Experimental Evidence for a High-Pressure Isostructural Phase Transition in Osmium

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We have measured the isothermal 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 this data using a third-order Birch-Murnaghan EOS yields an isothermal bulk modulus $K_0 = 411 \pm 6$ GPa, showing osmium is more compressible than diamond. Most importantly, we have documented an anomaly in the compressibility around 25 GPa associated with a discontinuity in the first pressure derivative of the c/a ratio. This discontinuity plausibly arises from the collapse of the small hole-ellipsoid in the Fermi surface near the L point.

Recently, there has been much interest the high-pressure properties of zinc and most specifically the nature of a possible Lifshitz [1] or electronic topological transition (ETT) near 10 GPa. This type of phase transition arises when distortion of the electronic band structure results in a topological singularity of the Fermi surface. Interestingly, while the experimental data remain somewhat ambiguous [2–5], simulations suggest an ETT indeed exists in this pressure range [6–8]. Recently, Steinle-Neumann *et al.* [8] have suggested 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. This suggests one might expect other hcp metals to exhibit similar phenomena. The platinoid 5*d* transition elements (e.g., Re, Os, and Ir) are known to be the densest and stiffest metals [9,10], suggesting they might in fact be poor candidates in which to look for such effects. However, experimental and theoretical results for Os [11,12] have shown the existence of small local maxima in the band structure just above the Fermi energy near the L point on the zone boundary [11]. Thus, the potential exists that these structures might upon compression fall below the Fermi energy and give rise to an ETT. Furthermore, recent equation of state (EOS) measurements by Cynn *et al.* [13] have suggested that Os has a bulk modulus (K_0) and first derivative of the bulk modulus (K_0') equal to 462 GPa and 2.4, respectively, and is less compressible 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, is less compressible than the covalent bond, where bonding electrons are localized. The difficulty in supporting such a claim, however, arises due to the fact that in EOS studies and especially those of low-

compressibility materials, where the maximum experimental pressures are only a small fraction of the value of K_0, there exists a strong inverse correlation between the values of K_0' and those of K_0 in the numerical inversion of the volume as a function of pressure data. In order to accurately investigate the magnitude of K_0 and K_0' simultaneously in materials such as Os, one needs to undertake a high-resolution study in the low-pressure region (K_0) and also obtain 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 with ultrahigh accuracy. Great care was taken to compress the samples hydrostatically to obtain the most accurate pressure measurements and to minimize both the stress distribution on the sample and the error in the bulk modulus. Pressure on the sample was measured by ruby fluorescence before and after the x-ray diffraction data were collected to ensure there was no pressure drift during the measurement. Of great help in that endeavor was the extremely short acquisition time (~ 4 s of x-ray exposure per diffraction pattern) available on third generation synchrotron sources. The samples (commercially available osmium with a 325 mesh) were loaded in three separate membrane actuated diamond anvils cells (DAC) and one symmetrical Mao-Bell–type DAC. One cell was set up for very high resolution in the low-pressure regime (up to 26 GPa; 0.5 GPa per point) to better constrain K_0. In this cell, we used 350 μm diamond culets, neon as a pressure transmitting medium, and a stainless-steel gasket [16]. The remaining cells were optimized for higher pressure experiments (up to 75 GPa) by using 150 μm $\times$ 350 μm beveled diamond culets, helium as the pressure transmitting medium, and rhenium gaskets [16]. In our low-pressure run, pressure was measured using both the NaCl EOS 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. Above the B1-B2 phase transition at 29 GPa [18], NaCl can no longer be used reliably as an internal pressure standard.

Angle-dispersive x-ray diffraction measurements were recorded at ID09A of the European Synchrotron Radiation Facility, Grenoble, France [19]. 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 from our experiment; the narrow diffraction lines even at the highest pressure indicate the near absence of nonhydrostatic stresses and pressure drift during the measurement. No less than 12 reflections from osmium are resolved on each pattern, enabling us to minimize the errors on the lattice parameters using a crystal structure refinement procedure. The Rietveld structural refinements were performed using GSAS (General Structural Analysis System) [20]. Over this pressure range, our data confirm that no first order structural phase transition occurs. The errors on the volumes derived from our data are at most $5 \times 10^{-3} \, \text{Å}^3$.

