Osmium has the Lowest Experimentally Determined Compressibility

Hyunchae Cynn, John E. Klepeis, Choong-Shik Yoo, and David A. Young
Lawrence Livermore National Laboratory, University of California, Livermore, California 94550
(Received 8 June 2001; published 14 March 2002)

On the basis of high pressure diamond-anvil compression studies for the precious metals Ru, Ir, and Os we report the surprising discovery that metallic osmium has a lower compressibility than covalently bonded diamond. We also find that Ir and Ru are as incompressible as Re. In addition, we have performed first principles calculations that confirm the trend in the measured transition metal compressibilities.

DOI: 10.1103/PhysRevLett.88.135701 PACS numbers: 64.30.+t, 31.15.Ar

Compressibility (reciprocal of the bulk modulus) is an important physical property of a material, providing useful information about material strength, chemical bonding, and electronic structure. Strongly bonded materials have short interatomic distances and correspondingly strong repulsive interatomic forces, leading to high bulk moduli. The bulk modulus has been correlated empirically with the interstitial electron density [1], cohesive energy [2], and mechanical hardness [3].

Diamond is the hardest known material and also has the highest known bulk modulus, $B_0 = 443$ GPa (or the lowest compressibility, $\beta = 0.226$ Mbar^{-1}) [4]. Recent studies on quenched high density ZrO_2 and TiO_2 report bulk moduli of 444 and 431 GPa, respectively [5]. A newly discovered polymeric form of carbon dioxide also shows a high bulk modulus of 365 GPa [6], similar to that of cubic boron nitride, 369 GPa [7]. We note that most of these materials are metastable phases quenched from high pressures and temperatures. However, 5*d* transition metals also have very high bulk moduli, with an early estimate for osmium on the basis of trends in cohesive energies indicating a value close to that of diamond [8]. In addition, the Vickers hardness number for Os is the highest among the metals [9]. It is intriguing that a light, covalently bonded element such as diamond and a heavy, metallic element such as osmium, with very different chemical bonding, would both have large values of the bulk modulus. However, osmium is one of the least studied of the elements and to date no high-pressure experiments have been carried out in order to directly measure the bulk modulus.

We report diamond-anvil cell compression studies to 60 GPa for the transition metals ruthenium, iridium, and osmium. Os and Ru occur in the hexagonal close-packed (hcp) structure while Ir has the face-centered cubic (fcc) structure. In addition to the equation of state (EOS), we have also measured the c/a ratios to high pressure for the hcp metals Os and Ru. Our experimental results are also compared with the results obtained by first principles electronic structure calculations of the EOS for C, Os, Ir, Re, Ru, and W. Re has been reported as a strong metal [10] and is used in gaskets for ultra-high-pressure diamond-anvil cell experiments. W and Re are often used as internal pressure standards for high-pressure experiments.

The Friedel model describes parabolic trends in the equilibrium volume and cohesive energy as a function of *d*-band filling for each of the rows of transition metals in the periodic table [11]. In order to verify this trend in 5*d*-transition metals, it is necessary to measure the EOS to high pressures and at room temperature. We believe that to date there is no experimentally measured compressibility data at high pressures available for Os, although there are two theoretical estimates of 476 GPa [12] and 419 GPa [13] for the bulk modulus. An early experimental study showed that Ir is a stiff metal [14] and B_0 was estimated to be 306 (± 23) GPa on the basis of compression to 65 GPa [15]. This value of B_0 is low compared to the 355 GPa estimate obtained by extrapolating the trend in the bulk modulus as a function of the cohesive energy for the transition metals [8]. This low measured value might be due to unknown additional x-ray diffraction peaks above 60 GPa [15]. Clendenen and Drickamer compressed Ru to 40 GPa [16], yielding $B_0 = 98$ GPa using a third-order Birch-Murnaghan EOS to fit the data. They also found anomalous values of the hcp c/a ratio. However, this work did not include the most important hcp (002) diffraction line in the estimate of the volumes and c/a ratio, which could negatively impact the accuracy of the data.

In our experiments condensed Ar was used as a pressure medium in order to reduce uniaxial compression of the sample, and ruby grains smaller than 3 μm in diameter were used as a pressure standard [17]. The samples were contained inside a small hole (80 μm in diameter) drilled into a rhenium gasket. The Os, Ru, and Ir powder samples had grain sizes less than 5 μm (99.8+ purity, Alfa Aesar). The measured diffraction patterns were dispersed either in energy using unfocused white x rays from the superconducting wiggler beam line X17C at the National Synchrotron Light Source (NSLS), or in angle using focused monochromatic x rays at 20 keV from the wiggler beam line 10-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). In both cases a small x-ray collimator (10–30 μm in diameter) was used to minimize diffraction lines from the Re gasket. In this study the diffraction patterns for Os, Ir, and Ru were obtained to 65, 55, and 56 GPa, respectively. The details of our x-ray experiments have been described elsewhere [18,19].

