an equation of state for Os to 207 GPa ($V/V_0 = 0.761$) at ambient temperature and compare our results with the previously published data.

Subjects: Earth Sciences; Physical Sciences; Materials Science

Keywords: transition metals; high pressure; equation of state; X-ray diffraction

ABOUT THE AUTHORS

The high-pressure structural studies on transition metal osmium to multi-megabar pressures is carried out by Yogesh Vohra's research group at the University of Alabama at Birmingham (UAB) and is supported by the US National Science Foundation (NSF). This is part of a larger study on structural, electronic, and magnetic transitions in transition metals, rare earth metals, and their alloys under extreme conditions of pressure and temperatures. Yogesh Vohra, PhD, is the founding director of UAB Center for Nanoscale Materials and Biointegration (CNMB) that houses a Diamond Microfabrication Laboratory. Yogesh Vohra's research group has also pioneering several enabling technologies used in studies of materials under extreme conditions including diamond anvils with embedded sensors (designer diamonds) and nanocrystalline diamond micro-anvils grown by chemical vapor deposition techniques to study materials to pressures exceeding 500 GPa.

PUBLIC INTEREST STATEMENT

The transition metal osmium is the most incompressible metal in the periodic table and its elastic stiffness rivals that of crystalline diamond. There is significant interest in high-pressure behavior of osmium as previous studies have reported structural anomalies that are attributed to changes in electronic structure induced by compression. The experimental studies on structural anomalies in osmium are particularly challenging as they require compression to several million atmosphere pressure in a diamond anvil cell. We present detailed structural analysis of X-ray diffraction data on osmium to over 2 million atmospheres (207 GPa) and found no evidence of structural anomaly at 150 GPa within the experimental errors inherent in the measurement. We present pressure-volume relationship or equation of state for osmium and show that even the most incompressible metal is compressed by 24% at the highest pressure of 207 GPa reached in our study.

1. Introduction

The study of transition metals under high pressure has historically attracted much attention due to the electron transfer effects induced by volume compression. The s-electron wave function is extended in space in transition metals as compared to relatively localized d-electron wave function and hence when pressure is applied the s-wave function will feel the effects of coulomb repulsion more than the d-electrons. This repulsive interaction due to s-electron overlap implies that the bottom of the s-band experiences an increase in energy with increasing pressure relative to the d-band leading to s → d electron transfer (Pettifor, 1977). This s–d electron transfer under high pressure is responsible for phase transformations and relatively high compressibility in early Group IV transition metals (Pettifor, 1977; Sikka, Vohra, & Chidambaram, 1982). This s → d electron transfer slows down near the middle of transition metal series for 5-d metal transition metal like osmium (Os) with atomic electronic configuration [Xe] 4f¹⁴ 5d⁶ 6s² and leads to low compressibility. The transition metal Os is the most incompressible metal in the periodic table. It retains a hexagonal close-packed structure at pressures exceeding 770 GPa (Dubrovinsky et al., 2015). There have been reports of three structural anomalies in the axial ratio *c/a*, notably at 25, 150, and 440 GPa, respectively. Occelli et al. (2004) observed a discontinuity in the first pressure derivative of *c/a* at 25 GPa and Dubrovinsky et al. (2015) observed a local minimum in the *c/a* value at 150 and 440 GPa. The compression anomalies at 25 GPa and 150 GPa, as observed by the *c/a* ratio change, have been attributed to electronic topological transitions (ETT) at ambient temperature and high pressures. The structural anomaly at higher pressure of 440 GPa has been attributed to pressure-induced interaction between 4-f and 5-p core electrons (Dubrovinsky et al., 2015). There is much disagreement over the existence and location of these discontinuities. For example, Kenichi (2004) has reported no anomaly in the *c/a* ratio at 25 GPa in Os. Our experimental study is motivated by further need to understand the electronic basis of these structural anomalies in transition metal Os under extreme conditions. We have collected high-pressure X-ray diffraction data for Os in very closely spaced pressure intervals to pinpoint these structural anomalies under high pressure. In addition Rietveld structural refinements were carried out at all pressures to obtain consistency in fitting procedures as well as reduce the uncertainty in determination of lattice parameters for hexagonal close-packed Os.

