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Synthesis of ruthenium hydride

M. A. Kuzovnikov[*] and M. Tkacz[†]
Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

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Ruthenium hydride was synthesized at a hydrogen pressure of about 14 GPa in a diamond-anvil cell. Energy-dispersive x-ray diffraction was used to monitor the ruthenium crystal structure as a function of hydrogen pressure up to 30 GPa. The hydride formation was accompanied by phase transition from the original hcp structure of the pristine metal to the fcc structure. Our results confirmed the theoretical prediction of ruthenium hydride formation under hydrogen pressure. The standard Gibbs free energy of the ruthenium hydride formation reaction was calculated assuming the pressure of decomposition as the equilibrium pressure.

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I. INTRODUCTION

Transition-metal hydrides have attracted the attention of many researchers due to their novel physical properties and important technical applications as hydrogen and energy storage materials. One of the most intriguing features of these hydrides is superconductivity, discovered for the first time in palladium hydride [1]. Due to the high-frequency optical phonons of hydrogen vibrations, the superconducting transition temperature in hydrides can reach as high as 200 K as recently found in the sulfur-hydrogen system at a high pressure of about 150 GPa [2].

Together with group III–V elements, palladium is the only transition metal which forms a hydride at ambient pressure. Many other transition metals form hydrides at high pressures when the chemical potential of hydrogen in the gas phase increases dramatically. There are three techniques available for compressing hydrogen up to several GPa: piston-cylinder chambers, used for the synthesis of Ni [3], Mn [4], and Cr [5] hydrides; toroidal chambers [6], for the production of a series of new hydrides of Fe, Co, Mo, Tc, Rh, and others [7,8]; and diamond-anvil cells (DACs). Utilization of the DAC technique for the compression of hydrogen has opened the way to the synthesis of new hydrides of transition metals that have been reluctant to react with hydrogen thus far. Recently, DACs were successfully used for the hydride synthesis of Cu [9,10], W [11,12], Re [13], and Pt [14,15]. Surprisingly, several new polyhydrides were produced: RhH_2 [16], IrH_3 [17], and FeH_3 [18].

Among the group III–X elements, only ruthenium and osmium were not found to form hydrides. The only experimental result to date on the ruthenium-hydrogen system at high pressures has been reported by the research group of Ponyatovsky [7]. They showed that the electrical resistance of ruthenium, charged with hydrogen at pressures up to 9 GPa at 250 C, increases significantly compared with the resistance of ruthenium in an inert medium. This behavior results from an increase in hydrogen concentration in the solid solution of hydrogen in ruthenium metal. However, they did not observe the formation of the hydride phase in the pressure region available at that time with the maximum solubility of hydrogen in ruthenium reaching $H/Ru = 0.03$. Their studies on quenched hydrogen solutions have shown that hydrogen suppresses superconductivity in ruthenium, and the T_c dependence on the hydrogen concentration can be expressed as $T_c = 0.495\text{ K}–(H/Ru) \times 1.4\text{ K}$ [19].

A theoretical assessment for RuH formation was performed in the work of Gao *et al.* [20]. They used the CALYPSO method [21,22] for crystal structure prediction to examine the possibility of the formation of noble-metal monohydrides at high pressures.

The calculations showed that with the exception of gold, all other noble metals can form monohydrides and fcc RuH is stabilized with respect to decomposition into constituents at pressures above 10 GPa.

In the recent work of Liu *et al.* [23] the stabilities of various hypothetical compounds in the ruthenium-hydrogen system were analyzed by *ab initio* calculations in the pressure range of 50–300 GPa. They found that NaCl-type RuH is stable with respect to decomposition into constituents over the whole pressure range. Under an excess of hydrogen they predicted the stable compound between 50 and 100 GPa to be RuH_6, and RuH_3 is stable at higher pressures.

In this study, we used a DAC with gas loading and *in situ* energy-dispersive x-ray powder diffraction to synthesize ruthenium hydride and characterize its properties at hydrogen pressures up to 30 GPa.

II. EXPERIMENTAL METHODS

We used a diamond-anvil cell of the modified brilliant type with a culet diameter of about 400 μm. A 200-μm hole was spark drilled in a rhenium gasket of ~50-μm thickness after the indentation of a 250-μm foil. Samples were made compressing 99.99% purity ruthenium powder to a thickness of about 10 μm. The pressure was calculated, measuring the shift of ruby luminescence [24] excited with a 633-nm HeNe laser and recorded with a THR1000 monochromator equipped with a Peltier-cooled CCD detector.