Figure 1a shows a typical energy-dispersive x-ray diffraction pattern for Os at 65 GPa, consisting of the diffraction lines from hcp Os and fcc Ar (pressure medium), and the x-ray emission lines from Os. The pressure was measured using the luminescence lines from ruby grains [17] at the center of the gasket, which agrees well with that determined from the Ar diffraction lines [20]. The strong appearance of the (002) diffraction line with a nearly ideal intensity for hcp indicates a relatively small uniaxial stress and thus a low degree of preferred orientation in the sample. This observation is also consistent with the small measured pressure gradient of 0.5 GPa per 100 μm. The synchrotron x-ray Debye-Scherrer diffraction ring pattern for hcp Ru at 56 GPa (Fig. 1b) shows a similarly strong appearance of the (002) reflection. Eight peaks were used to estimate the volume of Ru. In the case of fcc Ir we did not find any evidence for a phase change [14] or the appearance of a superlattice [15] up to 55 GPa.

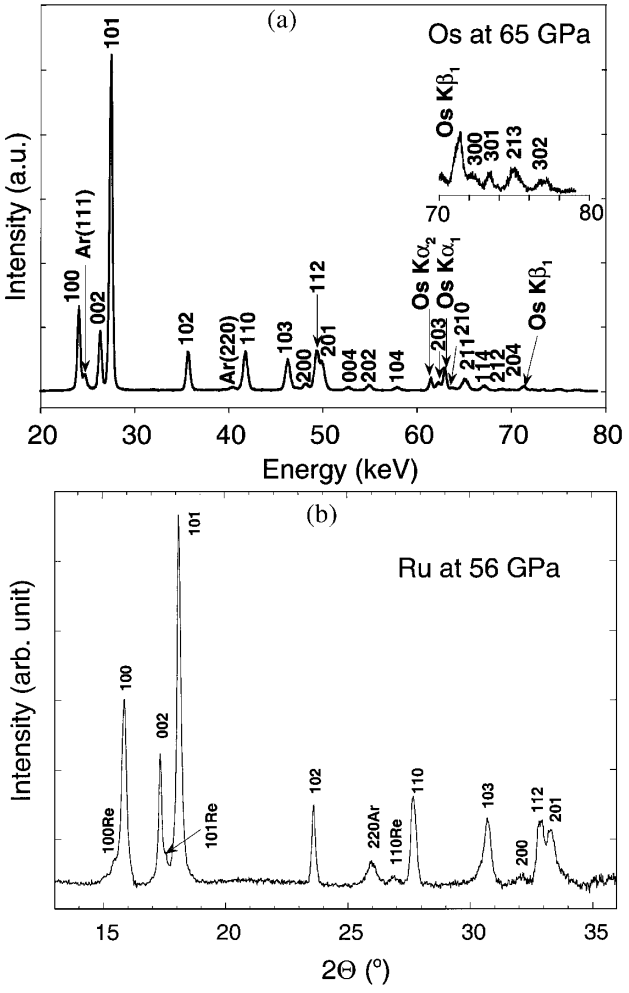

FIG. 1. Energy-dispersive x-ray diffraction pattern for hcp Os at 65 GPa in (a). Inset shows an expanded view from 70 to 80 keV. Angle-dispersive x-ray diffraction pattern for hcp Ru at 56 GPa in (b). The Ar and Re peaks are marked. The refined result for the lattice constants of Os is $a = 2.5907$ (± 0.0014) Å and $c = 4.1161$ (± 0.0017) Å.

The measured compression data for Os, Ir, and Ru were fit with third-order Birch-Murnaghan EOS and the resulting fit parameters are listed in Table I. Our EOS data and fits are shown in Fig. 2, together with the previous compression data for diamond [4], Re [21], and W [22] for the purpose of comparison. The trend shown among the EOS curves indicates that for the transition metals compressibility decreases in the order W $\rightarrow$ Ru $\rightarrow$ Re $\rightarrow$ Ir $\rightarrow$ Os. We note that our experimentally determined bulk modulus for Os at ambient conditions is 462 GPa, even greater than the value of 443 GPa for diamond (see Table I). In the case of the earlier diamond experiments [4] there is a large uncertainty in the magnitude of the first pressure derivative of the ambient bulk modulus (B_0') depending on the ruby pressure scale. However, B_0 was 444 GPa regardless of pressure scales. We chose the EOS parameters [4] obtained using the same ruby pressure scale [17] as ours to assure consistency to compare P-V/V_0 curve for diamond with others. It is notable that the P-V/V_0 curve for diamond is lower than the EOS fit for Os at high pressures (Fig. 2).

