

In Situ Diffraction Study of the Formation of Rhenium Hydride at High Pressure

T. Atou and J. V. Badding¹

Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802

Received October 20, 1994; in revised form January 17, 1995; accepted January 18, 1995

The formation of rhenium hydride from rhenium and hydrogen at high pressure has been studied using a diamond anvil cell and *in-situ* X-ray diffraction. Rhenium hydride forms by 5.3 GPa at room temperature. The hydride has an hcp structure with interstitial hydrogen. By 8.6 GPa, the stoichiometry of rhenium hydride saturates to $\text{ReH}_{0.38 \pm 0.04}$, a value significantly greater than found in earlier studies of quenched material. After saturation at 8.6 GPa, the interstitial hydrogen is "incompressible," such that the difference in the volumes between rhenium metal and rhenium hydride remains nearly constant up to at least 20 GPa. © 1995 Academic Press, Inc.

INTRODUCTION

There is currently great interest in metal–hydrogen systems because of their importance in a wide range of technological (1), fundamental (1–3), and geologic (4, 5) problems. With the development of techniques for compressing materials to ultrahigh pressures (>100 GPa) (6) it is now possible to synthesize bulk hydrides of metals that incorporate limited amounts of hydrogen at ambient pressure. After synthesis at high pressure, these hydrides can often be quenched to ambient pressure at temperatures in the range from 80 to 300 K. At pressures above 0.1 GPa the chemical potential of hydrogen increases steeply (2), allowing hydrogen to be implanted at or near equilibrium. In contrast, nonequilibrium techniques, such as ion implantation, often cause extensive lattice damage and amorphization (7) and do not implant as much hydrogen. Here we report an X-ray diffraction study of the rhenium–hydrogen system at high pressure using diamond anvil cell techniques. These measurements document the formation of rhenium hydride at high pressure with a stoichiometry greater than previously reported, an expansion in the unit cell volume of the metal upon reaction, and a constant volume difference between rhenium and rhenium hydride with increas-

ing pressure, similar to the incompressible behavior of hydrogen found in other transition metal hydrides (8).

Rhenium hydride was first synthesized using a large-volume pressure apparatus (9, 10). Formation of the hydride at 250°C and 2 GPa was detected by comparing the electrical resistivity of rhenium under high pressures of hydrogen with the resistivity of pure rhenium at high pressure. Rhenium hydride synthesized at high temperature and pressure loses much of its hydrogen when the pressure is released at room temperature, but it can be quenched in a metastable form at low temperature (~90 K) (10). Measurement of the amount of hydrogen evolved upon warming quenched samples showed that the hydrogen stoichiometry was variable, increasing from $\text{ReH}_{0.06}$ for material synthesized at 7 GPa and 250°C to $\text{ReH}_{0.13}$ by 9 GPa. At lower temperatures, more hydrogen was incorporated; the stoichiometry was $\text{ReH}_{0.22}$ for samples synthesized at 9 GPa and 170°C.

Low-temperature X-ray (9) and neutron diffraction measurements (9, 11, 12) on the quenched samples showed that the hydride retains the hcp crystal structure of pure rhenium, but with a larger unit cell volume that scales with the hydrogen stoichiometry. The neutron diffraction patterns did not contain extra peaks due to hydrogen, indicating that the hydride is a disordered solid solution. By comparison of calculated intensities from models for which the interstitial hydrogen was in both octahedral and tetrahedral sites with the measured intensities, it was concluded that the hydrogens must be octahedrally coordinated. No direct information, however, is available on the crystal chemistry or stoichiometry of the hydride in equilibrium with hydrogen at high pressure.

EXPERIMENTAL

Powdered Re (Aesar, 99.99%) was loaded together with hydrogen at 0.2 GPa at room temperature in a Mao–Bell-type diamond anvil cell (6). The molar ratio of hydrogen to rhenium was estimated to be larger than 10. Pressures were measured with ruby fluorescence (13). Because an excess of hydrogen was present throughout

¹ To whom correspondence should be addressed.

the experiment, the pressures remained quasi-hydrostatic (6).

