

# The Crystal Structure of High-Pressure Hydrides

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## *Crystal structure / Neutron diffraction / Metal hydrides*

Using the high-intensity neutron diffraction technique and micro-samples we have studied the crystal structure of Re, Tc and Mn (the metals of VII group) hydrides synthesized at high pressure of hydrogen. It has been shown that hydrogen atoms occupy the octahedral interstices in these metals. Technetium and manganese hydrides have the layer superstructure of anti-CdI<sub>2</sub> type near the Me<sub>2</sub>H composition.

Die Kristallstrukturen der Metallhydride der VIIten Gruppe (Re, Tc und Mn), die unter hohen Wasserstoff-Drucken dargestellt worden waren, wurden an kleinen Proben mit Neutronenstreuung untersucht. Es wurde nachgewiesen, daß die Wasserstoffatome in diesen Metallen Oktaederlücken besetzen. Technetium- und Manganhydrid weisen in der Nähe der Zusammensetzung Me<sub>2</sub>H eine Schicht-Überstruktur vom Anti-CdI<sub>2</sub>-Typ auf.

## 1. Introduction

Although there is a great interest in metal-hydrogen systems and intense studies in this field have been carried out, the available structural data on hydrides of transition metals of groups VI–VIII and their alloys (with the exception of palladium hydrides) has remained scant until lately. This was because of the very low equilibrium solubility of hydrogen in these metals at the moderate pressures of up to some tens of atmospheres which had usually been employed for synthesis of the hydrides. The situation changed crucially after the technique of compression of macroscopic volumes of hydrogen up to very high pressures had been developed [1].

## 2. Experimental

At the Institute of Solid State Physics of The USSR Academy of Sciences pressures up to 90 kbar are available at present.

At maximum pressures the volume of compressed hydrogen is 30–50 mm<sup>3</sup>, the samples are foils of 0.05–0.2 mm thickness and linear dimensions of about a few millimetres. This technique enabled synthesis of hydrides of all 3d- and 4d-metals (with the exception of Ru) as well as hydrides of many alloys based on these metals. The hydrides are characterized by a variety of physical properties, including magnetic properties and superconductivity. They also show varying stabilities at atmospheric pressure – their temperatures of rapid decomposition varying from about 130 K for iron hydride to about 400 K for manganese hydride.

The crystal structures of hydrides synthesized at high hydrogen pressures were studied at 80–300 K using the X-ray method to determine the arrangement of the metal atoms. At the same time, neutron diffraction experiments were required to determine the arrangements of the hydrogen atoms (such as the types of interstices occupied in the metal lattice and the presence or absence of superstructures). Such experiments have usually been carried out using samples of about 1000 mm<sup>3</sup> (with weights of the order of tens of grams). Recently, however, a new multidetector diffractometer DISC with high luminosity exceeding those of conventional devices by two orders of magnitude has been developed at the I. V. Kurchatov Institute of Atomic Energy. This has allowed the weights of samples necessary for structural studies to be reduced to some tens of milligrams and even to fractions of a milligram. Sufficiently detailed structure investigations of hydrides synthesized at high hydrogen pressures have thus become practically feasible. The circular registration system consisting of 224 detectors enables about 100 neutron diffraction patterns to be taken simultaneously, and the superposition registration principle [3] makes it possible to have such an advantage of the luminosity without any loss in the accuracy of measurements.

Thus, such progress in high pressure technology and developments of the neutron diffraction method have provided a basis for structural studies of new hydrides of transition metals of the VI–VIII groups. The present paper describes the results of crystal structural studies of the metal hydrides of group VII: rhenium, technetium and manganese. To prevent decomposition the samples were kept in liquid nitrogen. During the neutron diffraction experiments the samples were kept in a special nitrogen cryostat where they could be reloaded without preliminary heating. The duration of each experiment was from 4 to 30 h. To avoid errors associated with any loss of hydrogen during experiments the hydrogen content of the samples was determined after neutron diffraction investigation by measuring the volume of the gas evolved on thermal decomposition of the hydride. The accuracy of these determinations was 0.03 (H/Me).

### 3. Rhenium hydride

The sample of ReH<sub>0.23</sub> ( $m \approx 50$  mg) was synthesized at 90 kbar and 600 K (for 48 h).

The diffraction pattern of ReH<sub>0.23</sub> (Fig. 1) shows peaks indexed on the basis of the hexagonal close-packed (h.c.p.) cell with the parameters  $a = 2.801 \pm 0.002$  Å,  $c = 4.465 \pm 0.005$  Å in accordance with X-ray data [4]. The absence of any additional peaks indicates that the hydride is a disordered solid solution with H-atoms randomly distributed over the Re lattice interstices.

