



Nonstoichiometric molybdenum hydride



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ABSTRACT

The molybdenum-hydrogen system was studied in a diamond anvil cell at high hydrogen pressure up to 30 GPa at room temperature by X-ray diffraction. At pressure around 4 GPa a phase transformation was observed of a bcc metal to a hydride with a hcp metal lattice and $H/Mo \approx 1.1$. Further hydrogen pressure increase resulted in a continuous increase of the hydrogen content of the hydride. At about 15 GPa the hydrogen content reached saturation, and no further hydrogen absorption occurred up to the maximal reached pressure. The saturation composition $H/Mo = 1.35$ (10) was estimated from volumetric considerations.

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1. Introduction

The most efficient way to produce hydrides is the use of high hydrogen pressure, which increases dramatically the chemical potential of hydrogen in a gas phase. Recent development of the diamond anvil cell (DAC) technique allowed a series of new transition metal hydrides to be synthesized: $WH_{1.3}$ [1,2], $ReH_{0.85}$ [3], PtH [4], RhH_2 [5], IrH_3 [6], FeH_3 [7] and RuH [8].

At present all transition metals in groups VI–X except osmium were found to form hydrides. Most of them form monohydrides with composition H/Me close to 1, when hydrogen atoms occupy all available octahedral interstitial positions in a close packed metal lattice [9]. The question is open if any of these metals other than rhodium, iridium, and iron can also form stoichiometric hydrides with $H/Me > 1$.

The molybdenum-hydrogen system has been thoroughly studied at hydrogen pressures up to 6 GPa and temperatures up to 800 °C [10,11]. Maximum hydrogen solubility in a bcc solid solution does not exceed $H/Mo < 0.07$ [10], and the composition of a hcp hydride is $H/Mo = 1.10$ (3) [11]. Hydrogen atoms occupy octahedral interstitials in the hcp hydride, forming NiAs-type structure as

confirmed by neutron diffraction [12]. The location of additional over-stoichiometric hydrogen in the crystal structure is unclear, but it is reasonable to assume that the tetrahedral interstitials are partially occupied.

An existence of a stability field of a fcc MoH reported in Ref. [10] at high temperatures was recently refuted in Ref. [11].

The closest analog of the molybdenum-hydrogen system is the tungsten-hydrogen system, previously studied in Refs. [1] and [2]. Tungsten hydride formation, like molybdenum one is accompanied by a bcc to hcp phase transformation. The hydride formation pressure of 24 GPa is considerably higher than that for molybdenum hydride, which is about 4 GPa [13]. Unrealistically high bulk modulus of tungsten hydride, obtained from the equation of state fit in Ref. [2], was interpreted there as a result of its composition being variable, continuously increasing with pressure. From the volume considerations the maximal composition of tungsten hydride was estimated as $H/W \approx 1.3$, but no dihydride formed in the tungsten-hydrogen system up to 115 GPa, contrary to the theoretical predictions in Refs. [14] and [2].

In the recent work [15] the crystal structures and stabilities of the hypothetical molybdenum hydrides with $H/Mo > 1$ were studied. It was found that MoH should be stable in the hydrogen pressure range of 0–9 GPa and MoH_2 should be stable above 9 GPa. The predicted crystal structures of MoH_2 share the same hcp arrangement of metal atoms with MoH, differing only in nonzero fraction of tetrahedral interstitials occupied by hydrogen.

Since the discovery of the superconductivity in H_2S at 203 K [16]

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there was a renewed interest in the superconductivity of hydrogen-rich materials. Molybdenum hydride is a superconductor with $T_c = 0.9$ K ($T_c = 1.1$ K for a deuteride and $T_c = 0.9$ K for pure Mo) [17].

In the present work we used a DAC with gas loading and an in-situ energy-dispersive X-ray powder diffraction to verify the formation of the molybdenum hydride with $H/Mo > 1$ under high hydrogen pressure.

2. Experimental

Diamonds of the modified brilliant cut type with flat culets of about 400 μm in diameter were used. Rhenium gasket was pre-indentated at pressure about 12 GPa to about 50 μm thickness, and laser drilling was used to make a hole 200 μm in diameter. Ruby luminescence pressure scale for quasi-hydrostatic condition [18] was used. Sample was made of 99.96% purity molybdenum powder pressed to about ~ 10 μm thickness.