Two sets of diffraction experiments were performed. In the first, energy dispersive diffraction measurements at line X17C of the National Synchrotron Light Source were collected to a pressure 16 GPa. For these experiments diamonds with 600- μm -diameter culets, a T301 stainless steel gasket, and a 200- μm gasket hole were used. The energies of the diffraction peaks were derived from fits to pseudo-Voigt profiles (14). Angular dispersive diffraction measurements also were performed at pressures up to 19.2 GPa, using a conventional X-ray source and a focusing diffraction technique. Diamonds with 400- μm culets, a rhenium gasket, and a 150- μm gasket hole were used. $\text{MoK}\alpha$ radiation from a Rigaku rotating anode was focused in the horizontal plane with a Johansson-type curved quartz monochromator to a width of 100 μm (15). The beam was constrained in the vertical direction to a height of 75 μm by a brass collimator located close to the diamonds. Diffraction patterns were collected on a curved film oriented vertically. The focusing technique

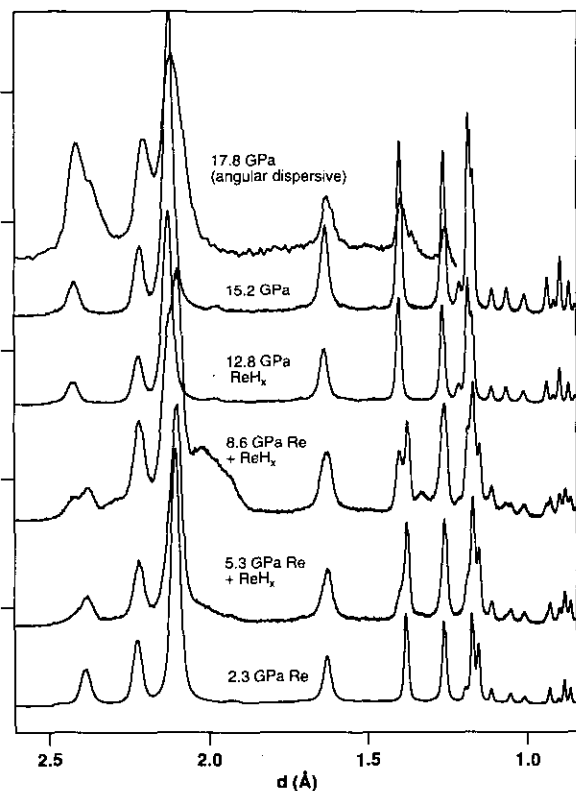


FIG. 1. Energy dispersive (bottom five curves) and angular dispersive (top curve) diffraction patterns at different pressures. The additional peaks on the curve at 8.6 GPa are due to diffraction from the steel gasket, which was formed a hydride (5). At 17.8 GPa, the weak shoulders on the right side of the diffraction peaks are due to the rhenium gasket.

TABLE 1
Observed and Calculated Interplanar Distances for Rhenium Hydride at 10.2 GPa

d_{obs} (Å)	d_{calc} (Å)	Δd (Å)	hkl
2.4246	2.4262	-0.0016	1 0 0
2.2211	2.2202	0.0009	0 0 2
2.1282	2.1291	-0.0009	1 0 1
1.6368	1.6379	-0.0011	1 0 2
1.4006	1.4008	-0.0002	1 1 0
1.2635	1.2636	-0.0001	1 0 3
1.2129	1.2132	-0.0003	2 0 0
1.1851	1.1847	0.0004	1 1 2
1.1705	1.1703	-0.0002	2 0 1

Note. The lattice parameters derived from the fit to the hcp structure are $a = 2.801 \text{ \AA}$ and $c = 4.440 \text{ \AA}$.

increases the intensity of the X-ray beam as compared with a simple collimator and removes the $K\alpha_2$ line. Since the beam is monochromatic with a small vertical angular divergence, improved resolution and signal to noise (15) are obtained. Typical exposure times were between 12 and 24 hr. The films were digitized with a scanner and collapsed into diffraction profiles using the computer program of Jeanloz *et al.* (16).

