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A new Lifshitz transition and the equation of state of Osmium

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Abstract

We have measured the equation of state (EoS) of osmium to 75 GPa under hydrostatic conditions at room temperature using angle dispersive x-ray diffraction. A least-squares fit of the data using a third order Birch-Murnaghan EoS yields K_0=411±6 GPa and K_0'=4.0±0.2, showing osmium is in fact more compressible than diamond. Most importantly, we have documented an anomaly in the compressibility at 20.3 GPa associated with a large discontinuity in the first pressure derivative of the c/a ratio. This discontinuity likely arises from the collapse of the small hole-ellipsoid in the Fermi surface near the L point.

There has been much interest in the possibility of a Lifshitz [1] or electronic topological transition (ETT) in zinc at high-pressure near 10 GPa. Interestingly, while the experimental data remain somewhat ambiguous [2-5], most simulations suggest the ETT exists in this pressure range [6-8]. Recently, Steinle-Neumann et al. [8] have shown that the transition arises from changes in the band structure near the high-symmetry point K where three bands cross the Fermi surface upon compression. Thus one might expect that other *hcp* metals should exhibit similar phenomena. The hcp 4*d* and 5*d* transition elements Re, Os and Ru are known to be among the densest and stiffest metals [9,10] suggesting that these might in fact be poor candidates in which to look for such effects. In osmium however, experimental and theoretical results [11,12] have shown the existence of small local maxima in the band structure just above the Fermi energy near the high-symmetry point L on the zone boundary [11]. These structures might potentially fall below the Fermi energy upon compression and give rise to an ETT. Osmium is of further interest as recent EoS measurements by Cynn *et al.* [13] have suggested that Os (K_0=462 GPa and K_0'=2.4) has the lowest known compressibility, lower even than diamond (K_0=446 GPa and K_0'=3) [14]. This conclusion has strong implications for the nature of the metallic bond in Os and paradoxically implies that the latter, where bonding electrons are delocalized, can be less compressible than the covalent bond, where bonding electrons are localized. The difficulty in supporting such a claim arises due to the fact that in all EoS studies of low compressibility materials, where the maximum experimental pressures are only a small fraction of the value of K_0, there exists a direct trade off between low values of K_0' and high values of K_0. Accurate investigations of K_0 and K_0' simultaneously in materials such as Os requires very high resolution studies in the low pressure region (K_0) and high pressure data to constrain K_0' [15].

In order to clarify these points, we have undertaken an experimental study of the EoS of osmium using angle dispersive x-ray diffraction (ADX) with ultra-high accuracy. Great care was taken to compress the samples hydrostatically to obtain the most accurate pressure measurements and to minimize the stress distribution on the sample, thus minimizing the error on the bulk modulus. Pressure on the sample was measured before and after x-ray diffraction data was collected to ensure there was no pressure drift during the measurement. Of great help in that endeavor was the very short acquisition time (4 seconds of x-ray exposure for a diffraction pattern) available on very high brilliance third

generation synchrotron sources. The samples (commercially available osmium powder with a 325-mesh grain size) were loaded in three separate membrane actuated diamond anvils cells (DAC) and one symmetrical Mao-Bell type DAC. One of our cells was set up for very high-resolution in the low-pressure regime (up to 26 GPa) to produce very small pressure steps (0.5 GPa per point) to best constrain K_0. In this cell, we used 350 μm diamond culets, neon as a pressure transmitting medium, and a stainless-steel gasket. The remaining cells were optimized for higher pressure experiments (up to 75 GPa) by using 150 μm x 350 μm beveled diamond culets, helium as the pressure transmitting medium, and rhenium gaskets. In our low-pressure run, pressure was measured using both the NaCl EoS [16] by placing a small amount of NaCl in the sample chamber as an internal pressure marker and by ruby fluorescence [17]. In the high-pressure runs, pressure was measured using only ruby fluorescence. While NaCl is the best candidate pressure standard (using x-ray diffraction) whose diffraction peaks do not overlap with those of Osmium, NaCl can no longer be used reliably above 29 GPa, because of the B1–B2 phase transition [18].