Our new EOS is shown in Fig. 2 using the third-order Birch-Murnaghan [21] equation; $P = 3/2K_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}]\{1 + 3/4(K'_0 - 4)[(V/V_0)^{-2/3} - 1]\}$, where V is the volume, V_0 is the zero pressure volume, K_0 is the isothermal bulk modulus, and K'_0 is the first pressure derivative of the isothermal bulk modulus. The least-squares fit to our data yields $K_0 = 411 \pm 6$ GPa, $K'_0 = 4.0 \pm 0.2$, and $V_0 = 27.941 \pm 0.008 \, \text{Å}^3$. Using a stochastic minimization algorithm on the third-order Birch-Murnaghan EOS, which gives a more robust estimate of the parameters as well as the correlation matrix, we find $K_0 = 410.9 \pm 1.2$ GPa, $K'_0 = 3.97 \pm 0.04$, and $V_0 = 27.949 \pm 0.002 \, \text{Å}^3$. Further, the refined values of V_0 in osmium obtained in this study are equal to the reference value given by ICSD (Inorganic Crystal Structure Database) ($V_0 = 27.958 \, \text{Å}^3$) within 2σ, and our new results show that contrary to the conclusions of Cynn et al. [13], the bulk modulus of osmium is actually 8% smaller than that of diamond, with K'_0 close to 4 as is expected for a well-behaved incompressible material. Indeed, 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 [21]. Furthermore, the Birch-Murnaghan formulation itself is valid only where this value is sufficiently close to 4. 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 (LDA) and generalized gradient approximations (GGA-PW91) to electronic exchange and correlation on hcp-osmium and diamond-carbon crystal structures [23–26]. Table I shows our new calculations, which agree with the theoretical results presented by Cynn et al. [13]. Interestingly, while our conclusions are at odds with those published by Cynn et al. [13], they are in qualitative agreement with the theoretical calculations presented in that same study. In the latter, the theoretical bulk modulus of osmium was determined to be lower than the theoretical bulk modulus of diamond (cf. Table I), and K'_0 is in good agreement with our new experimental and theoretical results. The explanation of the differences in the conclusions of the present study with those of Cynn et al. [13] stems from the fundamentally different experimental approaches taken in the two studies. In their work on the EOS of osmium, Cynn et al. [13] used energy dispersive x-ray diffraction. This technique relies on the
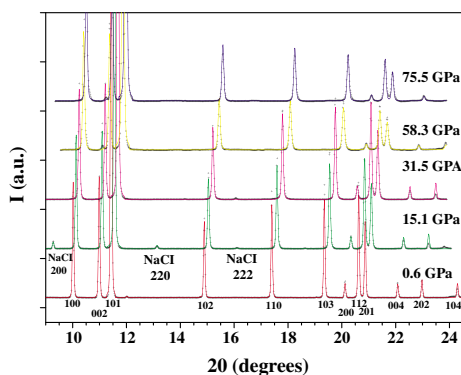

FIG. 1 (color online). Integrated angle-dispersive diffraction patterns recorded at various pressures. The experimental data are represented by a + symbol, and the curves are obtained from a Rietveld structural refinement of the data. The osmium reflections are labeled on the lowermost spectrum. NaCl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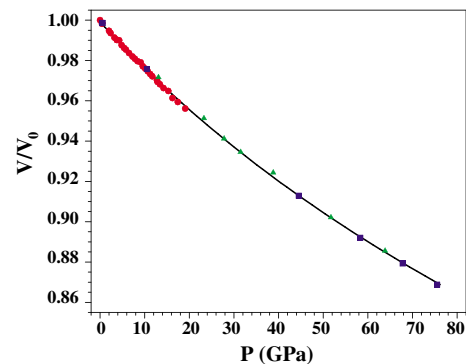

FIG. 2 (color online). The isothermal equation of state of Osmium at 300 K. The different symbols correspond to the three independent loadings (the size of the symbol is greater than the experimental errors both on pressure and volume). The solid curve is a third-order Birch-Murnaghan fit to the data yielding $K_0 = 411 \pm 6$ GPa, $K'_0 = 4.0 \pm 0.2$, and $V_0 = 27.941 \pm 0.008 \, \text{Å}^3$.

TABLE I. Third-order Birch-Murnaghan isothermal EOS parameters for osmium and diamond from various studies.

		Osmium		Diamond	
		K_0(GPa)	K_0'	K_0(GPa)	K_0'
This study	exp	411	4.0		
	LDA	437.3	4.46	464.0	3.65
	GGA	382.3	4.60	431.2	3.68
Cynn *et al.*	exp	462	2.4		
	LDA	444.8	4.4	467.1	3.6
Occelli *et al.*				446	3.0

use of an intense white beam, and while it was necessary for high-pressure diamond anvil experiments on second generation synchrotron sources, it results in low-accuracy volume refinements which are the critical parameter in EOS studies and even more crucial in the study of low-compressibility materials. Poor resolution on the volume refinements is further exacerbated by the use of stiff pressure media (such as argon above 30 GPa) that produce large pressure gradients and thus increase the error bounds. The quantitative discrepancy between these two studies, albeit small, does have 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 EOS indicates that there are no first order structural transitions, a more detailed analysis of the c/a ratio as a function of pressure [Fig. 3(a)] shows an interesting fea-