The h.c.p. Re lattice contains two types of interstices: octahedrons and tetrahedrons. Comparison of the calculated and measured intensities of all diffraction maxima observed shows that discrepancy factors  $R = \Sigma|I_{\text{exp.}} - I_{\text{theor.}}| / \Sigma I_{\text{exp.}}$  are 6.7% and 13.5% for the octahedron and

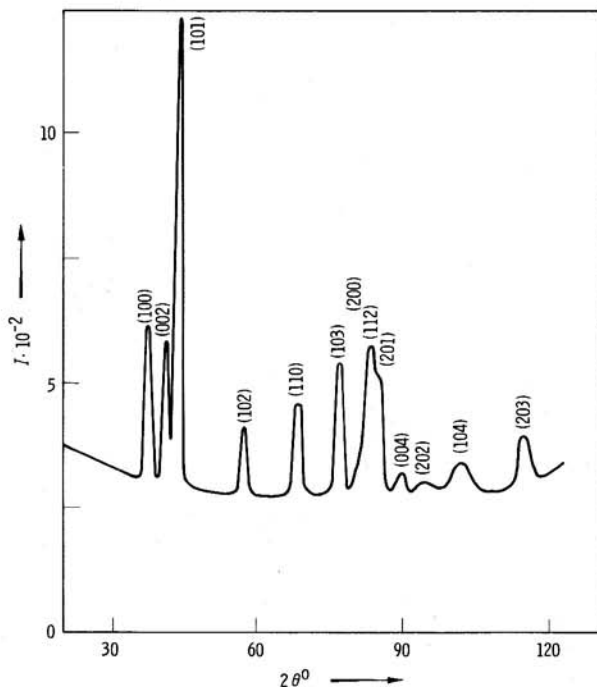


Fig. 1. The neutron-diffraction pattern of  $\text{ReH}_{0.23}$ ,  $T = 90 \text{ K}$ ,  $\lambda = 1.576 \text{ \AA}$

tetrahedron models, respectively. Since the average experimental accuracy is 7%, the tetrahedron model may therefore be considered as unsatisfactory. Minimization of the  $R$ -factor by the H concentration for the octahedron model gave the value  $\text{H/Re} = 0.20$ , which agrees well with that calculated from the amount of the gas evolved on decomposition of the hydride.

#### 4. Technetium hydride [5]

Samples of  $\text{TcH}_{0.45}$  and  $\text{TcH}_{0.69}$  ( $m \approx 100 \text{ mg}$ ) were synthesized at 570 K (12 h) and hydrogen pressures of 5.8 and 20.5 kbar, respectively. As technetium hydrides only decompose over a period of a few months under normal conditions, their study could be carried out at room temperature.

The peaks on the neutron diffraction patterns of these hydrides (Fig. 2) were indexed on the basis of the hexagonal cell with parameters  $a = 2.801 \pm 0.002 \text{ \AA}$ ,  $c = 4.454 \pm 0.005 \text{ \AA}$  and  $a = 2.838 \pm 0.002 \text{ \AA}$ ,  $c = 4.465 \pm 0.005 \text{ \AA}$ . For  $\text{TcH}_{0.45}$  the peaks (001), (111) and (003) were observed. Since these are forbidden for the h.c.p. lattice this indicates the existence of a superstructure. Cooling both samples down to the tempera-