ADX measurements were recorded at the high-pressure diffraction beamline ID09A of the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The x-ray beam was focused vertically with a Pt-covered Si-mirror and horizontally with an asymmetrically cut bent Si(111) Laue monochromator to a spot size of 15x15 μm FWHM. The energy was fixed at 30.006 keV, and the sample-to-detector distance was 362.618 mm. The images were recorded using a two-dimensional MAR345 detector and integrated using the Fit2D software package [19]. In order to minimize the errors on the EoS, a total of 33 diffraction patterns were recorded between 0 and 20 GPa, and 10 more points between 20 and 75 GPa. Figure 1 shows typical diffraction patterns recorded during the experiment, from the lowest to the highest pressure, and the narrow diffraction lines at the highest pressure indicate the quasi absence of non-hydrostatic stresses and pressure drift during the measurement. No less than twelve reflections from osmium are resolved on each pattern, which permits to lower *a minima* the errors on the lattice parameters using a crystal structure refinement procedure. The refinements were performed using the GSAS software package [20] ran by EXPGUI tool [21]. In addition, as the structure is very well constrained, we were able to confirm that no first order structural phase transition occurs in this pressure range. The error bars on the volume derived from our data set is at most 5.10^{-3} A^3, which is the highest one can expect using ADX.

The EoS derived from our data is shown in figure 2. The low degree of scatter about the EoS demonstrates the internal consistency of both the ruby pressure scale and the NaCl pressure scale, arguing these two pressure standards are equivalent. The least-square 3rd order Birch-Murnaghan fit to our data yields K_0=411±6 GPa, K_0'=4.0±0.2, and V_0=27.941±0.008 A^3 while the Vinet [22] fit yields K_0=410±6 GPa, K_0'=4.2±0.2, and V_0=27.942±0.009 A^3. An additional fit of our data using a stochastic minimization algorithm on the 3rd order Birch Murnaghan EoS yields K_0=410.9±1.2 GPa, K_0'=3.97±0.04, and V_0=27.9490±0.00014 A^3.

The most surprising result of the previous study of Cynn et al. [13] was the extremely low value of K_0' in Os (K_0'=2.4) obtained using a third-order Birch-Murnaghan EoS. Indeed, theory suggests that this value should be close to 4 in stiff materials [23]. Furthermore, the Birch-Murnaghan formulation itself is valid only where this value is sufficiently close to 4. This theoretical prediction does not however invalidate the finding of a low value of K_0' and while extremely rare, it would not be the first report of an incompressible material with a low value of K_0'. In an EoS study of diamond, Aleksandrov *et al.* [24] derived K_0=444±3 GPa and K_0'=1.9 and suggested that this anomalous value arose not because of intrinsic values of the physical properties of diamond but through inaccuracies in the ruby pressure scale. They further suggested, that the difference between the EoS of diamond based on K_0'=4 and K_0'=1.9 was an absolute measure of the accuracy of the ruby pressure scale. These results, suggested an 11% inaccuracy of the ruby pressure scale in the megabar pressure range. This conclusion is in direct contradiction with absolute pressure scale calibrations obtained from an extrapolation of combined Brillouin spectroscopy and x-ray diffraction data [25], which places the inaccuracy of the ruby pressure scale at 4%. In contradiction to the claim that diamond in fact has a K_0'=4, a recent study [14] has shown that diamond has an anomalously low value of K_0' (K_0'=3). In added proof, this low K_0' is also consistent with thermodynamic relations linking K_0' to the thermal Grüneisen parameter γ_h [23]. This not only supports the validity of the ruby pressure scale, but further shows that the low value of K_0' in diamond is a specific property of this covalently bonded material, and likely arises from increased electron delocalization with compression.