Hydrogen was loaded into the gasket hole at an initial pressure of about 0.4 GPa by the technique described previously [25]. Unless otherwise stated, hydrogen was in significant excess in all the experiments. The presence of the H_2 vibron

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[*] On leave from Institute of Solid State Physics RAS, Chernogolovka, Moscow District, 2 Academician Ossipyan Street, 142432 Russia.

[†] mtkacz@ichf.edu.pl

was monitored by a spectrometer. Thus, hydrogen served both as a reagent and as a pressure-transmitting medium.

X-ray powder diffraction was measured by the energy-dispersive method with white radiation from a conventional tungsten target tube [26] collimated down to about 100 μm to avoid diffraction from the gasket material. The scattering angle 2θ was set at about 20°, corresponding to $Ed \approx 35$ keV Å. The scattering angle was calibrated using the diffraction pattern of hydrogen-free ruthenium metal. The energy scale was calibrated independently for each diffraction pattern by $K\alpha$ and $K\beta$ x-ray fluorescence lines of Ru assuming a linear dependence between the channel number of the multichannel analyzer and the photon energy. All experiments were conducted at room temperature.

III. RESULTS AND DISCUSSION

The typical x-ray diffraction patterns of ruthenium in a hydrogen atmosphere during compression and decompression are presented in Figs. 1 and 2, respectively. The patterns were arbitrarily renormalized to put them on the same intensity scale because each pattern had a different accumulation time, typically from 4 to 20 h. Pressure was measured by the ruby fluorescence method before and after x-ray-diffraction experiments. The markings above each pattern indicate the pressures as measured after x-ray-diffraction experiments.

Ruthenium fluorescence lines, always present in the patterns, were used as internal markers for the energy scale calibration. The Ru $K\beta$ fluorescence line on every pattern had a shoulder towards the higher energies. Its presence did not depend on the value of 2θ, showing that the shoulder was a characteristic feature of the $K\beta$ absorption edge, and was not of diffraction origin. Coincidentally, the (102) diffraction line from the hcp ruthenium was in the same energy range for the chosen diffraction angle; however, its contribution to the profile of the Ru $K\beta$ line is small.

A significant increase in the lattice volume of hcp ruthenium was observed, starting from about 10 GPa of hydrogen pressure up to 14 GPa when the phase transformation to the fcc structure took place as a result of hydride formation. This behavior was observed in two independent runs. The hydride formation was accompanied by a pressure drop, resulting from hydrogen consumption by the sample. As a result, in the first run the pressure after the completion of hydride formation (14.3 GPa in Fig. 1) was lower than that when the phase transition had not yet started (14.4 GPa in Fig. 1). The cubic phase remained stable up to the highest pressure of about 30 GPa, obtained in the first run.

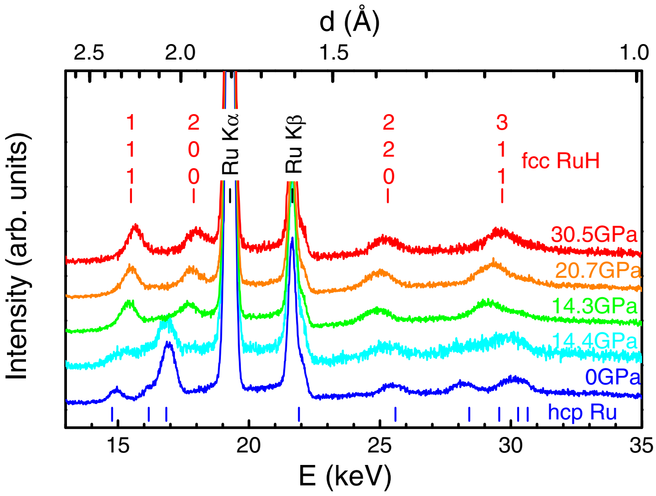

FIG. 1. Energy dispersive x-ray diffraction patterns of ruthenium as a function of hydrogen pressure taken during pressure increase. For clarity only selected patterns are presented here. The scattering angle corresponds to $Ed = 34.8$ keV Å.

