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Ab initio study of high-pressure behavior of a low compressibility metal and a hard material: Osmium and diamond

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We performed Density-Functional electronic structure calculations in order to investigate the high pressure behavior of Os beyond what is tractable experimentally with a diamond-anvil cell. In addition to the room-temperature and pressure structure hcp, two hypothetical structures of Os have been considered: fcc and ω (hexagonal phase with three atoms by unit cell). Phase transitions are suggested by these calculations. For calculating the bulk modulus, the reciprocal of the compressibility, of Os and that of diamond, the computed total energies vs volume curves were fit to three different equations of state. Several volume ranges have been considered during the fitting procedure. First, it is shown that the claim of Cynn and co-workers [Phys. Rev. Lett. **88**, 135701 (2002)] is confirmed at weak compression. Osmium is less compressible than diamond which is known as the hardest and the least compressible material. However, with increasing pressure osmium becomes more compressible than diamond. At strong compression, osmium transforms to the ω phase. It is also shown that the reconstructive phase transition hcp→fcc could be induced by cooling in this low compressibility material.

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I. INTRODUCTION

Diamond is the high-pressure high-temperature polymorph of a light element, namely carbon. It exhibits several exceptional properties two of which are the hardness and the compressibility. With a hardness of 8400 HV, it is the hardest known material. It is also the least compressible material. This means that diamond can withstand high hydrostatic pressure and large shear stress without volume and shape changes. These elastic and mechanical properties are associated with the strong directional covalent bonds of diamond (see also Table I).

Osmium is a precious metal belonging to the platinum group (Pt, Pd, Rh, Ir, Ru)—so-called because these 4*d* and 5*d* transition metals commonly occur together as native alloys. Applications of platinum-group metals are numerous: catalytic converters for automobiles, catalysts in the chemical and petroleum industries, corrosion resistant components, high temperature components, thick-film resistors and conductors, dental alloys, jewelry, etc.[1] Osmium is the heaviest known metal. Taylor *et al.*[3] reported that the hardness of osmium is about 530 HV; when annealed it is the hardest of the platinum group. It is primarily used as an alloying element to increase the hardness of other metals and in particular the platinum group metals. It has been predicted for a long time that osmium is a low compressibility material.[4] This is correlated with the average number of electrons/atom in the *d*-band.[5] To date, the phase diagram of osmium is unknown. Two reasons can be invoked to explain the absence of polymorphs of Os. First, it has bad press. The solid metal is not affected by air at room temperature but the powdered metal slowly oxidize to form the tetroxide OsO_4 which boils at 130 °C (265 °F) and is extremely toxic.[1] The second reason is that very high pressures are required to transform the structure of this low compressibility metal (see below). In the pioneer work of Cynn *et al.*,[6] osmium has been compressed to 65 GPa with no indication of any phase change. Room-temperature high-pressure compression data were fit with the third-order Birch-Murnaghan equation of state by the authors who found that the bulk modulus of osmium is equal to 462(12) GPa while that of diamond is equal 443 GPa. The bulk modulus is the reciprocal of the compressibility. It expresses the material resistance to hydrostatic pressure. According to Cynn and co-workers,[6] osmium is the least compressible material. A new value of the buk modulus of Os, 395 GPa, has been proposed recently by Kenichi who employed helium as pressure-transmitting medium in the diamond anvil cell.[7] According to the author, the difference with the result of Cynn *et al.*,[6] who used argon, is due to better quasi-hydrostatic conditions, i.e., the magnitude of the

TABLE I. Some data of diamond and osmium associated with the strength of the chemical bonds (Refs. 1 and 2).

Property	Diamond	Osmium
Crystal structure	fcc	hcp
Atomic number	6	76
Coordination number	12	12
Lattice constants (a.u.)	6.72742	5.16802; 8.16229
Interatomic length (a.u.)	4.11969	5.0555
Atomic volume (cm^3/mol)	3.42	8.49
Melting point (°C)	3820	3050
Hardness, HV	8400	530
Bulk modulus (GPa)	443	
Shear modulus (GPa)	535	
Elastic constants (Mbar)		
C_{11}	107.6	
C_{12}	12.5	
C_{44}	57.7	