Given the relatively small differences between the ambient bulk moduli of diamond and Os, we have carried out a number of checks in order to confirm the robust nature of our results. In addition to the Birch-Murnaghan EOS, we have also fit our data using the EOS forms proposed by Holzapfel [22] and Vinet *et al.* [22]. We obtain almost identical results for Ru, Ir, and Os. The particular choice of the EOS form would thus appear to have very little effect on our reported values of B_0. The previous compression data for diamond used the same Birch-Murnaghan EOS form by Aleksandrov *et al.* (1992) [4] and also found that the bulk modulus was insensitive to the precise details of the fitting.

As an independent check we have also considered the bulk moduli obtained at zero pressure using other experimental methods. The ultrasonic results of the zero-pressure adiabatic bulk modulus of diamond yields a value of 443 GPa by McSkimin and Bond [4]. Unfortunately, we are not aware of a similar experimental result for Os. However, by using the measured Young's modulus and an estimate for the shear modulus of Os, Narayana and Swamy [23] extracted an ultrasonic velocity and an adiabatic bulk modulus of 451 GPa for Os at ambient conditions. This result is also larger than the value measured for diamond and provides independent evidence that Os does indeed have a lower compressibility than diamond. However, the indirect and approximate nature of this zero-pressure result for Os does not allow for an unambiguous conclusion by itself.

In order to provide yet another independent check we have carried out full-potential linear muffin-tin orbital [24,25] calculations of the EOS for fcc Ir, hcp Os, hcp Re, hcp Ru, body-centered cubic (bcc) W, and diamond-structure C. The calculations are based on the local

TABLE I. Third-order Birch-Murnaghan parameters from fits to experimental and theoretical EOS for low-compressibility elements. The standard deviations for the experimental fits are given in parentheses. References are in brackets. The form of the third-order Birch-Murnaghan EOS is as follows: $P = (3/2)B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}]\{1 - (3/4)(4 - B_0')[(V/V_0)^{-2/3} - 1]\}$.

	Experiment				Theory			
	V_0 (Å^3/at)	B_0 (GPa)	B_0'	c/a	V_0 (Å^3/at)	B_0 (GPa)	B_0'	c/a
Os	13.978 [26]	462 (12)	2.4 (0.5)	1.580	13.749	444.8	4.4	1.584
Ir	14.145 [27]	383 (14)	3.1 (0.8)		13.880	402.7	4.8	
Re	14.713 [28]	372 [21]	4.05 [21]	1.613 [21]	14.403	400.5	4.3	1.617
Ru	13.574 [26]	348 (18)	3.3 (0.8)	1.584	13.138	364.0	4.8	1.584
W	15.854 [27]	308 [22]			15.450	332.8	4.3	
C	5.672 [28]	443 [4], 444 [4]	1–2.5 [4]; 4 [4]		5.505	467.1	3.6	

density approximation (LDA) and are scalar-relativistic. Spin-orbit interactions were not included. In the case of the three hcp metals, the total energy was minimized as a function of c/a at a range of fixed volumes in order to determine the theoretical values of c/a as a function of volume.

The trend in the ordering of the transition metal bulk moduli is the same for both the experimental measurements and the theoretical calculations, as shown in Table I. The fits to the calculations use the same third-order Birch-Murnaghan form as was used for the experimental data, although in the case of the experimental fits the volumes at ambient conditions (V_0) were constrained using previously measured values [26–28]. We note in particular that Re is more compressible than Os and Ir, in contrast to a previous report that Re has the highest bulk modulus among metallic elements [10]. With the exception of Os, the theoretical bulk moduli are 5%–8% larger than the experimental values. This difference is due in part to the fact that the theoretical bulk moduli are calculated at the theoretical equilibrium volumes, which are systematically underestimated within the LDA (see Table I). The neglect of spin-orbit interactions may also play a role in the case of the 5d transition metals. Although the theoretical value of B_0 for diamond is higher than that for Os, the difference is within the range of uncertainty in the LDA, and does not change our conclusion, which is based on our experimental results. Moreover, the calculations do confirm that the bulk modulus of Os is the largest among the transition metals and that it is comparable to that of diamond.