RESULTS

The diffraction pattern (Fig. 1) at 2.3 GPa and room temperature is characteristic of rhenium metal. At 5.3 GPa, shoulders begin to appear on the hcp rhenium diffraction peaks due to the formation of hydride. In view of earlier results on the electrical resistivity of rhenium under high pressures of hydrogen (9), it is likely that hydride formation begins below 5.3 GPa, but cannot be seen by diffraction because it forms only a small portion of the sample. By 8.3 GPa, two phases can clearly be seen. The coexistence of metal and hydride at room temperature has also been observed in other metal-hydrogen systems (2). The new diffraction peaks can be fit to an hcp structure (Table 1). The octahedrally coordinated interstitial hydrogens cannot be detected by X-ray diffraction. As the pressure is increased further, the proportion of rhenium hydride increases until, by 12.3 GPa, the sample is entirely hydride. Up to 19.2 GPa, the highest pressure attained, the structure remains hcp. Upon releasing the pressure at room temperature, the diffraction pattern remains that of an hcp metal, but with a slightly larger cell volume than pure rhenium.

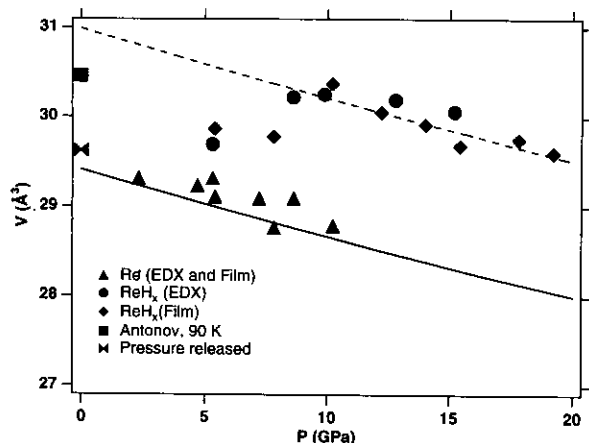


FIG. 2. Unit cell volumes of rhenium and rhenium hydride as a function of pressure. The dashed line is a fit to the data of the Birch-Murnaghan equation of state (18) with the bulk modulus (K_0) constrained to that of rhenium (372 GPa) and K_0' constrained to be 4. The resulting zero pressure volume is $31.0 \text{ cm}^3/\text{mole}$. The solid line is the rhenium equation of state from Ref. (17).

DISCUSSION

The volume of rhenium hydride (Fig. 2) increases from 5.3 GPa to about 8.6 GPa, then begins to decrease at still higher pressures. This behavior can be attributed to changes in stoichiometry as more hydrogen is incorporated with increasing pressure. Because no further increase in volume occurs above 8.6 GPa, it is likely that the sample has become saturated with hydrogen near this pressure. The differences in the unit cell volumes of rhenium hydride and rhenium (Fig. 3) can be used to estimate the stoichiometry of the hydride. It has been found empirically that many metals exhibit an almost constant increase in unit cell volume per hydrogen incorporated. For hcp and bcc metals which have the interstitial hydrogen in an octahedral site, the increase in the unit cell volume is almost always $2.1 \pm 0.2 \text{ \AA}^3$ per H atom incorporated (2). For example, the increase in unit cell volume of $\text{ReH}_{0.23}$ quenched to low temperature amounts to 2.0 \AA^3 per H (9, 12). After saturation, the average difference in the unit cell volumes between rhenium and the hydride is 1.58 \AA^3 , which gives a stoichiometry of $\text{ReH}_{0.38 \pm 0.04}$. This is a significantly greater hydrogen stoichiometry than was found in earlier quenching experiments (maximum H stoichiometry, 0.23 H per Re) (9) in which the hydride was synthesized at higher temperatures ($>120^\circ\text{C}$). At temperatures lower than room temperature, even more hydrogen might be incorporated, though the kinetics of the formation of the hydride might become slow. Because many octahedral sites remain unoccupied, it is plausible that more hydrogen could be incorporated.

Thus, at present, the ultimate limit to the hydrogen stoichiometry of rhenium hydride is uncertain.