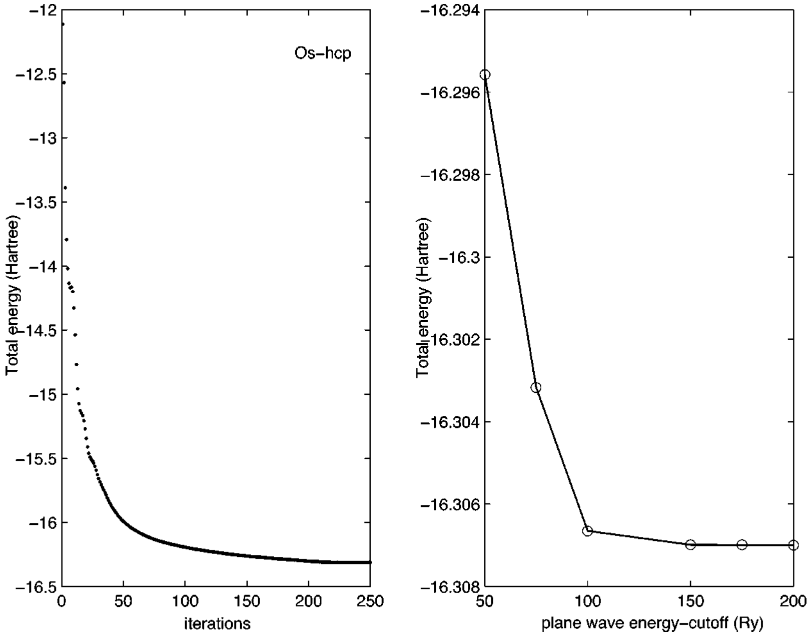

FIG. 1. Total energy convergence (fhi98md package, Ref. 13). Computed total energy of osmium as function of basis set size (right) and electronic self-consistency iterations (left).

residual uniaxial stress superimposed on the hydrostatic pressure is reduced. As the bulk modulus is often correlated to the hardness,[8] it has been considered for a long time as the best guide in the search of superhard materials. Cynn *et al.*[6] suggested that osmium compounds are potential candidates as superhard materials. The latter are intensively investigated because they have many industrial applications. Several transition metals are already involved in the formation of hard materials (Ti-, Nb-, W-, Zr—C, etc.). The purpose of the present theoretical work is to study the compressibility and the structural stability of Os at high pressure. The motivation is the search of new hard materials. Pressure-induced phase transitions can lead to new hard materials. For example, diamond, cubic boron nitride, and the stishovite are obtained under hydrostatic pressure from C_{60}, hexagonal BN and silicon dioxide SiO_2.[9–11] In the case of BN, heating is also required. High-pressure phases of transition metals can be also more harder than the zero-pressure phases. For example, the high-pressure ω phase of titanium is two times harder than the hcp phase. Moreover, the superconducting properties of ω phases are remarkable.[12] We then investigated the occurrence of the ω-Os phase under compression. Compressibility of osmium is calculated and compared to that of diamond. In this aim, the energy of these materials has been calculated as a function of the volume in the framework of the density functional theory (DFT). In order to calculate the bulk modulus of Os and diamond, the obtained curves were fit with equations of state. As the results are sensitive to the type of equation of state and to the volume range, three different equations of states and several volume ranges have been then considered.

The paper is organized as follows: In the next section, we first give the computational details and then develop the method of calculation of the compressibility. The stability of Os under compression is also studied. The main results are summarized in the third section.

II. STRUCTURAL PROPERTIES

A. Computational details

Total energy calculations were carried out in the framework of the DFT using the fhi98md package.[13] The valence electron wave functions were expanded in plane waves with the kinetic energy cutoff, E_{cut}, of 200 Ry and 250 Ry for osmium and diamond, respectively. Norm-conserving pseudopotential of Hamann[14] type in the fully separable form of Kleinman and Bylander[15] were employed. The pseudopotentials were generated with the $5d^6 6s^2$ and $2s^2 2p^2$ atomic configurations of osmium and carbon, respectively. The exchange and correlation terms were described with the local density approximation (LDA) of Ceperly and Adler[16] by the parameterization of Perdew and Zunger.[17] Damped Joannopoulos algorithm has been used to solve the minimization problem. For the Brillouin zone sampling we used a $4\times4\times4$ Monkhorst-Pack[18] mesh. For lack of information on osmium, the contribution of the vibrations of the lattice has been omitted. The numerical results given below correspond to the zero-temperature results. Figure 1 shows the total energy convergence as function of basis set size and electronic self-consistency iterations.

