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Bulk modulus of osmium: High-pressure powder x-ray diffraction experiments under quasihydrostatic conditions

Takemura Kenichi*
National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

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High-pressure powder x-ray diffraction experiments have been carried out on Os at room temperature under quasihydrostatic conditions with a He-pressure medium. By fitting the pressure-volume data up to 58 GPa, the bulk modulus and its pressure derivative are determined to be $B_0 = 395(15)$ GPa and $B_0' = 4.5(5)$. The bulk modulus of Os is smaller than that for diamond, in contrast with the conclusion drawn in a recent work [H. Cynn, *et al.* Phys. Rev. Lett. **88**, 135701 (2002)].

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Osmium is one of the heavy transition metals located in the middle of the Periodic Table. It has an hcp structure and the highest density among the elements under ambient conditions of pressure and temperature. Dense substances are incompressible, and hence one may expect a large bulk modulus for Os. The Friedel model explains that the cohesive energy of Os is high due to the half filling of the *d* bands, giving rise to a large bulk modulus.[1] Indeed, recent experiments by Cynn *et al.*[2] showed that the bulk modulus for Os is 462 GPa, higher than that for diamond (442–446 GPa).[3,4] It should be mentioned, however, that the experiments were done with Ar as a pressure-transmitting medium, which is known to give large nonhydrostatic stress above about 9 GPa.[5,6] Nonhydrostatic stress produces a systematic error in volume determined by powder x-ray diffraction experiments.[7,8] Pressures determined by the ruby luminescence method are also affected by the nonhydrostatic stress.[9] In this regard, it is important to carry out x-ray diffraction experiments on Os under better quasihydrostatic conditions. In the present study we have employed helium as a pressure medium, which offers the best quasihydrostatic conditions. We show that the bulk modulus for Os is actually high, but does not exceed the value for diamond.

High-pressure powder x-ray diffraction experiments were carried out with a diamond-anvil cell (DAC). Two experimental runs were done up to a maximum pressure of 58 GPa. Run A covered the pressure range up to 15 GPa. Although helium solidifies at about 12 GPa at room temperature, the stress conditions can safely be considered as purely hydrostatic in this pressure range. We used diamond anvils with 600 μm culet, and a spring steel gasket with a hole of 250 μm diameter and 110 μm thickness. Run B extended the pressure to 58 GPa. The stress conditions were quasihydrostatic in this case. The degree of nonhydrostaticity was, however, found to be negligibly small as explained later. We used diamond anvils with 310 μm culet, and a Re gasket with a hole of 100 μm diameter and 46 μm thickness.

A fine powder of Os with stated purity of 99.8+% (Alfa Aesar) was used without further treatment. The average particle size was less than 5 μm. A small amount of the Os powder was put in the gasket hole together with tiny ruby spheres (less than 4 μm in diameter) for pressure measurement. Helium was loaded to the DAC at room temperature by using a high-pressure gas-loading system operating at a gas pressure of 180 MPa.[10] After loading helium, the diameter of the gasket hole decreased to about 70%, but we still observed transparent light coming through the area surrounding the sample. This ensured that enough of an amount of the He-pressure medium filled the gasket hole. We used a diamond backing-plate for the support of the diamond anvil to observe full diffraction rings.[11] Pressures in the DAC were determined with the ruby luminescence method with precision of ±0.1 GPa on the basis of the hydrostatic ruby pressure scale.[12] It is known that the pressure in the DAC varies with time due to the relaxation of the gasket deformation after each pressure change. We thus took diffraction patterns at least after 30 min from a pressure change in order to stabilize the pressure. Angle-dispersive powder x-ray diffraction patterns were taken on the multipole wiggler beamline BL-13A at the Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK). The incident x rays were monochromatized to a wavelength $\lambda = 0.4252$ (run A) or 0.4248 (run B) Å, and collimated to the size of 75 μm (run A) or 15 μm (run B) in diameter. Diffraction patterns were recorded on imaging plates, and analyzed with the pattern integration program PIP.[13] Typical exposure times were 2 min. All the experiments were done at room temperature.