Hydrogen was loaded into the gasket hole at room temperature and pressure of about 0.3 GPa by the technique described elsewhere [19]. Hydrogen served both as a reagent and as a pressure transmitting medium. Hydrogen was always in excess, and its presence in the cell was monitored both visually and by Raman spectroscopy.

After initial clamping of hydrogen in a DAC the compression force was increased in steps by a lever mechanism. Each step resulted in a pressure drift due to gasket relaxation and hydrogen consumption by the sample and the gasket. This drift slowed down with time. The pressure was measured before and after each X-ray diffraction measurement was done, and the difference between these values was typically about 1 GPa at pressures about 10 GPa and higher. The pressures referred further are the pressures after the X-ray measurements.

X-ray powder diffraction patterns were measured by the energy-dispersive method with a polychromatic radiation from a conventional tungsten target tube and a 100 μm homemade collimator. X-ray technique is described in more details elsewhere [20]. The cathode voltage of the tube was -40 kV, and the tube current was 20 mA. The scattering angle was calibrated using the diffraction pattern of hydrogen-free molybdenum and assuming its lattice parameter to be $a = 3.145$ Å. Two runs were performed: run 1 for reaching maximal pressure and run 2 to better study the decomposition process. For both runs 2θ value was 21.5 (1°), corresponding to $E \cdot d = 33.2$ keV·Å. The energy scale was calibrated independently before and after each pattern was taken by measuring the positions of the $\text{CuK}\alpha$ and $\text{InK}\alpha$ X-ray fluorescence lines from separate standards, and assuming linear dependence between the channel number of the multichannel analyzer and the photon energy. Additional control of energy calibration was provided by using $\text{MoK}\alpha$ and $\text{MoK}\beta$ fluorescence lines always present in the spectra as an internal standard. Accumulation time was different for each pattern, typically in the range from 2×10^4 – 10^5 s. All experiments were conducted at room temperature.

3. Results and discussion

The powder diffraction patterns for compression in run 1 are presented in Fig. 1, and the decompression patterns for run 2 are shown in Fig. 2.

Phase transformation from the bcc to the hcp metal lattice, corresponding to the hydride formation was first observed at a pressure of $P_{\text{bcc} \rightarrow \text{hcp}} = 4.2$ (1) GPa in agreement with previous data [13]. At pressure between 6 and 15 GPa the diffraction peaks anomalously shifted with pressure to higher d values (see thin black lines in Fig. 1), indicating continuous increase in the H/Mo composition of the hydride. At higher pressures the peaks shifted as

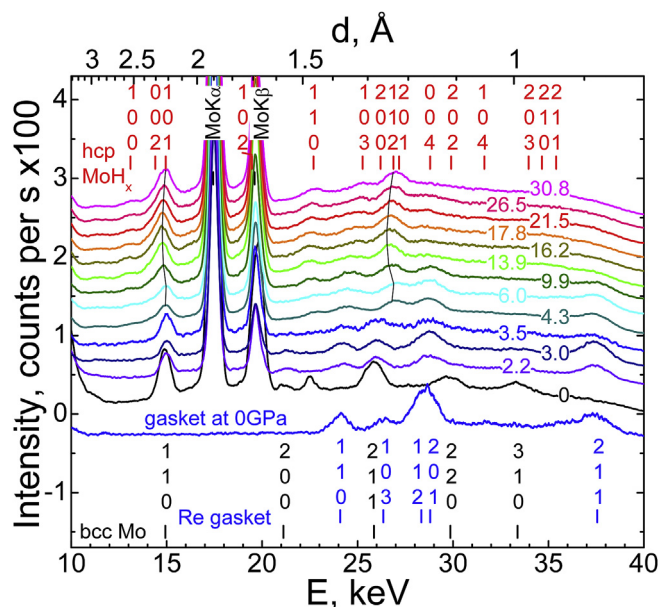


Fig. 1. Energy-dispersive powder diffraction patterns of Mo in a hydrogen atmosphere, taken during pressure increase in run 1. The numbers indicate hydrogen pressure in GPa; the black, red and blue marks indicate the peak positions of the bcc molybdenum, the hcp molybdenum hydride and the textured hcp rhenium gasket respectively. The X-ray fluorescence lines of Mo are marked as $\text{MoK}\alpha$ and $\text{MoK}\beta$. A peak at 22.5 keV and an intensity below 11 keV in the spectrum at 0 GPa are measurement artefacts of non-diffraction origin, caused by unexpected detector power shutdown. The thin black lines show pressure evolution of the (101) and (112) peaks of molybdenum hydride. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

