Bulk modulus of Os by experiments and first-principles calculations

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Introduction

Osmium is an hcp metal located in the middle of the *5d* transition metal series in the periodic table. Recent powder x-ray diffraction experiments (Cynn *et al*. 2002) showed that the bulk modulus of Os is 462 GPa, exceeding the value for diamond, 443 GPa (Occelli *et al*. 2003). Since such a high value of bulk modulus is rare for metals, the report stimulated further experimental and theoretical studies. Here we report the results of our powder x-ray diffraction experiments with a He-pressure medium and first-principle calculations.

Experimental methods & results

Angle-dispersive powder x-ray diffraction experiments have been carried out with a diamond-anvil cell (DAC) at room temperature. The He-pressure medium was loaded to the DAC by using a gas-loading apparatus (Takemura *et al.* 2001). Diffraction patterns were taken on the beam line BL13 of the Photon Factory with monochromatic x-rays with energy of 30 keV and an imaging plate. We have employed a diamond-backing plate for the DAC to get better powder statistics (Takemura and Nakano 2003). Pressures were determined on the basis of the hydrostatic ruby pressure scale (Zha *et al*. 2000). More experimental details are given elsewhere (Takemura 2004).

Two experimental runs were done up to the maximum pressure of 58.2 GPa. Figure 1 compares the diffraction pattern of Os taken in the present experiment and that from the literature (Cynn *et al*. 2002). The angle-dispersive method used in the present experiment, combined with the excellent hydrostaticity of the He-pressure medium, gives diffraction patterns with high peak resolution. The lattice parameters *a* and *c* were determined with precision of +-0.02%. Ruby fluorescence spectra remained sharp up to the highest pressure investigated, with a negligible change in the R_1-R_2 peak separation, indicating good hydrostatic conditions (Chai and Brown 1996).

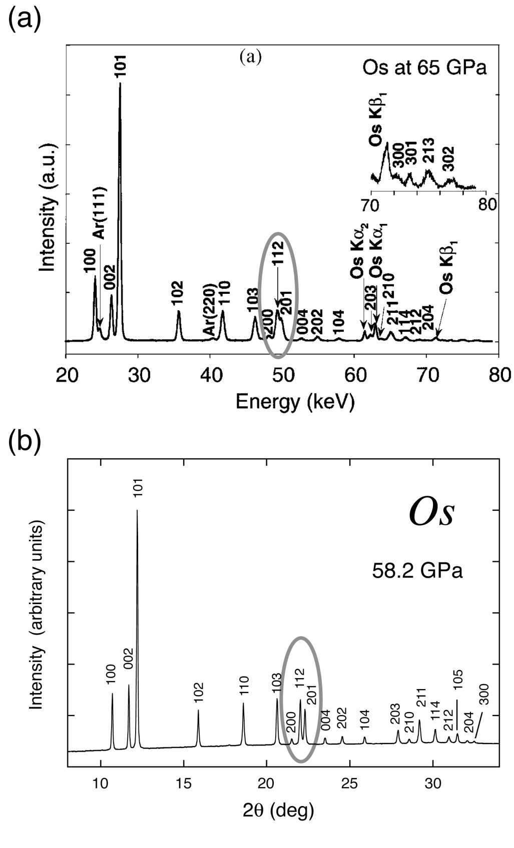

Fig. 1. Powder x-ray diffraction patterns of Os at high pressures by (a) energy-dispersive method with an Ar-pressure medium (Cynn *et al*. 2002) and (b) angle-dispersive method with a He-pressure medium (Takemura 2004). Difference in the peak resolution is seen, for example, at the circled positions.

Figure 2 shows the pressure-volume relationship. By fitting the Birch-Murnaghan equation of state, the bulk modulus and its pressure derivative were determined as 395(15) GPa and 4.5(5), respectively. Figure 3 shows the change of the *c/a* axial ratio with pressure. The axial ratio continuously increases from 1.580 to 1.586 without any anomaly.