It is important to achieve hydrostatic (or quasihydrostatic) conditions in order to get reliable values of bulk modulus and its pressure derivative. The stress conditions in the present experiments are checked in the spectral shape of the ruby luminescence line.[9] The peak width of the R_1 line and the R_1-R_2 splitting showed no change with pressure in run A. In run B, the peak width and splitting remained constant up to 40 GPa, above which they slowly increased with pressure. The increase in the R_1 peak width and the R_1-R_2 splitting amounted to about 25 and 12%, respectively, at 58 GPa. These values are considerably small compared with those under nonhydrostatic conditions. With a methanol-ethanol mixture, for example, the increase becomes 5–10 times larger at the same pressure. We therefore conclude that good quasihydrostatic conditions are maintained in the present experiments.

Figure 1 shows the two-dimensional diffraction pattern and the integrated diffraction profile taken at the highest

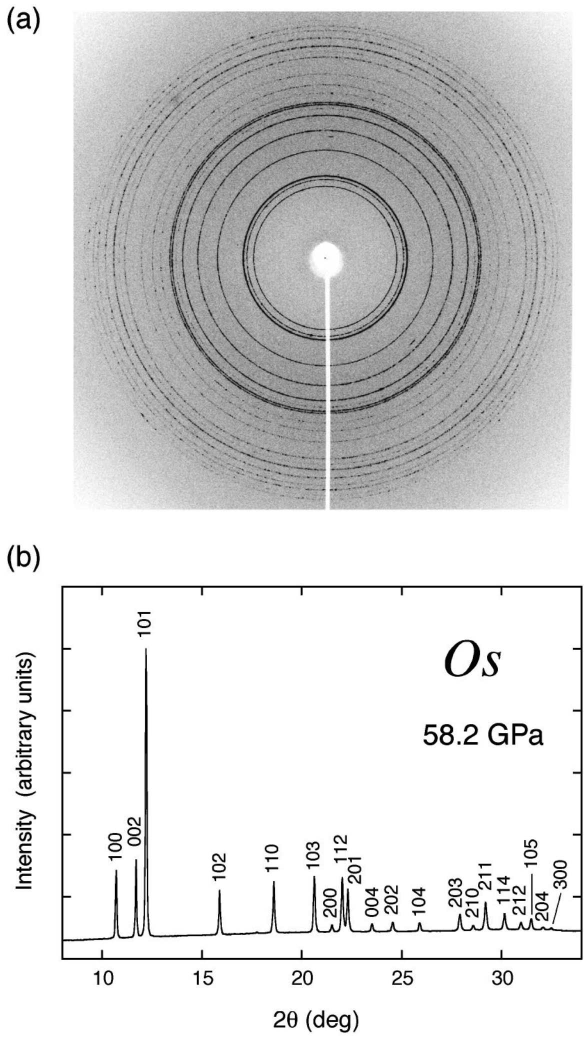

FIG. 1. Powder x-ray diffraction pattern of Os at 58.2 GPa. The x-ray wavelength was 0.4248 Å. (a) Two-dimensional diffraction pattern taken on an imaging plate and (b) the integrated diffraction profile.

TABLE I. Structural data of Os under high pressure. The lattice parameters and the axial ratio at atmospheric pressure are taken from Ref. 14: $a=2.7348(9)$ Å, $c=4.3193(6)$ Å, and $c/a=1.5794(6)$. The errors in a, c, c/a, and V/V_0 given in parentheses are from least-squares fits. The run AD indicates the data taken on decreasing pressure.