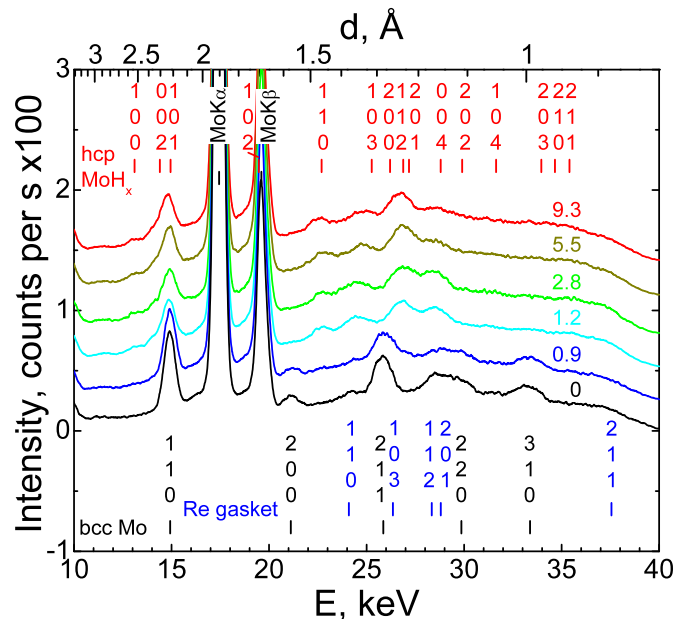


Fig. 2. Energy-dispersive powder diffraction patterns of Mo in a hydrogen atmosphere, taken during pressure decrease in run 2.

usual. No two-phase mixtures were detected in any pattern, which was a result of relatively fast kinetics.

Decompression measurements have shown this behavior to be reversible. The decomposition of the hydride was first observed at $P_{\text{hcp} \rightarrow \text{bcc}} = 1.0$ (1) GPa. This is considerably less than previous estimate $P_{\text{hcp} \rightarrow \text{bcc}} = 1.8$ GPa from Ref. [13], but close to the

extrapolation of high temperature data for equilibrium $P_{\text{hcp} \rightarrow \text{bcc}} = 0.7$ GPa [21,11]. We think that the data of Ref. [13] probably have suffered from hydrogen leakage during the decompression, which affected the decomposition process. The equilibrium conditions for hydride formation reactions are always much closer to the decomposition ones than to the midpoint between formation and decomposition (see Ref. [21] for discussion and explanation of this asymmetry of the hysteresis loop).

Atomic volumes, calculated from the powder diffraction patterns are plotted in Fig. 3 as a function of hydrogen pressure. The positions of the (100), (002), (101), (110), (200), (112) and (201) diffraction peaks of hcp-MoH_x were used to calculate its volume.

Volume-pressure dependence for bcc Mo at hydrogen pressure below 4.3 GPa does not differ from that for Mo in a neon atmosphere within data uncertainties. Volume discontinuity at 4.3 GPa is $\Delta V_{\text{bcc} \rightarrow \text{hcp}} = 2.2$ (2) Å³ per Mo atom, which agrees with previous estimates 2.1 Å³ per Mo atom [10] and 2.08 (2) Å³ per Mo atom for a hydride with MoH_{1.10(3)} composition [11]. The ratio $c/a = 1.60$ (2) for MoH_x is virtually pressure-independent (see the bottom part of Fig. 3), being smaller than the ideal value 1.633 in agreement with previous estimates 1.620 (1) [11] and 1.62 [10].

A continuous increase of the H/Mo content in the pressure range from 6 to 15 GPa is reminiscent of continuous hydrogen content increase in the hcp tungsten hydride [2]. Similar behavior is found in the metal-hydrogen systems with the hcp structure of primary hydrogen solution, such as Co-H [23], Ru-H [8], Tc-H [24], and Re-H [3] systems.