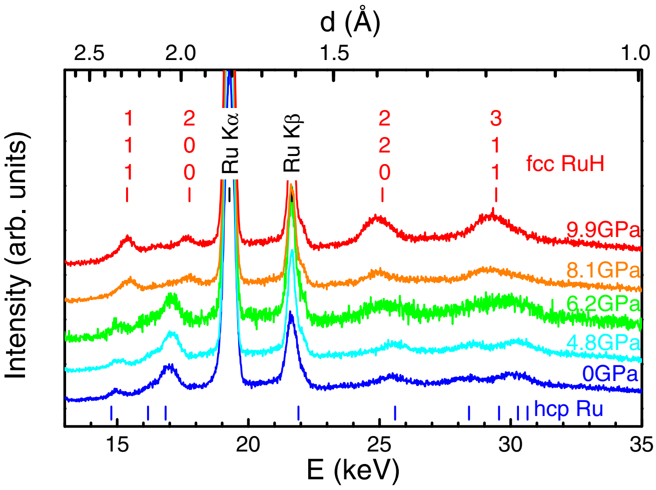

FIG. 2. Energy dispersive x-ray diffraction patterns of ruthenium as a function of hydrogen pressure taken during pressure decrease. The scattering angle corresponds to $Ed = 34.9$ keV Å.

When the pressure was lowered from the highest value down to 10 GPa a complete transition to the original hcp metal structure was observed. We think that the hydrogen escaped during the decompression process in this run as a result of heavy plastic deformation of the gasket, which was subjected to a pressure of 30 GPa.

In the second run, when the maximum pressure was below 20 GPa, we were able to retain hydrogen during decompression. In this run, we observed the cubic structure down to 8 GPa, and then the next decompression step caused almost complete decomposition of the hydride at a pressure of 6.2 GPa. We think that this estimate of the decomposition pressure is more accurate than that obtained in the first run.

The lattice volumes as a function of hydrogen pressure, obtained from x-ray-diffraction experiments on the Ru-H system, are presented in Fig. 3 (symbols) together with the literature data [27] for pure Ru in an inert medium (blue curve).

The pressure-volume relationships for the fcc ruthenium hydride and the pure hcp ruthenium were fitted in the pressure region of interest by the Birch-Murnaghan equation of state with the fixed pressure derivative of bulk modulus $B_0' = 4$. Table I presents a comparison of structural parameters at ambient pressure and bulk moduli of ruthenium hydride and pure ruthenium.

Interestingly, the bulk modulus of ruthenium hydride $B = 290(30)$ GPa was found to be close to that of pure ruthenium $B = 320(5)$ GPa. Evidently, there is no further hydrogen concentration increase with pressure. Such behavior is typical for stoichiometric transition-metal hydrides [28].

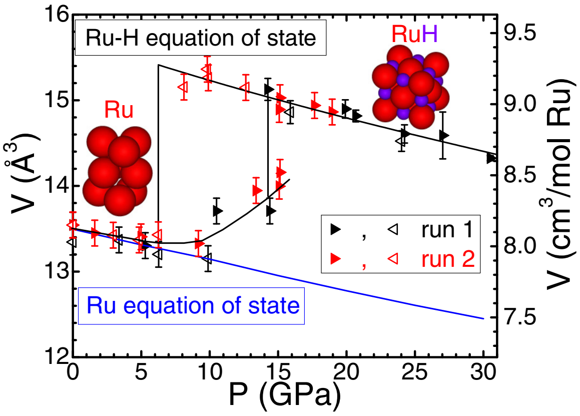

FIG. 3. Pressure-volume relationships for the ruthenium-hydrogen system (symbols and black curves) and pure ruthenium (blue curve) [27]. The solid triangles denote compression data, and the empty ones indicate decompression. The left Y axis corresponds to the volume calculated per one metal atom, and the right axis shows molar volumes.

Only limited data are available on the direct determination of the hydrogen content of hydrides formed under high pressure. Three methods are available for this purpose—volumetry in piston-cylinder high-pressure chambers, thermal desorption of quenched samples, and neutron diffraction on deuterides. The typical accuracy of the latter method is on the order of 10%, and the other two methods provide accuracies of up to a few percent. The second method requires samples weighing at least a few milligrams, the former and the latter—hundreds of milligrams. The two latter methods are applicable for the samples synthesized with toroidal high-pressure chambers [6], which can be used to compress hydrogen up to 9 GPa [29], but none of them are applicable for hydrides synthesized with the DAC, which provides space for 0.01 mg of the sample or less.