P (GPa)	a (Å)	c (Å)	c/a	V/V_0	Run
1.2(1)	2.7313(1)	4.3155(2)	1.5800(1)	0.9966(1)	A
2.1(1)	2.7286(1)	4.3119(1)	1.5802(1)	0.9938(1)	A
3.0(1)	2.7268(1)	4.3094(2)	1.5804(1)	0.9919(1)	A
4.0(1)	2.7249(1)	4.3068(1)	1.5806(1)	0.9899(1)	A
5.1(1)	2.7228(1)	4.3035(1)	1.5805(1)	0.9876(1)	A
6.2(1)	2.7202(1)	4.3000(1)	1.5808(1)	0.9850(1)	A
7.3(1)	2.7182(1)	4.2971(1)	1.5809(1)	0.9828(1)	A
8.1(1)	2.7164(1)	4.2946(1)	1.5810(1)	0.9810(1)	A
9.1(1)	2.7129(1)	4.2895(2)	1.5812(1)	0.9773(1)	A
10.0(1)	2.7119(1)	4.2878(1)	1.5811(1)	0.9761(1)	A
11.0(1)	2.7100(1)	4.2847(2)	1.5811(1)	0.9741(1)	A
11.9(1)	2.7077(1)	4.2817(1)	1.5813(1)	0.9717(1)	A
13.0(1)	2.7056(1)	4.2785(1)	1.5813(1)	0.9695(1)	A
14.0(1)	2.7036(1)	4.2759(1)	1.5815(1)	0.9675(1)	A
15.1(1)	2.7013(1)	4.2726(1)	1.5817(1)	0.9651(1)	A
9.6(1)	2.7122(1)	4.2881(1)	1.5811(1)	0.9764(1)	AD
3.0(1)	2.7278(1)	4.3098(1)	1.5800(1)	0.9927(1)	B
8.4(1)	2.7158(1)	4.2935(1)	1.5809(1)	0.9802(1)	B
13.6(1)	2.7045(1)	4.2776(1)	1.5816(1)	0.9685(1)	B
18.1(1)	2.6955(1)	4.2644(1)	1.5820(1)	0.9591(1)	B
22.3(1)	2.6877(1)	4.2532(1)	1.5825(1)	0.9511(1)	B
29.3(1)	2.6752(1)	4.2357(3)	1.5833(1)	0.9384(1)	B
34.2(1)	2.6669(1)	4.2233(2)	1.5836(1)	0.9299(1)	B
39.3(1)	2.6579(1)	4.2112(1)	1.5844(1)	0.9209(1)	B
44.0(1)	2.6506(1)	4.1996(1)	1.5844(1)	0.9134(1)	B
48.9(2)	2.6431(1)	4.1891(2)	1.5849(1)	0.9059(1)	B
53.6(2)	2.6358(1)	4.1789(2)	1.5854(1)	0.8987(1)	B
58.2(3)	2.6295(1)	4.1693(3)	1.5856(1)	0.8923(1)	B

pressure. Sharpness of the diffraction peaks is another indication of good quasihydrostaticity. The lattice parameters a and c are determined with precision of ±0.02% from the well-resolved twenty reflections. Table I lists the lattice parameters, axial ratio, and relative volume as a function of pressure.

Figure 2 shows the pressure-volume relationship of Os. Runs A and B give consistent results. The scatter of the present data is much smaller compared with the previous data.[2] The pressures by Cynn *et al.* are systematically higher than the present ones by about 2–4 GPa. The bulk modulus B_0 and its pressure derivative B_0' at atmospheric pressure are determined by fitting the Birch-Murnaghan equation of state (EOS) to the present data. First, the relative volume at atmospheric pressure is fixed to 1, as is frequently done in the EOS fitting. If we fit the data under hydrostatic conditions up to 15 GPa (run A), we obtain $B_0=384(9)$ GPa and $B_0'=5.8(17)$. The errors in parentheses simply indicate the fitting errors. The pressure derivative B_0' contains large uncertainty due to the small pressure range fitted. It is better constrained by fitting all the data in runs A and B. The fit gives $B_0=395(2)$ GPa and $B_0'=4.5(1)$. The values fitted with the Vinet-type EOS[15] agree with these within the fitting errors. Second, we allow the relative volume at atmospheric pressure to be variable. We then obtain the values $B_0=406(4)$ GPa, $B_0'=4.2(2)$, and $V/V_0=0.9994(2)$ for the data set from runs A and B. By considering the differences in the first and second fitting procedures, we estimate the maximum uncertainty in B_0 to be about ±15 GPa. The final value of the bulk modulus of Os is hence $B_0=395(15)$ GPa with $B_0'=4.5(5)$, which is considerably smaller than the previous determination $[B_0=462(12)\text{ GPa}]$.[2] The bulk modulus of diamond and its pressure derivative have recently been determined to be $B_0=446(1)$ GPa and $B_0'=3.0(1)$ with a He-pressure medium.[16] The EOS for diamond calculated with these values is shown in Fig. 2. It is clear that Os is more compressible than diamond.

