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Brief Reports

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High-pressure x-ray diffraction studies on rhenium up to 216 GPa (2.16 Mbar)

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Energy-dispersive x-ray diffraction techniques using a synchrotron source were used to study rhenium. The hcp structure is stable up to the highest pressure used 216 GPa (volume fraction $V/V_0=0.734$), and the axial ratio (c/a) is independent of pressure within experimental errors. The present study represents the first x-ray measurement above 2 Mbar, and diffraction patterns with 12 peaks were used to confirm the structure. This is also the first case in which x rays were used to obtain a pressure profile across the diamond face. The suitability of rhenium as a gasket material in ultrahigh-pressure experiments is also discussed.

Rhenium (Re) is a group-VII transition metal with a half-filled d band (electronic configuration $6s^2 5d^5$). The systematics of cohesive energies, bulk moduli, and equilibrium atomic volume for transition metals as the d bands are filled is well understood.[1,2] The half-filled d-band metals are characterized by high cohesive energy, low atomic volume and low compressibility. The early high-pressure work of Bridgman[3] indicated that rhenium is the least compressible of all metals. Re crystallizes in the hexagonal-close-packed (hcp) structure and retains this structure up to its melting temperature of 3180 °C. From thermodynamic studies of binary alloys of various transition metals including rhenium, Mo-Re, Nb-Re, and Ta-Re, Kaufman[4] estimated by extrapolation the difference in the Gibbs free energies for the pure hcp and bcc phases in rhenium to be −520 cal/mol at 300 K, and that the bcc phase is denser than hcp. Therefore it was speculated[4] that hcp Re might transform to a bcc phase under high pressure. The high-pressure x-ray diffraction study on Re up to 35 GPa by Liu, Takahashi, and Bassett[5] did not reveal any phase transition. It should be added that no approximate first-principle calculations of crystal phase stability under high pressures have been carried out on Re. Recently there has also been interest in the high-pressure behavior of Re because of its use as a gasket material in high-pressure diamond-anvil-cell experiments. For a particular diamond shape and geometry, a gasket made of a higher yield-strength material (such as rhenium) will produce high center pressures and will also help avoid "punch through" at the corners of diamond until higher pressures are reached.[6,7]

The purpose of the present experiment was twofold: to look for the possible phase transition in Re at pressures of the order of megabars, and to test the usefulness of Re as a gasket material for ultrahigh pressures.

The Re was studied by energy-dispersive x-ray diffraction techniques in a diamond-anvil cell to pressures of 216 GPa using the Cornell High Energy Synchrotron Source (CHESS). The details of the experimental technique are described by Brister, Vohra, and Ruoff.[8] Diamonds of 300-μm culet diameter with a central flat of 50–60 μm diameter (not quite a regular 16-sided tip) and 10° bevel angle were used in the present experiments. Re was used as a gasket material and also as a sample. Re foil of 99.99% purity and 250-μm thickness was preindented to 20-μm thickness. A ruby chip of 5–10-μm diameter was placed on the top of the gasket at the center of the cell. The cell was then taken to higher pressures based on the pressure measurement by ruby fluorescence technique. The primary calibration of ruby has been carried out to a pressure of 180 GPa (1.8 Mbar) by Bell, Xu, and Mao.[9] The calibration of ruby to these pressures is based on the isothermal equation of state of Au and Cu obtained from shock-wave data. The ruby pressure measurements between 1.4 and 2.8 Mbar are obscured by the strong diamond fluorescence emanating from the stressed region of the diamond anvil.[10] However at pressures above 2.8 Mbar the diamond fluorescence diminishes and the ruby fluorescence reappears strongly.[11] Because of this uncertainty in detection between 1.4 and 2.8 Mbar and lack of ruby calibration above 1.8 Mbar, the pressures above 2 Mbar are based on the isothermal equation of state of Re deduced from shock-wave Hugoniot measurements up to 3 Mbar pressure.[12] The pressures obtained in this way are accurate and the errors are largely determined by the reduction process of shock Hugoniot data to isothermal compression.

The isothermal equation of state for Re of Ref. 12 was fitted to the following Birch-Murnaghan equation of state

$$P/B_0=3/2(x^{7/3}-x^{5/3})[1+\tfrac{3}{4}(B_0'-4)(x^{2/3}-1)] , \quad (1)$$

where $x=V_0/V$, B_0 is the bulk modulus, and B_0' is the pressure derivative of the bulk modulus at zero pressure. For Re, the least-squares fit gives $B_0=372$ GPa and $B_0'=4.05$.