2. Experimental details

High-pressure studies were carried out using diamond anvils with central flat of 35 μm in diameter, a bevel angle of 7.5 degrees to a culet size of 300 microns in diameter. This diamond design provides reproducible access to pressure exceeding 200 GPa. A sample hole of 20 μm in diameter in a pre-indented 40 μm thick spring steel gasket served as the sample chamber. High purity Osmium (99.95%) and Platinum powders (99.9%) from Alfa Aesar were mixed and ground together and the powder mixture was placed in the sample chamber assembly to provide for X-ray diffraction experiments. Angle-dispersive X-ray diffraction was then performed on the sample at the HPCAT 16 ID-B beamline at the Advanced Photon Source at Argonne National Laboratories in Chicago, Illinois. A beam of X-rays with a wavelength of 0.40663 Å was collimated to a spot size with Full Width at Half Maximum (FWHM) of 5 × 7 μm. The X-ray sample to detector distance was 170.69 mm and the system was calibrated using a cerium oxide diffraction pattern as a standard. The Os and Pt sample was located in the X-ray beam by moving an X-ray sensitive diode behind the sample in the x and y direction to identify the point of minimum transmission on the central flat of diamond before the spectrum is acquired. A Diacell iGM Controller was used to control the gas membrane pressure.

The resulting diffraction patterns were collected using a Pilatus 1 M detector. Reitveld refinement was then carried out on the spectra using EXPGUI interface for GSAS (Larson & Von Dreele, 2000; Toby, 2001). A total of 141 diffraction patterns were obtained to analyze structure parameters of Os between ambient pressure and 207 GPa. The most common oxide for osmium is osmium tetroxide, which forms a monoclinic C2/c structure with lattice parameters *a* = 4.515 Å, *b* = 5.205 Å, *c* = 8.084 Å, *α* = 77.677°, *β* = 73.784°, and *γ* = 64.294° (Krebs & Hasse, 1976). Osmium dioxide can form a cubic fluorite structure with lattice parameter *a* = 4.8 Å (Liang, Li, & Song, 2010). The diffraction patterns did not indicate the presence of these or any other oxide in our sample.

3. Results and discussion

Pressures were calculated from the (111), (200), and (220) diffraction peaks of the platinum pressure marker, using the third-order Birch–Murnaghan equation of state:

$$p = 3B_0 f(1 + 2f)^{\frac{5}{2}}(1 + a_1 f)$$

$$f = \frac{1}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]$$

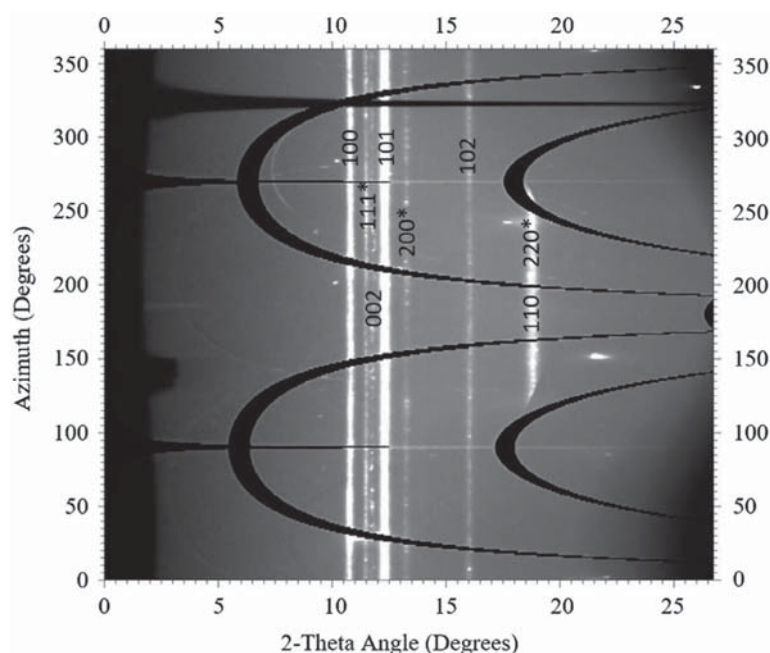
$$a_1 = \frac{3}{2}(B'_0 - 4)$$

where B_0 is the bulk modulus of the material, B'_0 is the pressure derivative of B_0 , and V_0 is the unit cell volume at ambient conditions. We have employed the equation of state of platinum from ref (Yokoo et al., 2009) with a bulk modulus $B_0 = 276.4$ GPa, pressure derivative $B'_0 = 5.12$, and an initial volume per atom of $V_0 = 15.097$ Å³. This Pt equation of state employed for pressure calibration in our experiment is valid up to the highest pressure of 550 GPa (Yokoo et al., 2009). A maximum pressure of 207 ± 1 GPa was reached in the present study at a gas membrane pressure of 51 bars consistent with the present design of diamond anvil and the sample was subsequently decompressed to ambient conditions.

Figure 1 shows the X-ray diffraction image of Os and Pt mixture at a pressure of 150 GPa obtained with Pilatus 1 M detector. The X-rays wavelength is 0.40663 Å. The diffraction lines are labeled with the corresponding Miller indices (hkl) and the platinum lines are marked by asterisk (*). The vertical axis shows the intensity variation along the azimuthal direction for various diffraction rings and shows presence of some preferred orientation in both Os sample as well as Pt marker. In particular, integrated intensity of (002) peak from Os is weaker than predicted by theoretical structure factor due to texturing; a phenomenon that is normally observed in compression of several *hcp* metals.

Figure 1. X-ray diffraction image of osmium and platinum mixture obtained with Pilatus 1 M detector at a pressure of 150 GPa. The X-rays wavelength is 0.40663 Å. The diffraction lines at various 2-Theta angles are labeled with the corresponding Miller indices (hkl) and the platinum lines are marked by asterisk (*).

Note: The vertical axis shows the intensity variation along the azimuthal direction for various diffraction rings.



The integrated angle-dispersive X-ray diffraction spectra from Os and Platinum mixture at various pressures between ambient pressure and 207 GPa are shown in Figure 2 where Os is in the hexagonal close-packed (*hcp*) phase and Pt is in the face-centered cubic (*fcc*) phase. All the diffraction peaks in Figure 2 move to the right with increasing pressure with noticeable weakening of (002) diffraction peak for *hcp* phase of Os as discussed earlier. The diffraction peaks from the Os sample were indexed using the (100), (002), (101), (102), and (110) peaks of the *hcp* phase. The (111), (200), and (220) diffraction peaks from the *fcc* phase of platinum are marked with an asterisk *. The (110) peak of osmium is merged with the (220) of platinum at high pressure. The measured lattice parameters of the *hcp* phase of the Os sample at 207 GPa were $a = 2.496 \pm 0.001$ Å and $c = 3.954 \pm 0.002$ Å with measured volume compression $V/V_0 = 0.761$. The lattice parameter of the platinum pressure marker was measured to be $a = 3.521 \pm 0.001$ Å with measured volume compression $V/V_0 = 0.723$.

Figure 3 shows the measured axial ratio (c/a) of Os as a function of pressure between ambient to 207 GPa pressure. We also show the location of anomalies reported in the literature at 25 and 150 GPa by dashed lines in Figure 3. It is clear that given the uncertainties in the axial ratio (c/a) it is difficult to assign structural anomalies at the reported values of 25 and 150 GPa. The c/a axial ratio shows an initial increase at low pressures consistent with an earlier published data (Kenichi, 2004). This initial increase is followed by a slight decrease and then gradual increase above 75 GPa to the highest pressure of 207 GPa. The c/a axial ratio does have appearance of several local minima in Figure 3 including the one reported at 150 GPa (Dubrovinsky et al., 2015), however, considering the error bars it is not possible to assign any definitive structural anomalies. It is important to add that the overall variation in the c/a ratio shown in Figure 3 between ambient pressure and 207 GPa is less than 1% and any claims of structural anomalies have to consider uncertainties in experimental determination of lattice parameters. There is experimental evidence of preferred orientation under non-hydrostatic conditions showing that the *c*-axis of osmium is aligned parallel to the load axis in the diamond cell. This manifests itself as a weak (002) reflection from the *hcp* Os (Figure 2). This can have some impact in depressing c/a axial ratio at high pressures between 25 and 75 GPa.