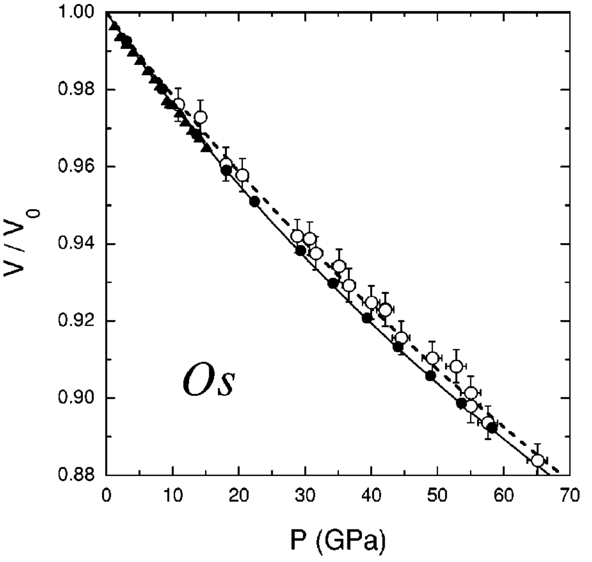

FIG. 2. Pressure-volume relationship for Os. Solid triangles and circles represent the present data in runs A and B, respectively. Open circles are the data by Cynn *et al.* (Ref. 2). The experimental errors in volume and pressure in the present data are smaller than the size of the symbols. Solid curve is a fit of the Birch-Murnaghan EOS to the present data with $B_0=395$ GPa and $B_0'=4.5$. The broken curve shows the EOS for diamond calculated with the Vinet formula with $B_0=446$ GPa and $B_0'=3.0$ (Ref. 16).

Since helium atom is so small, it would be necessary to discuss whether the helium-pressure medium diffuses into the Os lattice and eventually affects the equation of state. Unlike hydrogen, the solubility of helium in metals is extremely low.[17] As seen in Table I, the lattice parameters obtained at low pressures smoothly connect the values at atmospheric pressure from the literature. The data taken on decreasing pressure agree with the data taken on increasing pressure. These facts indicate that no diffusion occurs at least at low pressures. A high-pressure experiment on forsterite, however, suggests that the helium-pressure medium possibly diffuses into the crystal lattice at high pressures.[18] If we assume that the diffusion of helium also occurs for Os above some critical pressure, the volume of Os above the pressure should become systematically larger than that without helium diffusion. It follows that the presently determined bulk modulus is larger than the "correct" one, and Os without hypothetical helium diffusion is even more compressible than diamond.

Figure 3 shows the change in the c/a axial ratio with pressure. The present data smoothly connect the value at atmospheric pressure from the literature. The c/a axial ratio increases with pressure, in qualitative agreement with the previous results.[2]

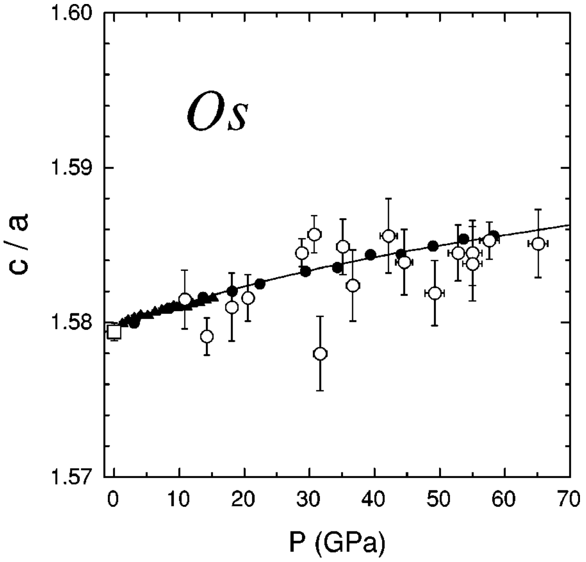

FIG. 3. The change in the c/a axial ratio of Os with pressure. Solid symbols show the present data and have the same meaning as in Fig. 2. Open circles are the data by Cynn *et al.* (Ref. 2). Open square indicates the value at atmospheric pressure (Ref. 14). Solid curve is a guide to the eyes.

In the powder x-ray diffraction experiments with a DAC, bulk moduli determined under nonhydrostatic conditions are larger than those obtained under hydrostatic conditions. This is due to the combined effects of the anisotropic deformation of the crystal lattice under nonhydrostatic stress and the particular x-ray diffraction geometry.[19] Cynn *et al.* reported an unusually small pressure derivative of the bulk modulus $B_0'=2.4$. This is seen in Fig. 2 as the approach of their data to the present ones in the high-pressure region. Similar trends are often observed in the pressure-volume curves measured under nonhydrostatic conditions. One of the plausible explanations is the decrease of nonhydrostatic stress in the sample chamber due to the elastic deformation of diamond anvils at high pressures. We infer that the experiments by Cynn *et al.*[2] suffered from nonhydrostatic stress, yielding a systematically large bulk modulus and small pressure derivative.

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*Electronic address: takemura.kenichi@nims.go.jp

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