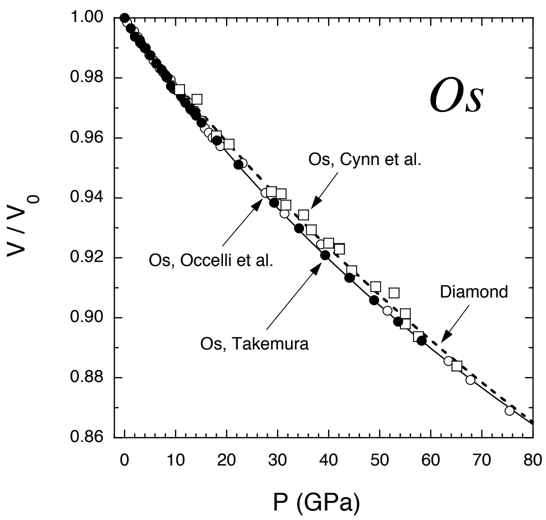

Fig. 2. Experimental equation of state for Os: squares (Cynn *et al*. 2002), filled circles (Takemura 2004), and open circles (Occelli *et al*. 2004). The equation of state for diamond (Occelli *et al*. 2003) is shown by the broken line.

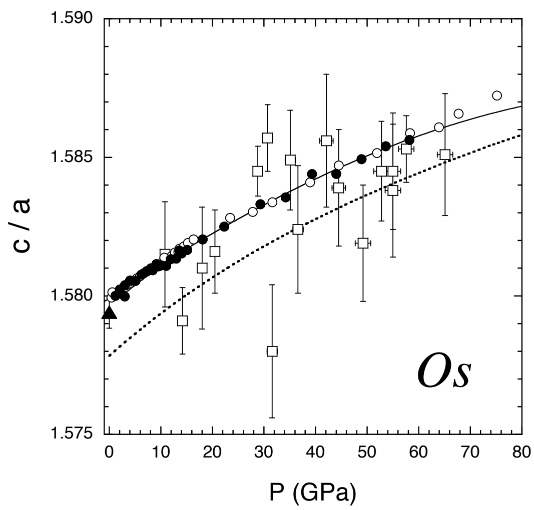

Fig. 3. The change in the *c/a* axial ratio of Os with pressure: squares (Cynn *et al*. 2002), filled circles (Takemura 2004), and open circles (Occelli *et al*. 2004). The dotted line shows the present calculation in the case B-GGA given in Table 1.

Computational methods & results

We performed first principles calculations on Os within density functional theory (Hohenberg and Kohn 1964, Kohn and Sham 1965). The exchange correlation energy functional (Exc) was treated with local density approximation (LDA) or generalized gradient approximation (GGA). To verify the accuracy, numerical calculations were performed with two types of computational schemes. The first is the all-electron type calculation, which incorporates core electrons in the self-consistent computations. We used WIEN2k (Blaha *et al*. 2001) package, which is based on the APW+lo method. The all-electron scheme has been considered to be the most accurate. However, it is difficult to evaluate stress directly. We must fit total energy as a function of volume to obtain the pressure. Thus, determination of bulk modulus B_0 and its derivative B_0' is less accurate. As another method, we used the pseudopotential scheme with wavefunctions expanded in plane waves. In this scheme, we treat valence electrons in first-principles pseudopotentials determined from atomic calculations. One advantage of the plane-wave pseudopotential (PWPP) method is that internal stress is directly obtained during the self-consistent calculations. Therefore, the shape of unit cell can be optimized through iterative methods such as molecular dynamics type simulations or conjugate gradient method.

The computational conditions are listed in Table 1. The case A is the computation with our own program code which implements the PWPP method with an optimized pseudopotential (Troullier and Martins 1991, Kobayashi 2001) in a separable form (Kleinman and Bylander 1982) and partial core correction (PCC) (Louie *et al*. 1982). The case B and C are the computations with ABINIT and WIEN2k packages. For all cases, calculated results were well converged about the number of k-points and the cut-off energy of wavefunctions.

Table 1. The computational conditions.