The refined values of V_0 in osmium obtained in this study are equal to the reference given by ICSD database (V_0=27.9582 A^3) within 2σ and our new estimates of K_0 and K_0' show that contrary to the conclusions of Cynn *et al.* [13], the bulk modulus of osmium is 8% smaller than that of diamond, with K_0' close to 4 as expected for a well-behaved incompressible material. To date then, diamond remains the most incompressible material known. As a further check on our experimental results, we have performed first-principles pseudopotential plane-wave total-energy calculations within the local density approximation (LDA) and generalized gradient approximation (GGA-PW91) to electronic exchange and correlation on the *hcp* osmium and *diamond* carbon crystal structures [26,27,28]. Vanderbilt ultrasoft pseudopotentials were generated for osmium and carbon. The electronic degrees of freedom were minimized using a preconditioned conjugate-gradient method and cell parameters for *hcp* osmium were optimized at all volumes. A plane-wave energy cutoff of 400 eV was found sufficient to converge the energies of both the osmium and carbon structures. A Monkhorst-Pack grid of [16 16 10] was used for hcp-osmium and [4 4 4] was used for diamond-carbon. Bulk moduli were then calculated using a third-order Birch-Murnaghan equation of state. Table 1 shows our new calculations; it is interesting to note, that while our experimental data show a large discrepancy with those published by Cynn *et al.* [13], they are in qualitative agreement with the theoretical calculations presented in the same study where the theoretical bulk modulus of osmium (K_0=444.8 GPa) is lower than the theoretical bulk modulus of diamond (K_0=467.1 GPa), and K_0' (4.4) is in good agreement with our new experimental and theoretical results. The differences between the present study and that of Cynn et al. [13] arise from the fundamental nature of the experimental approaches taken in the

different studies. In their work on the EoS of osmium, Cynn *et al.* [13] used energy dispersive x-ray diffraction, this technique is characterized both by a poor signal-to-noise ratio due to large Compton scattering from the anvils and, the impossibility to refine the crystal structures using peak intensities. While energy dispersive x-ray diffraction using a white beam was necessary for high pressure diamond anvil experiments on second generation synchrotron sources, its use results in low-accuracy volume refinements which is the critical parameter in EoS studies and even more crucial in the study of low-compressibility materials. Above all, accurate EoS measurements can only be performed using quasi-hydrostatic pressure transmitting media; argon is known to be a very strong solid at high pressure. The quantitative discrepancy between these two studies, albeit small, has drastic consequences on the physical interpretation of the nature of the chemical bond in osmium.

Aside from the straightforward determination of the EoS of osmium, our new data present a most surprising and novel result; although a simple analysis of the equation of state indicates that there are no first order structural transitions, a more detailed analysis of the c/a ratio as a function of pressure (figure 3a) shows an interesting feature at 20.3 GPa. Two distinct compression regimes can be identified below and above 20.3 GPa. Attempts to fit c/a vs. pressure with simple functional forms such as a single linear, quadratic or cubic function all yielded highly correlated errors. However, a two-piece linear fit provides the simplest statistically valid description of the data. Importantly, these two regimes are not resolvable as a function of volume (figure 3b) but only as a function of pressure (figure 3a). When plotted as a function of volume, the c/a ratio, exhibits a monotonous and continuous behavior (figure 3b) over the whole pressure range, and can be approximated by a unique linear function. This means that the modulus, namely $\frac{\partial P}{\partial V}$, and the equation of state V(P) must also exhibit the same discontinuity. This cannot be resolved in the data shown in figure 2, due to the lack of sensitivity of the EoS formulation to such changes. These features are in fact, the signature of a Lifshitz transition, where the first derivative of the compressibility presents a discontinuity at the transition pressure and the second derivative is not defined [1]. Such transitions have been suggested to arise through topologic singularities in the Fermi surface [1]. In the case of osmium, we suggest that the anomaly likely arises from the passage of the maxima in band h_7 below the Fermi energy with compression resulting in the collapse of the hole-ellipsoid. While non-trivial, our hypothesis can be tested experimentally by high-pressure de Haas–van Alphen measurements with recently developed diamond anvil techniques [29, 30]. Finally, our findings prove the importance of ultra-high accuracy measurements in the lattice constants in conjunction with close to ideal pressure conditions, and shows how these types of studies can help pinpoint, isolate, and even unveil peculiar behaviors in materials that could otherwise not be observed.