B. Compressibility of diamond

Before giving our predictions concerning osmium, we start with diamond for which first-principles equations of state (EOS) and data are available in the literature. We consider a large volume range, i.e., $V/V_o=0.4-1.6$. V_o is the volume at zero pressure. Equal compression and decompression have been considered during the fitting procedure. However for sake of simplicity, we will omit to mention the decompression in what follows. On the left, Fig. 2 shows the total energy vs volume curves of diamond. Our results, open circles, computed with a very large basis set coincide with that of Chelikowsky and Louie[19] (crosses). At large compres-

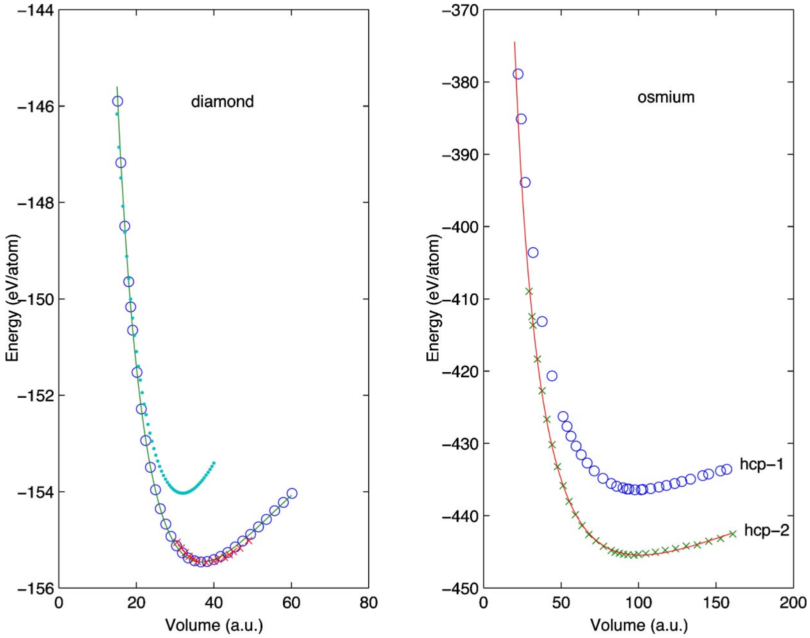

FIG. 2. (Left) Total energy of diamond as a function of volume (open circles). For comparison, results obtained by two other groups are reported [crosses (Ref. 19) and dots (Ref. 20)]. Solid line is the best fit which can be achieved with Vinet or Poirier-Tarantola EOS. (Right) Total energy of osmium as a function of volume with a small basis set (hcp-1) and a more larger basis set (hcp-2).

sion, they also coincide with the results of Biswas *et al.*[20] (dots). These latter authors used a small and a large basis set and found that the two curves approach each other closely as the volume is reduced. This behavior is attributed by the authors to the increase of the kinetic energy under compression. The solid line corresponds to the best fit of all open circles which can be achieved with Vinet EOS,[21]

$$E(\eta) = E_o + \frac{2B_oV_o}{(B_o'-1)^2} \times (2-(5+3B_o'(\eta-1)-3\eta)e^{-3(B_o'-1)(\eta-1)/2}) \quad (1)$$

or Poirier-Tarantola EOS,[22]

$$E(\varrho) = E_o + \frac{B_oV_o\varrho^2}{6}(3+\varrho(B_o'-2)), \quad (2)$$

where $\eta=(V/V_o)^{1/3}$ and $\varrho=-3\ln(\eta)$. V_o, B_o, B_o', and E_o, the total energy at zero pressure, are the fitting parameters. The results of the fits are summarized in Table II. It gives the bulk modulus at zero pressure, B_o, and its pressure derivative, B_o', for several volume ranges. V_o and E_o are not given explicitly but can be read directly on the curves. The Birch-Murnaghan[23] EOS

$$E(\eta) = E_o + \frac{9B_oV_o}{16}(\eta^2-1)^2(6+B_o'(\eta^2-1)-4\eta^2) \quad (3)$$

is based on the pressure expansion of the bulk modulus and consequently is valid only at moderate compression. In the

TABLE II. Bulk modulus at zero pressure B_o, in units of GPa, and its pressure derivative B_o' for six volume ranges and three different EOS. V_o is the equilibrium volume.

		Volume V/V_o					
EOS	Material	0.8–1.2	0.75–1.25	0.7–1.3	0.6–1.4	0.5–1.5	0.4–1.6
Vinet	Os	489	428	403	352	343	366
		8.2	6.2	5.1	3.9	3.8	3.2
	diamond	459	461	461	462	463	463
		3.6	3.6	3.6	3.6	3.6	3.7
Birch-Murnagnan	Os	497	426	397	350		
		8.0	6.3	5.1	3.7		
	diamond	457	460	459	457		
		3.6	3.5	3.6	3.5		
Poirier-Tarantola	Os	510	453	420	358	351	364
		7.0	6.1	5.1	4.1	3.9	3.1
	diamond	460	463	464	466	470	475
		3.6	3.6	3.6	3.6	3.7	3.7