Extrapolation of our measured hcp c/a ratios to ambient conditions for Os and Ru gives 1.580 and 1.584, respectively (Table I and Fig. 3). These values are in excellent agreement with the theoretical c/a ratios, further validating the comparison between experiment and theory in the case of the trends in the bulk moduli. The measured c/a ratios appear to increase slightly with increasing pressure, moving closer to the ideal c/a of 1.633, although the changes are still within the experimental uncertainties (Fig. 3). The calculations (not shown) exhibit the same trend of increasing c/a with increasing pressure. We note that the c/a ratios for Os and Ru deviate substantially from the ideal value and that the same is true for hcp Fe with a measured c/a of 1.603 [29]. The measured deviations from the ideal c/a among the

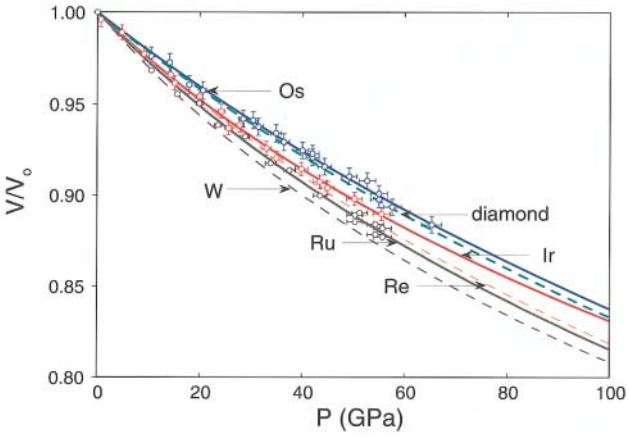

FIG. 2 (color). Volume compressions for Os, Ir, Re, Ru, W, and C. Previously measured Re (orange dashed line) [21], W (purple dashed line) [22], and diamond (green dashed line) [4] data were included for comparison. Error bars are shown for Os, Ir, and Ru.

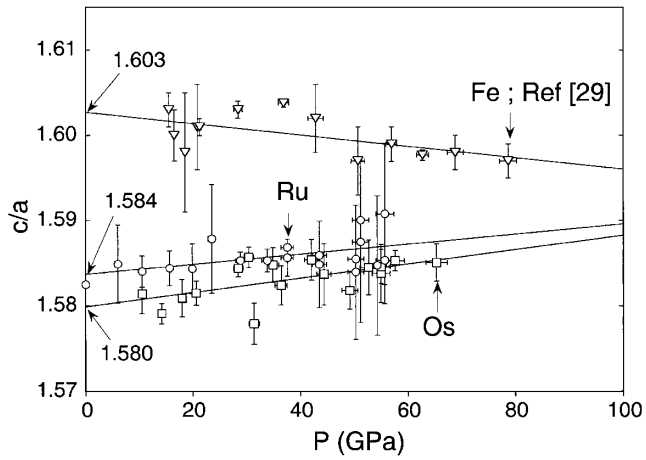

FIG. 3. Plot of experimentally measured c/a ratios for Fe (inverted triangles) [29], Ru (open circles), and Os (open squares) at high pressures and including error bars. The solid lines are linear fits to the data and are shown as guides to the eye.

hcp Group VIIIA elements increase in the following progression: $3d(\mathrm{Fe}) \rightarrow 4d(\mathrm{Ru}) \rightarrow 5d(\mathrm{Os})$. A recent study of trends in c/a for the transition metals indicates that the contribution of the d electrons to the chemical bonding results in a minimum in c/a for Group VIIIA elements [30]. It is well known that this same d-electron bonding contribution is also responsible for the large bulk moduli observed in the middle of the transition metal series [12]. Our experimental results and LDA calculations of c/a and the bulk moduli are consistent with this theoretical description through the pressure range we have studied.

In conclusion, we find that the transition metal Os has the lowest compressibility yet measured, including that of covalently bonded diamond. This result provides impetus for a continued search for superhard materials, including transition metal carbides, nitrides, and oxides.

We thank V. Iota and B. Baer for their assistance in data collection at NSLS and SSRL. We also appreciate help from Dr. J. Hu at NSLS. Part of this work was performed at SSRL operated by DOE, OBES. This work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

[1] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[2] D. G. Pettifor, *Solid State Physics,* edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1987), Vol. 40, p. 43.

[3] S. Vepřek, J. Vac. Sci. Technol. A **17**, 2401 (1999).