Instead of a direct determination of the composition of hydrides, the hydrogen content can be estimated on the basis of the volume expansion of the metal lattice during hydrogen absorption. The expansion of a metal lattice during monohydride formation for transition metals is typically 2.0 Å^3 per H atom [28]. However, this is only true for hydrogen atoms occupying octahedral interstitial sites in a close-packed metal lattice. For transition-metal dihydrides where hydrogen occupies tetrahedral interstitial sites, the volume expansion can vary from 2.2 Å^3 (for TiH_2) to 3.2 Å^3 (for RhH_2) [16] per H atom.

TABLE I. Structural parameters of ruthenium and ruthenium hydride, extrapolated to ambient pressure.

Material	Lattice parameters, Å	Molar volume, cm^3	Bulk modulus, GPa
Hcp ruthenium	$a = 2.7058(1)$ $c = 4.2816(1)$[a]	8.13(1)	320(5)
Fcc ruthenium hydride	3.98(1)	9.5(1)	290(30)

[a] Reference [39].

The difference in lattice volumes of ruthenium hydride and ruthenium, extrapolated to zero pressure, was measured to be 2.2(1) Å^3 per metal atom. The composition of the hydride was determined to be H/Ru = 1 on the basis of this volume, and the hydrogen sites were determined to be octahedral, corroborating the prediction of Gao *et al.* [20].

In all transition-metal-hydrogen systems there is a significant gap between the pressure of formation and the pressure of decomposition known as hysteresis. In the case of the ruthenium-hydrogen system this difference reaches 8 GPa.

The problem of equilibrium pressure determination for hydride formation reactions is essential for the calculation of the thermodynamic potentials of hydrides. According to one concept, the equilibrium pressure P_{eq}^{H} is equidistant from the formation and decomposition pressures [30,31]. However, experimental evidence on several metal-hydrogen systems [32,33] has shown that the decomposition pressure is much closer to P_{eq}^{H}. In the case of ruthenium hydride we accept $P_{eq}^{\mathrm{H}} = 6.2$ GPa. This is in reasonable agreement with the prediction of Gao *et al.* [20], where P_{eq}^{H} was estimated to be 10 GPa. Keep in mind, however, that the predicted formation pressures for other hydrides differ significantly from the experimentally observed values, e.g., theoretical estimation of the platinum hydride formation pressure is about 3 GPa, whereas the actual formation pressure is around 27 GPa [15,14]. The explanation of this discrepancy by a kinetic barrier seems to be rather unjustified and mostly comes from the accuracy overestimation of the method used for the calculations.

Gao *et al.* [20] tried to understand the formation of various transition-metal hydrides at ambient pressure by comparing the electronegativity of elements. This approach, however, can hardly be adopted for the formation of noble-metal hydrides at high pressures. Consider, for example, Ru, Pd, Os, and Ir, which have the same electronegativity value of 2.2 [20], but hydrogen pressure has a dramatically different effect on them: Ru forms a monohydride at 14 GPa (the present result), Pd forms a hydride at less than atmospheric pressure, Os hydride is yet to be discovered (and if it exists, it would require pressures higher than 9 GPa to form [8]), Ir reacts with hydrogen only at a pressure as high as 55 GPa, forming an unusual compound (tentatively a trihydride) with a simple cubic lattice of metal atoms [17]. An even larger difference is observed for the behavior of Pt and Rh, which have the same electronegativity of 2.28. Rhodium forms a NaCl-type monohydride at a hydrogen pressure of 4 GPa [34] when hydrogen atoms occupy octahedral interstitial sites in the fcc lattice of the metal atoms; at a pressure of 8 GPa [16] tetrahedral sites are filled instead, forming a dihydride with a CaF_2-type structure. Platinum reacts with hydrogen at pressures no less than 27 GPa, forming a NiAs-type monohydride [14].

The uncertain pressure effect on electronegativity adds further difficulty to this approach.

Recently, Dong *et al.* [35] suggested redefining electronegativity so that its value at $P = 0$ would be 4.44, 4.48, 5.02, 5.11, 5.51, and 5.87 for Ru, Rh, Pd, Os, Ir, and Pt, respectively. However, no clear monotonic correlation between electronegativity and behavior under hydrogen pressure can be seen.