Above 8.6 GPa, the interstitial hydrogen in rhenium hydride is incompressible, such that the difference in the volumes between metal and hydride remains nearly constant with pressure. This provides further evidence that the hydrogen stoichiometry has become constant by 8.6 GPa. Similar incompressible behavior of the hydrogen volume in several transition metals has been observed (2, 10, 17). The physical significance of this behavior and the relationship between the volume of hydrogen in a metallic environment and in elemental hydrogen at high pressure is beginning to be explored (2, 8).

The equation of state of a material is important for assessing its stability and structure-property relations at high pressure. Because the hydrogen stoichiometry of rhenium hydride does not saturate until about 8.6 GPa, the present data collected up to 20 GPa do not cover a sufficient range of pressures to fit a complete equation of state (18) (Fig. 2). However, since the compression curves for rhenium and rhenium hydride appear similar except for an offset in the volume (in other words, the hydrogen volume in the hydride is incompressible), the bulk modulus should be similar to that of rhenium (372 GPa) (19). The c/a ratio of the hcp hydride (Fig. 4) remains constant with pressure (~ 1.583), smaller than that for rhenium (~ 1.613) (20), which also has a c/a ratio independent of pressure.

After the release of pressure, the c/a ratio (1.58) of the sample is characteristic of the hydride, not pure rhenium. From the difference in the volume between pure rhenium and the pressure-released sample (Fig. 3), the stoichiometry

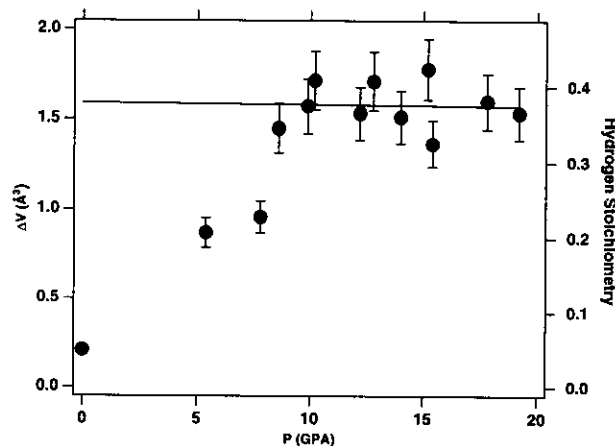


FIG. 3. Difference in the unit cell volumes of rhenium and rhenium hydride as a function of pressure. The error bars represent estimated uncertainties in the hydrogen stoichiometry due to uncertainty in the volume-stoichiometry relationship for hcp transition metal hydrides ($2.1 \pm 0.2 \text{ \AA}^3$ per H atom) (2).

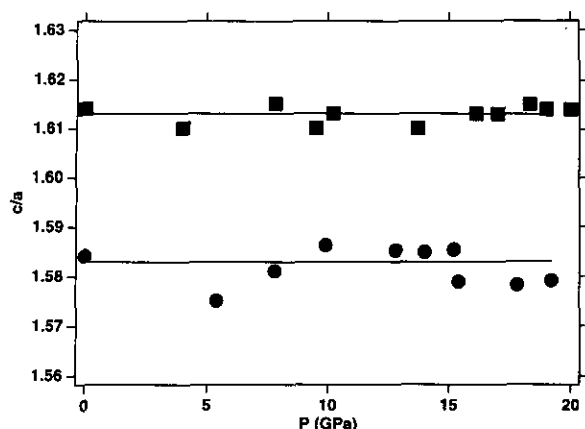


FIG. 4. c/a ratios for rhenium (squares) and rhenium hydride (circles) as a function of pressure.

etry of the metastable hydride at room temperature can be estimated to be $\text{ReH}_{0.05}$, in good agreement with previous quenching studies (10). With the exception of palladium hydride, hydride stability decreases from left to right in the transition metal series (21). Because some hydrogen remains incorporated at room temperature, rhenium hydride must be on the border of stability between stable hydrides to the left (e.g., TaH) (21) and those to the right that decompose completely at room temperature after synthesis at high pressure (e.g., FeH) (5).