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	hcp osmium		*diamond* carbon	
Method	K_0 (GPa)	K_0'	K_0 (GPa)	K_0'
LDA	437.3	4.46	464.0	3.65
GGA	382.3	4.60	431.2	3.68

Table 1: Third order Birch-Murnaghan EoS parameters derived from the *ab initio* calculations.

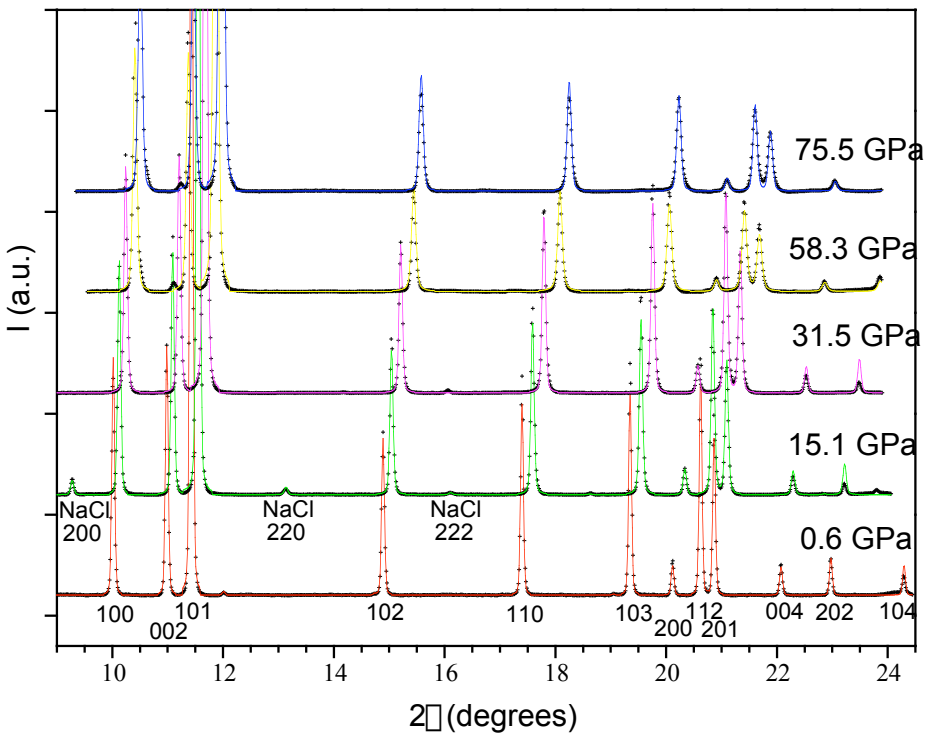

Fig. 1 : Integrated angle-dispersive diffraction patterns recorded at various pressures. The experimental data is represented by a + symbol, and the curves are obtained from a Rietveld structural refinement of the data. The osmium reflections are labeled on the lowermost spectrum. NaCl reflections are labeled on the second spectrum.