case of diamond, the values of B_o and B'_o are almost constants. They do not depend on the type of EOS and on the volume range. This is correlated with the high stability of diamond. The value of B'_o is less 5 as it is for a large variety of materials. In nonlinear elasticity, B'_o can be expressed by means of third-order elastic constants C_{IJK} and represents partially the anharmonicity of the materials.[24] C_{IJK} can be measured by means of ultrasonic techniques. With respect to experiment, the bulk modulus of diamond deduced with Vinet[21] and Poirier-Tarantola[22] EOS are overestimated by less than 5% and 7.5%, respectively. The limits of validity of Vinet equation and of the classical equations of states have been discussed elsewhere.[25] We found that Vinet equation fits accurately the computed total energy vs volume curves. Poirier-Tarantola[22] EOS is as efficient as Vinet EOS.

C. Compressibility of osmium

The high-pressure behavior of osmium is more complex. Its hexagonal closed-packet (hcp) structure $(P6_3/mmc = D^4_{6h})$ possesses two atoms per unit cell. An optimization of the c/a ratio must first be achieved. We found that at 0 K c/a is equal to 1.7. The difference with respect to the experimental value, 1.6, does not change significantly the total energy. On the right, Fig. 2 gives the computed total energy of osmium as a function of the volume using a small basis set $(E_{\mathrm{cut}}=75\ \mathrm{Ry})$ and a large basis set $(E_{\mathrm{cut}}=200\ \mathrm{Ry})$. The two curves tend to each other at large compression. The solid line is the best fitting curve which can be achieved with Vinet or Poirier-Tarantola EOS. Table II gives the fitted values of B_o and B'_o. As in the case of diamond, one expects that they are overestimated by less than 10% with respect to the experimental values. On the contrary to that of diamond, they exhibit some anomalies which are pointed out below. Again, we will omit to mention the decompression. For a small compression i.e., $V/V_o: 1 \rightarrow 0.8$ or $p < 115$ GPa (see Table II and Fig. 3), the bulk modulus of Os is higher than that of diamond, or in other words, osmium is less compressible than diamond. Cynn *et al.*[6] reported diamond-anvil cell compression data up to 65 GPa, corresponding to the volume range $V/V_o: 1 \rightarrow 0.86$. For this volume range, the authors are then right. However, we note that the value of B'_o is very high, i.e., >5 (see Table II). In the volume range 0.8–0.75, the values of B_o and of B'_o decreases rapidly. Os becomes more compressible than diamond. Further compression tends to normalize the value of B'_o. At a reduced volume equal to about 0.7, the value of B'_o becomes normal, i.e., $\simeq 5$, while the softening of B_o continues. For large compression, $V/V_o: 0.7 \rightarrow 0.4$, we note that the difference between the highest value of B_o of osmium, 366 GPa, and the lowest value of that of diamond, 457 GPa, is now important. The softening of the bulk modulus is a precursor sign of an isostructural phase transition, i.e., same point group. The bulk modulus is associated with the volume strain, $e_v = (e_{11} + e_{22} + e_{33})/\sqrt{3}$, which plays the role of the order parameter of the phase change or is coupled to some order parameter.[26] The strain components e_{ii} express the relative variations of the lattice constants. In what follows, we investigate the structural stability of osmium.

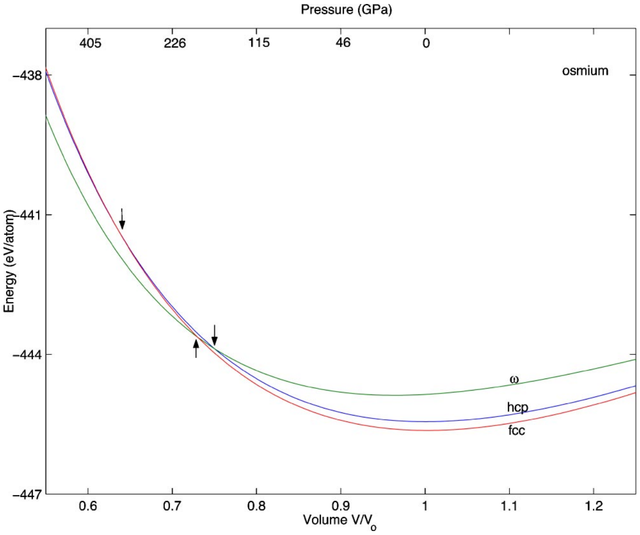

FIG. 3. Total energy vs volume for the hcp structure and two hypothetical structures of Os: fcc and ω $(D^1_{6h} = P6/mmm)$. V_o is the equilibrium volume of the hcp structure (see Fig. 2). Arrows show crossing points. Pressures at which occur phase transitions are given by the common tangents.