[4] H. J. McSkimin and W. L. Bond, Phys. Rev. **105**, 116 (1957); I. V. Aleksandrov, A. F. Goncharov, A. N. Zisman, and S. M. Stishov, Sov. Phys. JETP **66**, 384 (1987); I. V. Aleksandrov, A. F. Goncharov, E. V. Yakovenko, and S. M. Stishov, *High Pressure Research: Application to Earth and Planetary Sciences,* edited by Y. Syono and M. H. Manghnani (TERRAPUB, Tokyo/American Geophysical Union, Washington, DC, 1992), pp. 409–416. Note that B_0 for diamond obtained from ultrasonic velocity measurement at ambient conditions is almost the same as B_0 from EOS fits using x-ray compression data. The resulting B_0 using *B-M* EOS was 442 GPa assuming $B_0' = 4$, and it is similar to 444 GPa with B_0' ranging from 1 to 2.5 using Aleksandrov's EOS.

[5] S. Desgreniers and K. Lagarec, Phys. Rev. B **59**, 8467 (1999); L. S. Dubrovinsky, N. A. Dubrovinskaia, V. Swamy, J. Muskat, N. M. Harrison, R. Ahuja, B. Holm, and B. Johansson, Nature (London) **410**, 653 (2001).

[6] C.-S. Yoo, H. Cynn, F. Gygi, G. Galli, V. Iota, M. Nicol, S. Carson, D. Häusermann, and C. Mailhiot, Phys. Rev. Lett. **83**, 5527 (1999).

[7] C. M. Sung and M. Sung, Mater. Chem. Phys. **43**, 1 (1996).

[8] K. A. Gschneidner, Jr., Solid State Phys. **16**, 275 (1964).

[9] L. J. Cabri, *Platinum Group Metals Resources in Encyclopedia of Materials Sciences and Engineering* (Pergamon Press, New York, 1986), pp. 5 and 3577; metal data on physical properties in *Goodfellow Catalog* (Goodfellow Inc., New York, 1994), pp. 26–37.

[10] R. Jeanloz, B. K. Godwal, and C. Meade, Nature (London) **349**, 687 (1991).

[11] J. Friedel, *The Physics of Metals,* edited by J. M. Ziman (Cambridge University Press, New York, 1969), Chap. 8.

[12] L. Fast, J. M. Wills, B. Johansson, and O. Eriksson, Phys. Rev. B **51**, 17 431 (1995).

[13] J. C. Grossman, A. Mizel, M. Côté, M. Cohen, and S. G. Louie, Phys. Rev. B **60**, 6343 (1999).

[14] J. Akella, J. Phys. Chem. Solids **43**, 941 (1982).

[15] Y. Cerenius and L. Dubrovinsky, J. Alloys Compd. **306**, 26 (2000).

[16] R. L. Clendenen and H. G. Drickamer, J. Phys. Chem. Solids **25**, 865 (1964).

[17] H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[18] C.-S. Yoo, H. Cynn, and V. Iota, Phys. Rev. Lett. **84**, 4132 (2000).

[19] H. Cynn and C.-S. Yoo, Phys. Rev. B **59**, 8526 (1999).

[20] M. Ross, H. K. Mao, P. M. Bell, and J. A. Xu, J. Chem. Phys. **85**, 1028 (1986): EOS obtained fitting pressure and volume of solid argon is used here to cross-check ruby pressure.

[21] Y. K. Vohra, S. J. Duclos, and A. L. Ruoff, Phys. Rev. B **36**, 9790 (1987).

[22] W. B. Holzapfel, *High-Pressure Techniques in Chemistry and Physics: A Practical Approach,* edited by W. B. Holzapfel and N. S. Isaacs (Oxford University Press, Oxford, 1997), pp. 47–55; P. Vinet, J. Ferrante, J. R. Smith, and J. H. Rose, J. Phys. C **19**, L467 (1986).

[23] K. L. Narayana and K. M. Swamy, Mater. Sci. Eng. **18**, 157 (1975).

[24] M. Methfessel, Phys. Rev. B **38**, 1537 (1988).

[25] M. Methfessel, C. O. Rodriguez, and O. K. Andersen, Phys. Rev. B **40**, 2009 (1989).

[26] V. A. Finkel, M. I. Palatnik, and G. P. Kovtun, Phys. Met. Metallogr. **32**, 231 (1971).

[27] H. P. Singh, Acta Crystallogr. Sect. A **24**, 469 (1968).

[28] J. Donohue, *The Structures of the Elements* (John Wiley & Sons, New York, 1974).

[29] A. P. Jephcoat, H. K. Mao, and P. M. Bell, J. Geophys. Res. **91**, 4677 (1986); H. K. Mao, Y. Wu, L. C. Chen, and J. F. Shu, J. Geophys. Res. **95**, 21 737 (1990).

[30] J. X. Zheng-Johansson, O. Eriksson, and B. Johansson, Phys. Rev. B **59**, 6131 (1999).