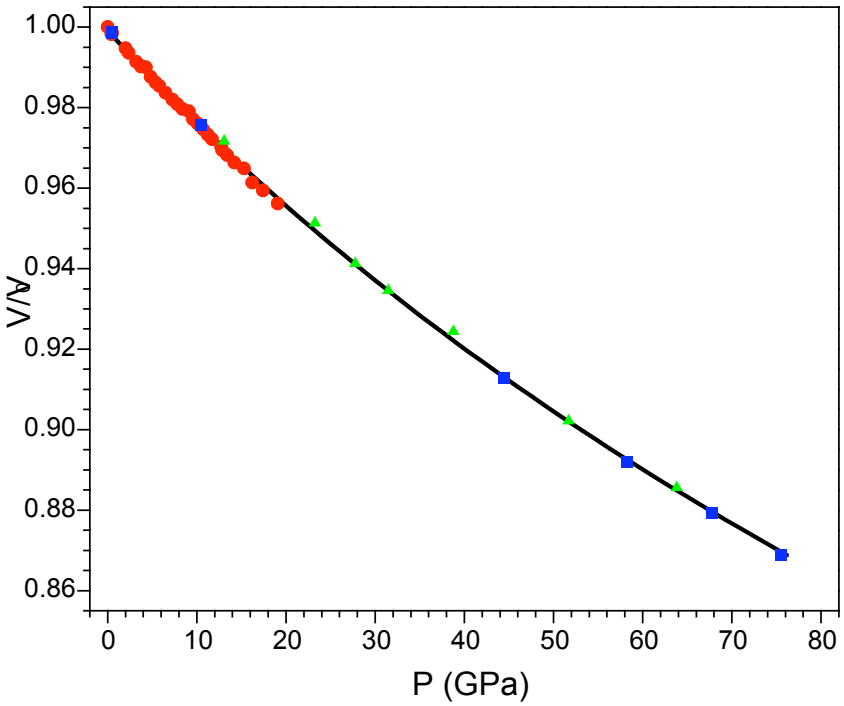

Fig. 2: The equation of state of Osmium. The different symbols correspond to the three independent loadings (the size of the symbol is greater than the experimental errors both on pressure and volume). The solid curve is a 3rd order Birch-Munaghan fit to the data yielding K_0=411±6 GPa, K_0'=4.0±0.2, and V_0=27.941±0.008 A^3.

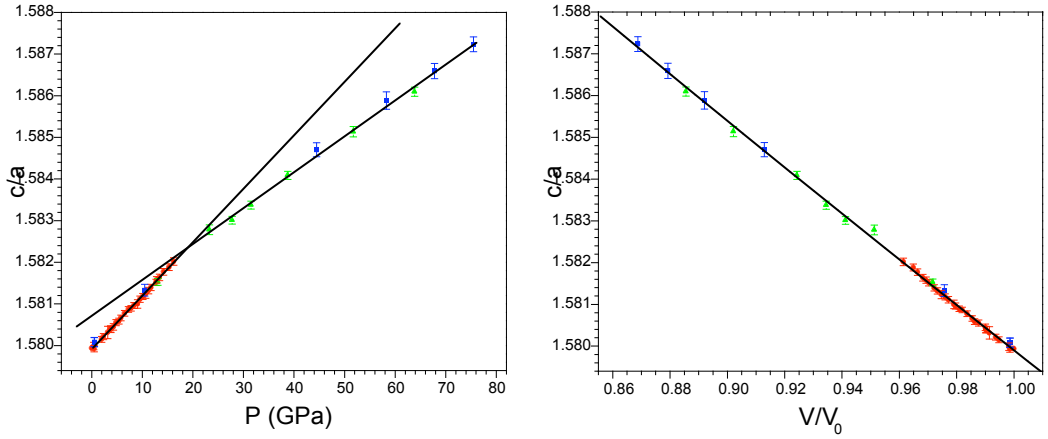

Fig. 3: The c/a ratio of osmium versus pressure (left panel), and volume (right panel). The symbols are the same as in figure 2. The linear fits to the c/a vs. pressure data yield $c/a=1.57993+1.25049.10^{-4}$ P(GPa) over the pressure range 0 to 20.3 GPa and $c/a=1.58071+8.65348.10^{-5}$ P(GPa) from 20.3 GPa to the highest pressure achieved in the study. The linear fit to the c/a vs. reduced volume data yields c/a=1.63504 - 0.0552 (V/V_0).