We have further investigated the presence of any shear strength anomalies in our data near 150 GPa in Os by examining the diffraction line broadening with increasing pressure and comparing them with the Pt pressure standard. Figure 4 shows the percent change in the Full Width at Half Maximum (FWHM) for the (100) diffraction peak of osmium (filled diamonds) and the (200) diffraction peak of platinum (open diamonds) as a function of pressure. The percent change plotted in

Figure 2. The integrated angle-dispersive X-ray diffraction patterns for osmium sample and platinum pressure standard at ambient pressure, 50, 100, 150, and 207 GPa. The diffraction peaks from the osmium sample are indexed to a hexagonal close-packed structure while the platinum peaks marked by asterisk (*) are indexed to a face centered cubic structure.

Note: The results of Rietveld refinement are also indicated in the 207 GPa pattern.

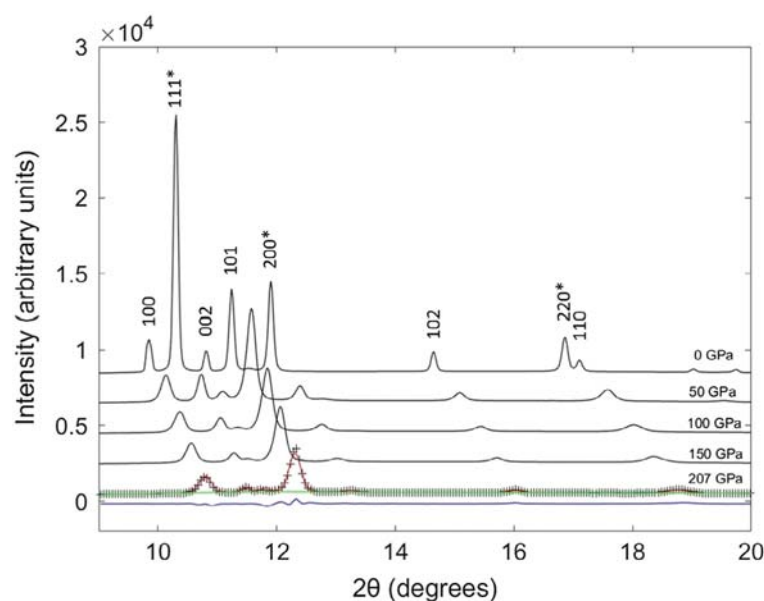


Figure 3. The measured c/a axial ratio versus pressure for the osmium sample. The vertical dashed lines represent the location of structural anomalies as reported by Occelli et al. (2004) and Dubrovinsky et al. (2015), respectively. The solid line represents the axial ratio reported by Kenichi (2004).

Note: Our data show a broad minimum at 75 GPa and the overall variation c/a axial ratio is below 1% over the entire pressure range.