D. Phase transitions of Os

Under ambient conditions, most of the elements of the periodic table crystallize in the hcp, fcc, and bcc structures. Osmium and ten other transition metals crystallize in the hcp structure. Their transformations under compression are given in Table III. The following sequence hcp$\Rightarrow\omega\Rightarrow$bcc is observed in group IV transition metals (Ti, Zr, Hf). Actually, the bcc phase of Ti has not been yet observed. The ω phase is an hexagonal structure $(P6/mmm = D^1_{6h})$ with three atoms per unit cell located at (000), $\left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2}\right)$ and $\left(\frac{2}{3}, \frac{1}{3}, \frac{1}{2}\right)$. The c/a ratio of this structure is equal to about 0.612. As already mentioned, the mechanical and superconducting properties of ω phase are remarkable. For example, ω-Ti phase is two times harder than the α-Ti phase.[12] A hcp-fcc phase transition can be induced in cobalt by ball milling technique[27] or by heating.[28] We recomputed the total energy as function of the volume for two hypothetical structures of Os: fcc and ω. The fitting curves are plotted in Fig. 3. Each arrow shows a crossing point. The pressure at which a phase transition occurs can be deduced from the common tangent. However, for pressure-induced phase transitions it is more suitable to consider the enthalpy $H = P + PV$. At very low temperatures the cubic structure (fcc) is more stable than the hcp structure. On cooling, the reconstructive phase transition hcp→fcc could then occur. This type of structural transformation usually requires large atomic displacements and drastic reordering. From the H vs P curves which are not shown, we found that hcp structure could transform directly to ω phase at 840 GPa, while the fcc structure, if it occurs at low temperature, transforms first to hcp at 350 GPa and then to ω phase at 635 GPa. These hydrostatic pressures are beyond what is tractable experimentally in a diamond-anvil cell. However, phase transitions can be accelerated by shear stresses. For example, the first structural transformation of silicon, i.e.,

TABLE III. High-pressure (HP) phases of transition metals with hcp structure at room temperature and pressure (RTP). P_t is the pressure or pressure range at which the phase transition occurs. Tc, Ru, Os, and Re have been compressed to 10, 56, 65, and 251 GPa, respectively, without phase change (Refs. 6 and 36). $9R$ is the complex hexagonal structure of Sm-type. ω is an hexagonal structure with three atoms per unit cell. (see also Ref. 37.)

Transition metal	RTP phase	HP	Phases		P_t (GPa)	Ref.
Sc	hcp→	bcc			23	31
Ti	hcp→	ω			212	32
Co	hcp					
Y	hcp→	$9R\rightarrow$	dhcp→	fcc	10;26;39	33
Zr	hcp→	$\omega\rightarrow$	bcc		2–6;30	34
Tc	hcp					
Ru	hcp					
Lu	hcp→	$9R\rightarrow$	dhcp		18;35	35
Hf	hcp→	$\omega\rightarrow$	bcc		38;71	32
Re	hcp					
Os	hcp→	ω			840	this work

diamond to β-tin, occurs at about 12 GPa in a diamond-anvil cell, but at only 4 GPa beneath a nanoindenter.[29] Nanoindentation combined with micro-Raman spectroscopy and/or conductivity measurements[30] could reveal these phase transitions. Shock waves is another mean to realize such transformations. Due to the elevation of temperature during this type of experiment, solid metal should be used.

III. CONCLUSION

We have computed the total energy of osmium and diamond as function of volume. The obtained curves have been fitted with Vinet, Poirier-Tarantola and Birch-Murnaghan EOS in order to obtain the bulk modulus B_o and its pressure derivative B_o'. Different volume ranges have been considered during the fitting procedure. In agreement with Cynn *et al.*,[6] we found that osmium is less compressible than diamond at low compression, i.e., $p<115$ GPa. With increasing pressure, the bulk modulus softens and osmium becomes more compressible than diamond. The hcp structure of Os is expected to convert to a cubic phase (fcc) by cooling while under strong compression, it transforms to the hexagonal phase ω. This latter transformation can be realized beneath a nanoindenter where high hydrostatic and shear stresses are present. The ω phase possesses remarkable mechanical and superconducting properties.[12] Conductivity measurements during the indentation process are then advised. From these calculations, a primary phase diagram of Os could be drawn roughly.

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