Case	Type	Program	Exc
A	PWPP	our own(kobayashi 2001)	LDA
B	PWPP	ABINIT	LDA and GGA
C	all-electron	WIEN2K	LDA and GGA

The calculated lattice properties are listed in Table 2. The equilibrium volumes are slightly scattered depending on the computational schemes. The deviations may be regarded as numerical errors contained within these calculations. However, the agreement of bulk modulus between calculations is rather good. We obtained the bulk modulus as 440~450 GPa with LDA and ~400 GPa with GGA. The LDA gives about 10% larger bulk modulus than that of GGA. It is well known that the LDA overestimates the cohesive energy and chemical bonding in solids. Therefore, the LDA gives larger bulk modulus. The calculated bulk modulus for GGA is close to the experimentally determined value 395 GPa (Takemura 2004). We have calculated lattice properties of diamond with the same computational condition for case B and C. It is found that diamond shows 5-10% larger bulk modulus than that of Os for all computational conditions. These results agree with experiment (Takemura 2004).

Table 2. Calculated equilibrium properties of hcp Os. Volume, *c/a* ratio, bulk modulus B_0, and its pressure derivative B_0' are tabulated for each calculation conditions.

Exc	Case	V (Å^3/atom)	c/a	B_0 (GPa)	B_0'
LDA	A	14.15	1.583	441	4.77
	B	13.79	1.577	451	4.82
	C	13.70	1.582	444	4.93
GGA	B	14.65	1.578	392	4.90
	C	14.26	1.580	404	4.67

The pressure derivative of bulk modulus B_0' of hcp Os is calculated as 4.67-4.90, which is higher than that of diamond. The higher B_0' means that Os may be less compressible than diamond at high pressures as shown in Fig. 4. As pressure increases, the calculated curves of diamond and Os cross at around 100 GPa.

Finally, relative stability of different crystal structures is evaluated by comparing hcp, fcc, and bcc Os. We found that the hcp structure is most stable as shown in Table 3. This is consistent with the experimental observation but not with the previous calculations (Hebbache and Zemzemi 2004). The fcc structure shows similar bulk modulus with the hcp but that of bcc is about 10% smaller than those for hcp and fcc.

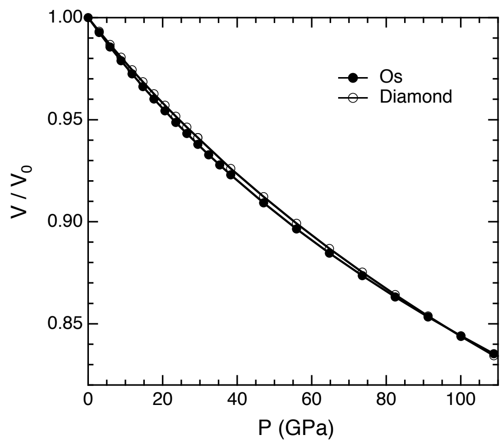

Fig. 4. The normalized volumes are plotted as a function of pressure for hcp Os (closed circle) and diamond (open circle). The results are taken from case B with GGA.

Table 3. Calculated equilibrium properties of Os with different crystal structures. Relative total energy (ΔE) from the hcp structure, unit cell volume V, bulk modulus B_0, and its pressure derivative B_0' are tabulated for each crystal structure. The computations were performed with case A.

	ΔE (eV/atom)	V (Å^3/atom)	B_0 (GPa)	B_0'
hcp	0	14.15	440.5	4.77
fcc	0.15	14.21	432.6	4.75
bcc	0.96	14.65	392.5	4.75

Discussion

The B_0 and B_0' values of Os determined by various experiments and theoretical calculations are summarized in Table 4, and plotted in Fig. 5. The present experimental and computational results are in excellent agreement with those by Occelli *et al*. (2004), in which the experiments were also done with the He-pressure medium. It should be noted that Cynn *et al*. (2002) used argon as a pressure medium, which is known to develop sizable nonhydrostatic stress at high pressures (Bell and Mao 1981). Nonhydrostatic stress distorts the crystal lattice, and hence the volume determined for such a distorted lattice can be different from the hydrostatic case (Singh *et al*. 1998). Another point to be mentioned is that the value of B_0' by Cynn *et al*. is 2.4, which is unusually small for metals. Since B_0' and B_0 are strongly correlated in the fitting procedure, a small change (increase) of B_0' in their fit will easily lower the B_0 value close to the present one and that by Occelli *et al*. Joshi *et al*. (2003) actually reanalyzed the data by Cynn *et al*. by assuming B_0' = 4, and obtained B_0 = 434 GPa.