Figure 1 shows the energy-dispersive x-ray diffraction pattern of Re at a volume compression of 0.734 as measured by the x-ray diffraction. This corresponds to a pressure of 216 GPa based on the isothermal equation of state of Re shown above. All the 12 diffraction peaks shown in Fig. 1 index to the hexagonal-close-packed structure. The hcp structure of Re is stable up to pressures of 216 GPa and no phase transition is seen. Table I shows the calculated and observed interplanar spacings at 216 GPa for hcp Re. The quality of the diffraction data can be judged from the fact that the average deviation of any observed diffraction-peak energy from the calculated one is

$$\left|\frac{d_{\text{obs}}-d_{\text{calc}}}{d_{\text{obs}}}\right|_{\text{av}}=0.0012 ,$$

which corresponds to

$$\Delta V/V=0.0036$$

which, from the bulk modulus obtained from the equation of state at this pressure corresponds to an error of pressure of

$$\Delta P=6 \text{ GPa} .$$

TABLE I. Comparison of observed and calculated interplanar spacings for rhenium at 216 GPa ($V/V_0=0.734$). The calculated interplanar spacings (d) are based on $a=2.491\pm0.003$ Å, $c=4.020\pm0.005$ Å and $c/a=1.614\pm0.004$. The excellent quality of diffraction data at this pressure is indicated by the small fractional deviation of the calculated line positions from the observed ones.

(hkl)	d_{obs} (Å)	d_{calc} (Å)	$\frac{d_{\text{obs}}-d_{\text{calc}}}{d_{\text{obs}}}$
100	2.154	2.157	−0.0014
002	2.004	2.010	0.0030
101	1.901	1.901	0
102	1.468	1.471	−0.0020
110	1.246	1.246	0
103	1.139	1.138	0.0009
200	1.078	1.079	−0.0009
112	1.056	1.059	−0.0028
201	1.043	1.042	−0.0010
202	0.9506	0.9504	0.0002
211	0.7996	0.7991	0.0006
114	0.7831	0.7821	0.0013

Figure 2 shows the variation of the axial ratio (c/a) with pressure up to 216 GPa. The earlier data of Liu *et al.*[5] up to 35-GPa pressure is also shown as is the averaged room-pressure c/a value of 1.615 for Re from Donohue.[13] The linear fit to the combined data gives

$$c/a=1.613+1.40\times10^{-6}P ,$$

where P is the GPa. It is clear that for all practical purposes the axial ratio is independent of pressure. This remarkable constancy of c/a implies that one can in principle determine the volume of Re (and hence pressure) by x-ray diffraction measurements by using only one

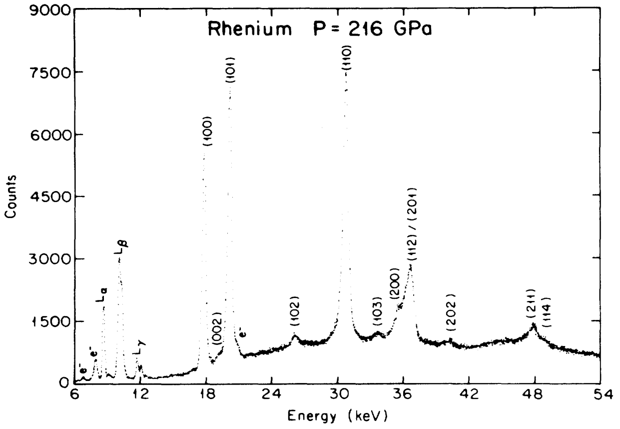

FIG. 1. The energy dispersive x-ray diffraction pattern of rhenium at 216 GPa. (Diffraction angle is 9.311°.) The twelve peaks in the spectrum are indexed according to a hexagonal-close-packed structure. The diffraction pattern was recorded with a 10-μm pinhole and the data collection time was 90 min. The spectrum shown is raw data.