ture around 25 GPa. Two distinct compression regimes can be identified, below and above $\sim$25 GPa. Attempts to fit c/a versus pressure with either a single linear, quadratic, or cubic function all yielded highly correlated errors. Only a two-piece linear fit provides a statistically valid description of the data. Importantly, these two regimes are not resolvable as a function of volume [Fig. 3(b)] but only as a function of pressure [Fig. 3(a)]. When plotted as a function of volume, the c/a ratio exhibits a monotonically increasing behavior [Fig. 3(b)] and can be approximated by a unique linear function. This means that the modulus, namely $\delta P/\delta V$, must also exhibit the same discontinuity as seen in the function $c/a(P)$. This further implies that $V(P)$ should also display this anomaly, and, in that respect, two independent Birch-Murnaghan EOS were fitted to the data below and above 25 GPa, as reported in Fig. 2. In that case, the reduced χ^2 drops by 60%, and using an F-test comparison the two-phase model is statistically significant at the 96% confidence level, strengthening our assumption (for a phase transition) from a statistical standpoint. It is noteworthy that in the latter case, both bulk moduli (392 ± 2 GPa and 400 ± 5.5 GPa for low-pressure and high-pressure data, respectively) are still lower than that of diamond, and actually lower (but within error bars) than the one obtained with one EOS fit of the entire data set.

These structural changes likely arise from changes in the electronic structure on compression and could be 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. Such transitions arise by passage of the Fermi surface through a topologic singularity [1]. In the most
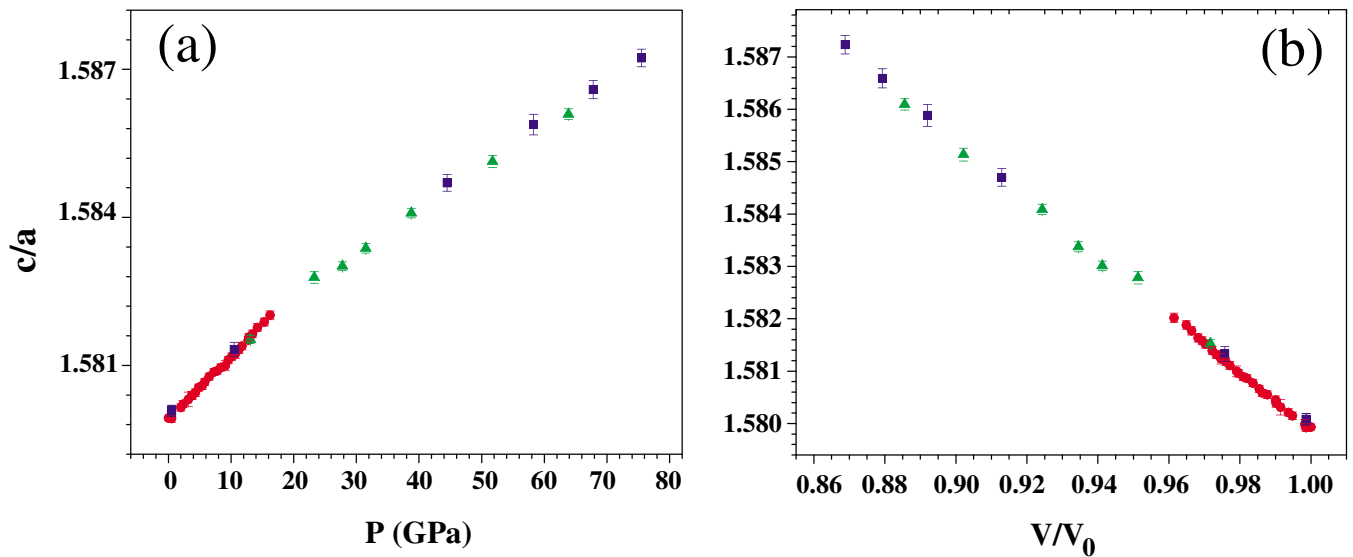

FIG. 3 (color online).   The c/a ratio of osmium versus pressure (a) and volume (b). The symbols are the same as in Fig. 2. The linear fits to the c/a versus pressure data yield $c/a = 1.57993 + 1.25049 \times 10^{-4} P + O(P^2)$ over the pressure range 0 to 25 GPa and $c/a = 1.58071 + 8.65348 \times 10^{-5} P + O(P^2)$ from 25 GPa to the highest pressure achieved in the study. The linear fit to the c/a versus reduced volume data yields $c/a = 1.63504 - 0.0552(V/V_0) + O(V^2)$.

studied example of zinc [8], recent calculations show that the transition arises from changes in the band structure near the high-symmetry point K where three bands, which lie above the Fermi level at zero pressure, cross the Fermi level upon compression. 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 small hole ellipsoid. While nontrivial, this hypothesis can now be experimentally verified either by single-crystal high-pressure inelastic x-ray scattering measurements or de Haas–van Alphen measurements with recently developed diamond anvil techniques [27,28]. Finally, our findings prove the importance of ultrahigh 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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[26] 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 the hcp-osmium were optimized at all volumes. A plane-wave energy cutoff of 400 eV was found to sufficient 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 thus calculated using a third-order Birch-Murnaghan isothermal equation of state.

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