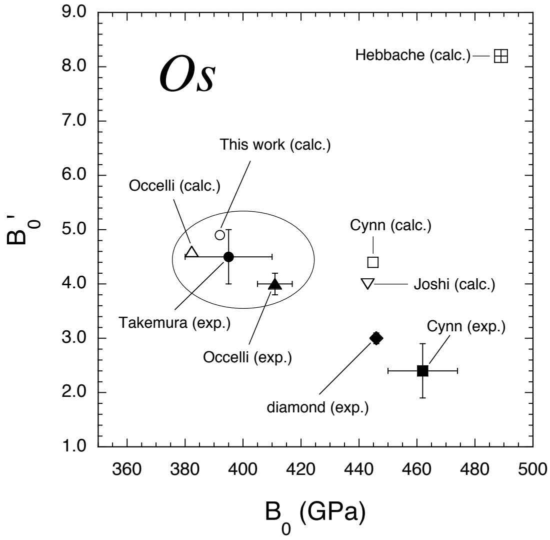

Fig. 5. Bulk modulus B_0 and its pressure derivative B_0' of Os by various expeiments and theoretical calculations. The values for diamond are from Occelli *et al*. (2003). The ellipsoid roughly indicates the most probable region of B_0 and B_0' for Os.

Theoretical calculations of the bulk modulus of Os by different groups are mostly in reasonable agreement as seen in Fig. 5. However, the recent calculation by Hebbache and Zemzemi (2004) significantly differs from others. In their calculation, B_0' and B_0 are strongly dependent on the volume range to be fitted; larger the volume range, both B_0' and B_0 become smaller. In our present calculation, we also observed the similar trend in the fitted values, although the variation of B_0' and B_0 was much smaller. This may indicate the inadequacy of the conventional equation of state formula for Os, suggesting further detailed investigations.

Finally, we like to mention that our experimental data do not support the suggestion by Occelli *et al*. (2004) that an electronic topological transition takes place in Os at about 25 GPa, evidenced by the change in the pressure derivative of the axial ratio. As seen in Fig. 3, the *c/a* ratio smoothly changes with pressure without any discontinuity. Our theoretical calculation of the change in the axial ratio qualitatively agrees with the experiment.

Table 4. Bulk modulus B_0, its pressure derivative B_0', and the equilibrium volume V_0 at atmospheric pressure of Os by experiments and theoretical calculations. The volumes in square brackets indicate the values from the literature, which were used to calculate the relative volume. The values by Hebbache and Zemzemi are for the volume range 0.8-1.2. The values in the present calculation are from B-GGA in Table 2.

	B_0 (GPa)	B_0'	V_0 (Å^3/atom)
Experiment (Cynn *et al*. 2002)	462(12)	2.4(5)	[13.978]
Experiment (Takemura 2004)	395(15)	4.5(5)	[13.988]
Experiment (Occelli *et al*. 2004)	411(6)	4.0(2)	13.971
Theory, LDA (Cynn *et al*. 2002)	444.8	4.4	13.749
Theory, GGA (Joshi *et al*. 2003)	443	4	14.336
Theory, GGA (Occelli *et al*. 2004)	382.3	4.60	
Theory, GGA (Hebbache and Zemzemi 2004)	489	8.2	
Theory, GGA (This work 2005)	392	4.90	14.65

Conclusion

We have determined the bulk modulus and its pressure derivative of Os as B_0 = 395(15) GPa and B_0'= 4.5(5), respectively, by powder x-ray diffraction experiments with a He-pressure medium. These values are in excellent agreement with those obtained by independent experiments with the He-pressure medium (Occelli *et al*. 2004). Our first-principles calculation with the FLAPW method gave values of B_0 and B_0' consistent with these results. We thus conclude that Os is actually stiff, but its bulk modulus does not exceed the value for diamond.

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