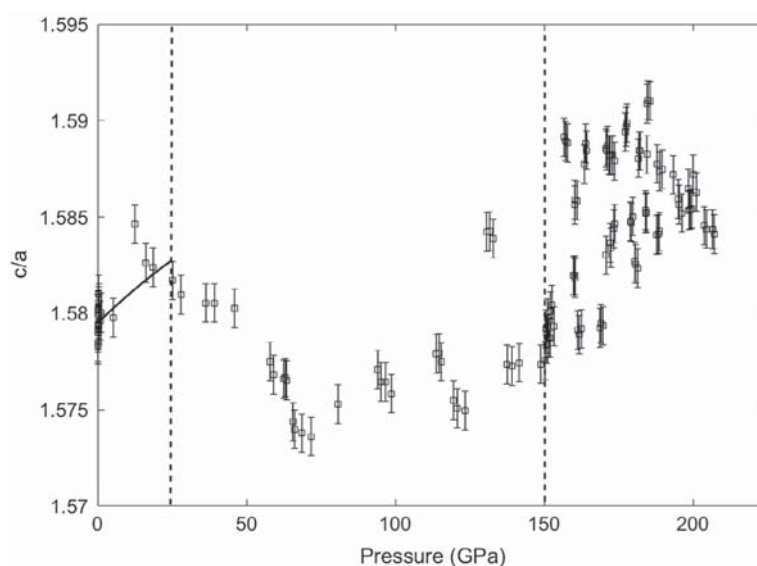


Figure 4. The percent change in the full width at half maximum (FWHM) for the (100) diffraction peak of osmium (filled diamonds) and the (200) diffraction peak of platinum (open diamonds) as a function of pressure.

Notes: The percent change is with respect to their corresponding values at ambient pressure. The solid line is drawn as a fit to all data and serves as a guide to the eye to show the relative change.

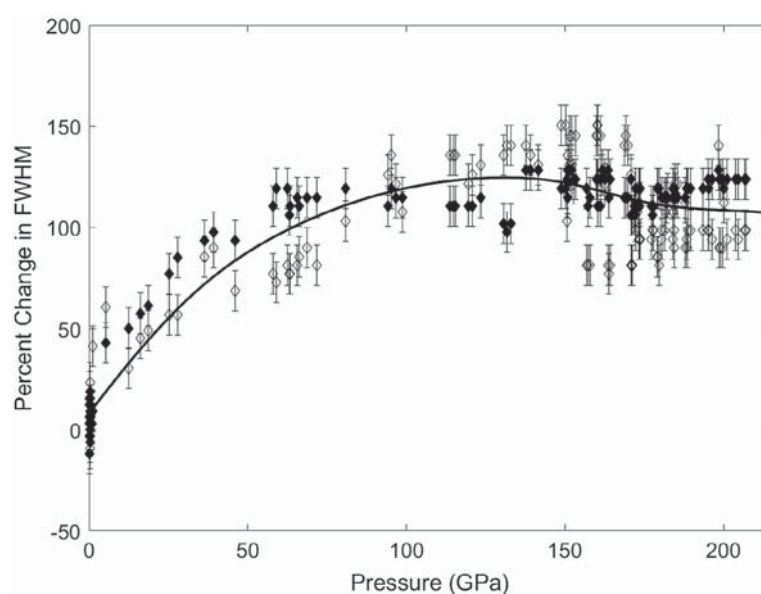
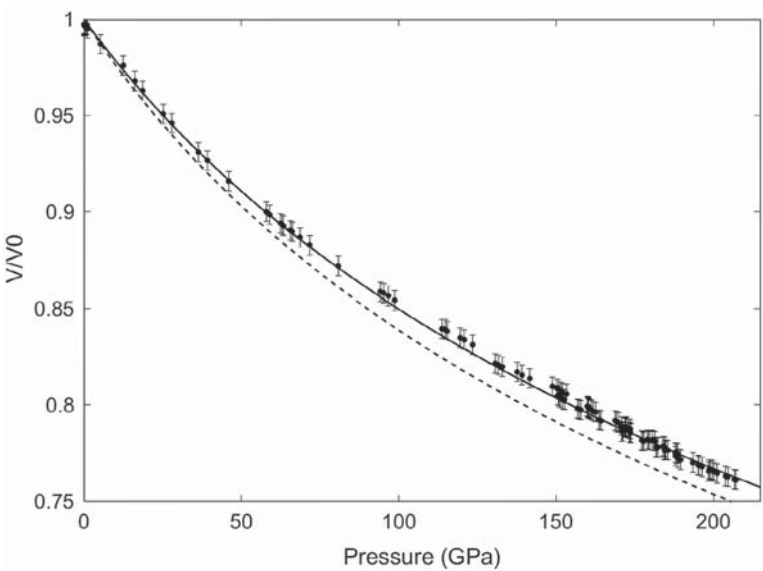