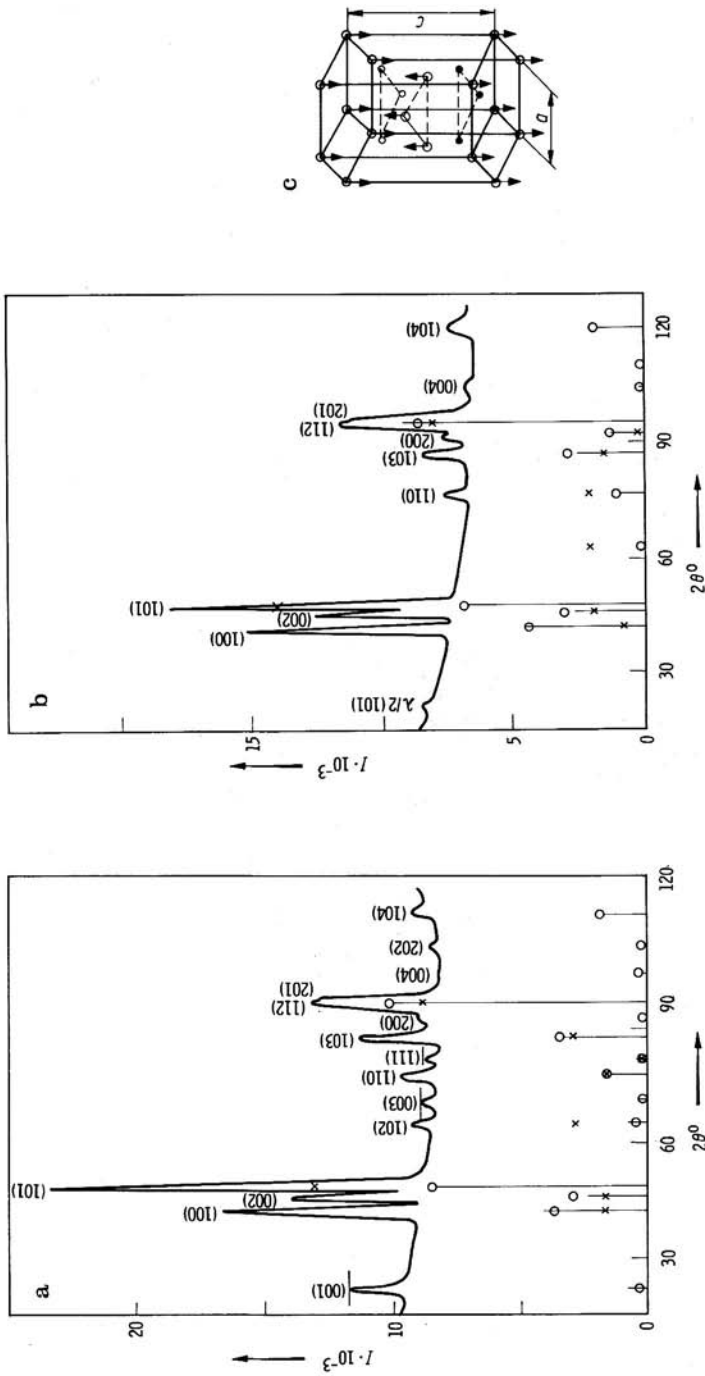


Fig. 2. The neutron-diffraction patterns of  $\text{TcH}_{0.45}$  (a) and  $\text{TcH}_{0.69}$  (b),  $T = 300$  K,  $\lambda = 1.759$  Å, the superstructural peaks are underlined. Below, the experimental peak intensities (vertical lines) are compared with the calculated ones for the tetrahedral ( $\times$ ) and the octahedral ( $\circ$ ) coordinations of hydrogen atoms. (c) Elementary cells of the disordered solid solution (L'3 type) and the superstructure (anti- $\text{CdJ}_2$  type).  $\circ$  Metal atoms,  $\times$ ,  $\bullet$  octahedral interstices occupied by hydrogen atoms in the disordered solid solution (with equal probabilities) and in the superstructure ( $\bullet$  alone). Arrows mark the displacements of the metal atoms in the superstructure from their positions in the disordered solid solution

ture of liquid nitrogen did not give any noticeable changes in the intensities, from which it may be concluded that no structure changes take place within the range from room to liquid nitrogen temperatures.

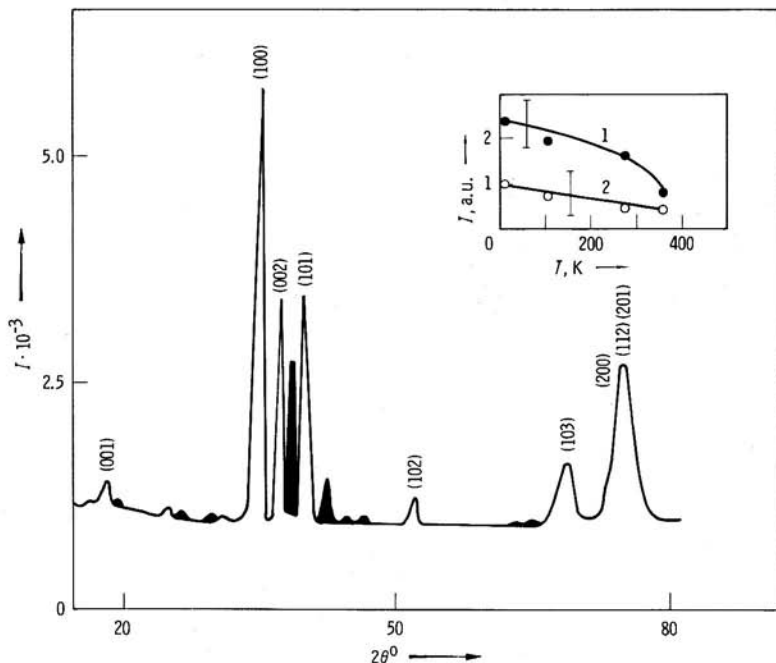
To determine the coordination of the H atoms the experimental intensities of the structural (h.c.p.) peaks of both hydrides were compared with those calculated for two models of disordered arrangement with H atoms in octahedral and tetrahedral interstices, respectively (in the case of hydrogen ordering these intensities change rather weakly). The results are shown in Fig. 2a, b, and it may be seen that the tetrahedral model does not give even a qualitative agreement with experiment. It may thus be concluded that the hydrogen atoms occupy the octahedral interstices in the technetium lattice.