These results have implications for the containment of hydrogen to ultrahigh pressures. Rhenium is increasingly being used as a gasket material to contain hydrogen in diamond cell experiments aimed at the metallization of hydrogen (22) and for the exploration of high-pressure hydride chemistry (5). Steel gaskets used in high-pressure hydrogen experiments in the diamond cell are disrupted and embrittled by the formation of a hydride with a stoichiometry close to FeH (5). The use of rhenium gaskets generally results in less hole deformation and higher sample stability (23). In the absence of hydrogen, both ferrous and rhenium gaskets behave well in ultrahigh pressure experiments. At high pressure, rhenium forms a hydride of stoichiometry $\text{ReH}_{0.34}$, which suggests that the superior properties of rhenium gaskets are due to the incorporation of less hydrogen and smaller changes in the materials properties of the metal.

ACKNOWLEDGMENTS

The synchrotron diffraction data were collected at line X17C of the National Synchrotron Light Source. We thank R. B. Baron and D. C. Nesting for assisting with sample loading and data collection. This research was supported by The David and Lucile Packard Foundation and the National Science Foundation.

REFERENCES

1. G. Alefeld and J. Vökl, (Eds.), "Hydrogen in Metals I." Springer-Verlag, New York, 1978.
2. Y. Fukai, "The Metal-Hydrogen System." Springer-Verlag, Berlin, 1993.
3. Y. Ebisuzaki and M. O. O'Keefe, in "Progress in Solid State Chemistry" (H. Reiss, Ed.), p. 187. Macmillan, New York, 1967.
4. Y. Fukai and T. Suzuki, *J. Geophys. Res.* **91**, 9222 (1986).
5. J. V. Badding, R. J. Hemley, and H. K. Mao, *Science* **253**, 421 (1991).
6. H. K. Mao, in "Simple Molecular Systems at Very High Densities" (A. Polian, P. Loubeyre, and N. Bocarra, Eds.), p. 223. Plenum, New York, 1989.
7. A. S. Soltan, P. Jung, and A. A. Gadallay, *J. Phys. Condens. Matter* **4**, 9573 (1992).
8. Y. Fukai, *J. Less-Common Met.* (1990).
9. V. E. Antonov, I. T. Belash, V. Y. Malyshyev, E. G. Ponyatovskii, and N. A. Tulina, *Dokl. Akad. Nauk SSSR* **269**, 617 (1983).
10. E. G. Ponyatovskii and V. E. Antonov, in "Problems in Solid State Physics" (A. M. Prokhorov and A. S. Prokhorov, Eds.), p. 109. MIR, Moscow, 1984.
11. V. A. Somenkov, V. P. Glazkov, A. V. Irodova, and S. S. Shilstein, *J. Less-Common Met.* **129**, 171 (1987).
12. S. S. Shilstein, V. P. Glazkov, A. V. Irodova, V. A. Somenkov, V. E. Antonov, and E. G. Ponyatovskii, *Z. Phys. Chem.* **146**, 129 (1985).
13. H. K. Mao, J. Xu, and P. M. Bell, *J. Geophys. Res., B.* **91**, 4673 (1986).
14. L. W. Finger, in "Modern Powder Diffraction" (D. L. Bish and J. E. Post, Eds.), p. 309. Mineralogical Soc., Washington, DC, 1989.
15. T. Atou and J. V. Badding, in press.
16. J. H. Nguyen and R. Jeanloz, *Rev. Sci. Instrum.* **64**, 3456 (1993).
17. B. Baranowski, in "Molecular Systems Under High Pressure" (R. Pucci and G. Piccitto, Eds.), p. 139. Elsevier/North-Holland, Amsterdam, 1991.
18. F. Birch, *J. Appl. Phys.* **9**, 279 (1938).
19. Y. K. Vohra, S. J. Duclos, and A. L. Ruoff, *Phys. Rev. B* **36**, 9790 (1987).
20. L.-G. Liu, T. Takahashi, and W. A. Bassett, *J. Phys. Chem. Solids* **31**, 1345 (1970).
21. N. N. Greenwood and A. Earnshaw, "Chemistry of the Elements." Pergamon, Oxford, 1981.
22. H. K. Mao and R. J. Hemley, *Rev. Mod. Phys.* **66**, 671 (1994).
23. R. J. Hemley and H. K. Mao, *Science* **249**, 391 (1990).