Figure 4 is with respect to their corresponding values at ambient pressure. The FWHM of diffraction peak is related to the pressure gradient over the $5 \times 7 \mu\text{m}$ sampling region of the incident beam in our experiments. The pressure gradient a material can support depends on the shear strength of material and the shear strength increases gradually with increasing pressure due to the pressure strengthening effect. The FWHM variation is very similar for both Pt and Os in the entire pressure range to 207 GPa. The FWHM increases rapidly with pressure below 50 GPa followed by a gradual increase and saturation at high pressure. This trend is correlated to increase in shear strength of material with increasing pressure. It is clear from Figure 4 that there is no anomalous change in FWHM of the Os near 150 GPa.

Figure 5 shows the measured equation of state of transition metal Os to 207 GPa and to volume compression $V/V_0 = 0.761$ at ambient temperature. These data were used to fit a third order

Figure 5. The measured Equation of State for osmium to 207 GPa at ambient temperature. The solid line is the unconstrained third-order Birch–Murnaghan fit with $B_0 = 444$ GPa and $B'_0 = 3.99$.

Note: The dashed line is the equation of state provided by Dubrovinsky et al. (2015) from their experimental data using $B_0 = 399$ GPa and $B'_0 = 4.04$.



Birch–Murnaghan equation of state to the osmium data. The unconstrained fitted equation of state produced a bulk modulus of $B_0 = 444$ GPa and pressure derivative $B'_0 = 3.99$, using an initial volume per atom of $V_0 = 14.01 \text{ \AA}^3$. This value of the bulk modulus is greater than the ultrasonic value of 411.9 GPa (Pandey, Singh, & Yadawa, 2009) and lies between the values of 399 and 462 GPa, as reported by Dubrovinsky et al. (2015) and Cynn, Klepeis, Yoo, and Young (2002), respectively. The calculated pressure derivative of the bulk modulus was not fixed and happens to be close to a value of 4. This agrees with Dubrovinsky et al. (2015), however, it is much greater than the value of 2.4, as presented by Cynn et al. (2002). The reported equation of state parameters for Os were compiled into Table 1 for ease of comparison.

Our experimental observation of lack of structural anomalies in Os is consistent with first-principle structural calculations at high pressures which predict a monotonous increase in c/a axial ratio with increasing pressure (Dubrovinsky et al., 2015). Our absolute value of c/a axial ratio of 1.59 for Os above 200 GPa is also consistent with other reported experimental measurements.

Table 1. Equation of state parameters for osmium			
Source	B_0 (GPa)	B'_0	V_0 ($\text{\AA}^3/\text{at}$)
Cynn et al. (2002)	462	2.4	13.978
Kenichi (2004)	395	4.5	13.989
Occelli et al. (2004)	411	4.0	13.971
Dubrovinsky et al. (2015)	399	4.04	14.01
This work	444	3.99	14.01

4. Conclusions

We have compressed 5-d transition metal osmium to a pressure of 207 GPa in a diamond anvil cell utilizing platinum as a pressure standard. The X-ray diffraction data were obtained at closely spaced pressure intervals to detect any potential structural anomalies at high pressures in the hexagonal close-packed phase. Rietveld analysis was performed to obtain consistent analysis of lattice parameters throughout the entire pressure range. We found no evidence of structural anomalies in osmium between ambient pressure and 207 GPa. The overall variation in c/a axial ratio is below 1% over the entire pressure range to 207 GPa. The analysis of pressure broadening of diffraction peaks show very similar behavior for osmium sample and platinum pressure marker and no evidence of any anomaly in the shear strength of material. The measured equation of state of Os at ambient temperature to volume compression $V/V_0 = 0.761$ yielded a bulk modulus of 444 GPa and its pressure derivative of 3.99 in general agreement with previous results.

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