The indices (001), (111) and (003) of superstructural reflections in the case of  $\text{TcH}_{0.45}$  indicate a twofold increase of the spacing ( $c$ ) between the basic layers of the hydrogen sublattice as compared to  $c/2$  in the disordered state. This condition is satisfied by one of the h.c.p. based superstructures, namely, the anti- $\text{CdJ}_2$  type, where only every second layer of octahedrons is occupied (Fig. 2c). This structure was chosen as the starting model for the ordered  $\text{TcH}_{0.45}$  hydride, especially as its composition is close to the ideal stoichiometry  $\text{Tc}_2\text{H}$ . The calculated peak intensities agree reasonably with the experimental data, but the calculated values for the superstructural reflections (001) and (111) are decreased by a factor of 1.5. This apparent discrepancy can be eliminated by allowing for displacements of metal atoms from the h.c.p. positions  $(\frac{2}{3}, \frac{1}{3}, Z)$ ,  $(\frac{1}{3}, \frac{2}{3}, \bar{Z})$  at  $Z = 0.25$  by  $\Delta Z = 0.01$ , while the agreement for the structural peaks remains equally good. The directions of the displacements are shown in Fig. 2c; they have a simple meaning — the metal layers separated by hydrogen atoms move apart from one another while those containing no hydrogen atoms draw closer to one another. Similar displacements have been observed earlier in other hydrogen superstructures [6]. The absence of superstructure in  $\text{TcH}_{0.69}$  is indicative that the ordered phase has only a relatively narrow region of existence.

## 5. Manganese deuteride

The first successful synthesis of a manganese hydride was reported in 1975 by Krukowski and Baranowsky [7].

The deuteride  $\text{MnD}_{0.5}$  ( $m \approx 100$  mg) was synthesized at 18 kbar and 620 K [8]. It is seen from the neutron diffraction pattern of  $\text{MnD}_{0.5}$  (Fig. 3) that metallic  $\alpha$ -Mn coexists with the hexagonal hydride whose lattice periods are  $a = 2.68 \text{ \AA}$  and  $c = 4.35 \text{ \AA}$ . The experimental intensities of the h.c.p. peaks are in good agreement with those calculated for the octahedral model for the composition  $\text{D/Mn} = 0.65$  ( $R = 3.9\%$ ) [8]. Additional peaks are seen at small angles. One of them is indexed in the hexagonal cell,



**Fig. 3.** The neutron-diffraction pattern of  $\text{MnD}_{0.65}$  [8],  $\lambda = 1.38 \text{ \AA}$ ,  $T = 300 \text{ K}$ . Dark peaks correspond to  $\alpha\text{-Mn}$ . Insert: temperature dependence of the superstructural peak intensities of  $\text{MnD}_{0.65}$ , 1 (001), 2 "magnetic" peaks

(001), and is indicative of a superstructure similar to that of  $\text{Tc}_2\text{H}$ . A relatively high stability of  $\text{MnD}_{0.65}$  permitted studies of structure to be carried out within the temperature range 4–350 K (insert Fig. 3). The peak intensity of (001) essentially decreases with increasing temperature, which suggests that the temperature of disordering in  $\text{MnD}_{0.65}$  is only slightly higher than 350 K. The rest of the additional peaks are not indexed in the hexagonal cell, and their intensities change weakly with temperature. They appear to be of a magnetic nature [9].

## 6. Discussion

The octahedral coordination of hydrogen atoms in solid solutions based on the metals of group VII (Re, Tc, Mn) agrees with earlier observations of changes from a tetrahedral coordination (in metals with large atom radii  $R_m$ ) to octahedral coordination (in metals with small  $R_m$ ) for "critical" values  $R_m = 1.34\text{--}1.37 \text{ \AA}$  [10]. These conclusions had mainly been formed with values available for hydrides with cubic lattice while no information

was available for the h.c.p. metals with  $R_m$  close to the "critical" value. Technetium and rhenium have  $R_m = 1.36 \text{ \AA}$  and  $1.37 \text{ \AA}$ , respectively, manganese has  $R_m = 1.30 \text{ \AA}$ . Therefore all the data obtained show that metals with the h.c.p. lattice and hydrides with the h.c.p. metal sublattice change the hydrogen coordination with decreasing  $R_m$  at  $R_m$  close to the "critical" values for cubic metals.

The Re, Tc and Mn hydrides are interstitial solid solutions of hydrogen with broad ranges of homogeneity. The examples of  $\text{TcH}_{0.45}$  and  $\text{MnD}_{0.65}$  show that these solutions may be ordered at some hydrogen concentrations.

The results obtained permit the hope that the present state of synthesis and investigation of hydrides will enable the crystal structures of all new high pressure hydride phases to be determined in the near future.

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