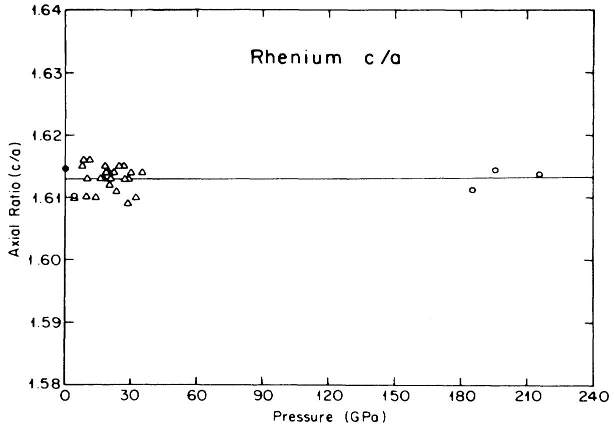

FIG. 2. The axial ratio (c/a) of rhenium as a function of pressure up to 216 GPa. Here Δ represents the data of Liu *et al.* (Ref. 5), ○ represents the results of the present experiment and ● is the room-pressure value of Donahue (Ref. 13). The solid line is the linear fit to all the data. (See text for details).

peak. In hcp materials the presence of growth or deformation faults causes only line broadening, whereas in fcc or bcc materials such faults cause shifts in peak positions as well, so that using only a single peak for lattice-parameter determination (and hence to measure pressure) could give an incorrect pressure.[14] This may have implications for use of Re as a gasket material where gasket pressure can be estimated rather quickly. When rhenium is used as a gasket material to achieve pressures of several megabars, it may be necessary to use a sample hole of very small diameter (in order to reach the pressure), in which case gasket peaks may also be present along with sample peaks. It is thus necessary to know accurately at which energies the gasket peaks appear at each pressure while analyzing the data.

Figure 3 shows the pressure profile on the rhenium gasket measured across the diamond face by x-ray diffraction techniques. The pressures were calculated from the measured volume of rhenium at various locations using the isothermal-shock equation of state. The distances shown are measured with respect to the center of the diamond or the highest-pressure region in the cell. The peak pressure for the profile shown is 183 GPa. There is a sharp drop in pressure at the edge of the central flat of 50–60-μm diameter and pressure is fairly homogeneous in the central region. The culet diameter of 300-μm is also shown in Fig. 3. This is the first pressure profile measured by x-ray diffraction technique whereas only optical techniques have been employed in the past.[10] The rapid drop in pressure at the edge of the flat region is unusual. It may be due to the large bevel of 10° on both diamonds. It may also be due to a low coefficient of friction between rhenium and diamond. Both of these factors may result in a slipping condition over most of the beveled area.[6] These two factors can give rise to a pressure profile such as shown in Fig. 3 where most of the applied force is concentrated on the central flat region.

We offer the following conclusions.

(1) The first x-ray diffraction studies at pressures above 2 Mbar have been carried out in the diamond-anvil cell. Rhenium, when subjected to pressures of 216 GPa (2.16 Mbar), retains its hcp structure. The structural determinations above 2 Mbar are based on 12 diffraction peaks.

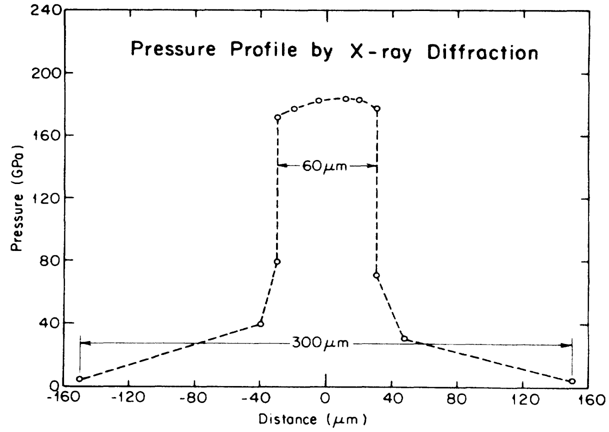

FIG. 3. The pressure profile on the rhenium gasket measured by x-ray diffraction techniques from the measured volume of rhenium at various locations. The distances shown are measured with respect to the center of the diamond or the highest-pressure region in the cell. The diamond central flat of 60-μm diameter and the culet of 300 μm are also indicated.

(2) The axial ratio (c/a) is remarkably constant throughout the pressure range up to 216 GPa.

(3) Pressure profiles by x-ray diffraction techniques have been measured on the diamond face at these very high pressures. These profile studies will eventually lead to an improved design of the diamond geometry.

(4) Use of a rhenium gasket in ultrahigh-pressure experiments appears promising.

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