The small sample size in a DAC does not allow for calorimetric determination of the thermodynamic properties of new materials, but it is possible to estimate them if the equilibrium conditions are known. Particularly, as soon as the Gibbs free energy of the formation reaction is zero in such conditions and $dG = \Delta V\, dP$ at a constant temperature, the standard Gibbs free energy can be calculated provided the pressure dependence of ΔV is known.

The standard Gibbs free energy for the reaction $\mathrm{Ru} + 1/2\mathrm{H}_2 \rightarrow \mathrm{RuH}$ at $P_0 = 1\,\mathrm{bar}$ and $T = 298\,\mathrm{K}$ was estimated as follows:

$$\Delta G^0_{\mathrm{H}} = \int_{P^{\mathrm{H}}_{eq}}^{P_0} \Delta V\, dP = \int_{P^{\mathrm{H}}_{eq}}^{P_0} \left(V_{\mathrm{RuH}} - V_{\mathrm{Ru}} - \frac{1}{2} V_{\mathrm{H}_2} \right) dP$$
$$\approx -\beta_{\mathrm{H}} P^{\mathrm{H}}_{eq} + \frac{1}{2} \int_{P_0}^{P^{\mathrm{H}}_{eq}} V_{\mathrm{H}_2} dP \approx +37(5)\,\mathrm{kJ/mol},$$

where $\beta_{\mathrm{H}} = 2.2\,\mathring{\mathrm{A}}^3/(\mathrm{H\,atom})$ is the volume difference between RuH and Ru, taken from Table I, and the hydrogen molar volume V_{H_2} was calculated using the equation of state from Ref. [36]. We neglected the solubility of hydrogen in hcp ruthenium at 6.2 GPa, which is a few atomic percent.

Typical values of standard Gibbs energy for the formation reactions of transition-metal hydrides are less than +20 kJ/mol, e.g., $\Delta G^0_{\mathrm{H}}(\mathrm{NiH}) = +12\,\mathrm{kJ/mol}$ [37] and $\Delta G^0_{\mathrm{H}}(\mathrm{MoH}) = +16\,\mathrm{kJ/mol}$ [33]. The considerably higher value obtained for RuH is consistent with the higher formation pressure of this compound.

It would be interesting to compare the ΔG^0_{H} value with the *ab initio* calculation result. Such a calculation would not require an accurate reproduction of pure hydrogen properties under high pressure, which is a major source of inaccuracy in the *ab initio* calculations of P^{H}_{eq}.

The best analog of the ruthenium-hydrogen system under high pressure is the cobalt-hydrogen system [38]. In both systems hydride formation is accompanied by a phase transition from a hydrogen solid solution in a hcp metal lattice to a monohydride with a NaCl-type structure. However, RuH should be nonmagnetic, unlike CoH. Although the extrapolation of the critical temperature dependence of superconductivity in the ruthenium-hydrogen system derived from the study of Bashkin *et al.* [19] at low hydrogen concentrations is discouraging, stoichiometric ruthenium hydride may display superconductivity. Therefore further studies, also carried out in an extended pressure range, are required to clarify the behavior of ruthenium hydride at low temperatures.

IV. CONCLUSIONS

We synthesized ruthenium hydride from ruthenium and hydrogen at room temperature and a pressure of 14 GPa. The hydride has a fcc structure of a metal lattice and a composition close to H/Ru = 1, judging by the volume expansion of the metal lattice. No further phase transitions were found up to 30 GPa. The bulk modulus of RuH is close to that of ruthenium.

The thermodynamic potential of RuH was accurately estimated, providing grounds for the refinement of theoretical calculations, which are important for the better understanding of metal-hydrogen interactions and the design of new hydrogen storage materials.

The possibility of the formation of unusual noble-metal polyhydrides under high hydrogen pressure remains an interesting open problem. So far only three polyhydrides of group VI–XI transition metals have been found: RhH_2 [16], IrH_3 [17], and FeH_3 [18], but the use of higher pressures and/or high temperatures could help to synthesize more. Our results demonstrate the importance of the high-pressure technique as an instrument for the synthesis of new noble-metal compounds, which can have unusual properties.

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