At pressures higher than 15 GPa the $V(P)$ dependence for MoH_x shows normal compression behavior and can be fit by a Birch-Murnaghan equation of state.

$$P = \frac{3B_0}{2} \left[\left(\frac{V(P)}{V_0} \right)^{-\frac{2}{3}} - \left(\frac{V(P)}{V_0} \right)^{-\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4}(B'_0 - 4) \left[\left(\frac{V(P)}{V_0} \right)^{-\frac{2}{3}} - 1 \right] \right\}$$

with fixed bulk modulus pressure derivative $B'_0 = 4$, where V_0 and

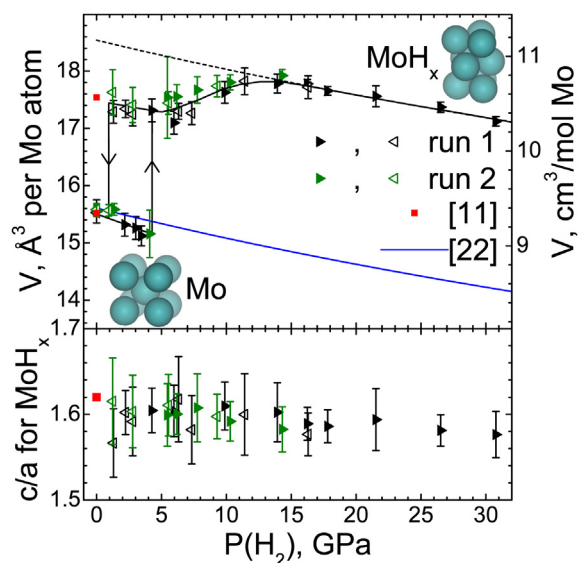


Fig. 3. Lattice volumes per metal atom (top) and the c/a ratios for hcp molybdenum hydride (bottom) as a function of hydrogen pressure. The solid and open triangles denote compression and decompression data respectively. The red squares are the literature data for molybdenum and its hydride at ambient pressure and $T = 85$ K [11], the blue line is an equation of state for molybdenum in a neon atmosphere [22]. The arrows show formation and decomposition pressures for MoH_x, and the solid black lines are guides for an eye. The dashed line is a fit of the $V(P)$ data at $P > 15$ GPa (see corresponding equation of state parameters in Table 1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

B_0 are volume at 0 GPa and bulk modulus respectively. The results of this fit are presented in Table 1 together with the V_0 for pure Mo (our data) and B_0 for Mo in a neon atmosphere, taken from the literature. The bulk modulus of MoH_x is comparable to that of pure molybdenum, which is typical for the hydrides with a fixed composition [25]. Thus, the hydrogen content H/Mo of the hydride saturates at 15 GPa and can be considered constant at higher pressures.

An estimation of the saturation composition of molybdenum hydride is possible from volumetric considerations. Since the volume expansion per Mo atom is measured directly by X-ray diffraction, a composition H/Mo of the saturated molybdenum hydride can be estimated by comparing this volume expansion with the expected volume expansion per H atom. Each hydrogen atom, placed in an octahedral interstitial site in a close-packed lattice of transition metal atoms expands the lattice by about 2.0–2.5 Å³ per H atom, whereas in a tetrahedral site the volume expansion is 2.2–3.2 Å³ per H atom (see Ref. [25] for particular values for different metals). More accurate estimate can be made based on the recent experimental [11] and theoretical [15] works.

The volume difference $V(\text{MoH}_{1.10}) - V(\text{Mo}) = 2.08$ (2) Å³ per Mo atom was accurately measured in Ref. [11] (the corresponding volumes are shown by the red squares in Fig. 3). Ab-initio calculations [15] gave $V(\text{MoH}) - V(\text{Mo}) = 1.9$ Å³ per Mo atom and $V(\text{MoH}_2) - V(\text{Mo}) = 5.2$ Å³ per Mo atom for a hypothetical MoH₂ compound at 0 GPa. In this hypothetical compound with the hcp metal lattice all octahedral and half of the tetrahedral interstitials are occupied, thus, the volume expansion caused by the occupation of the tetrahedral interstices is 3.3 Å³ per H atom. All these data together with our estimate $V(\text{MoH}_x) - V(\text{Mo}) = 3.0$ (2) Å³ per Mo atom are presented in Fig. 4.

If in a saturated molybdenum hydride observed at $P > 15$ GPa all octahedral interstices are occupied and the tetrahedral interstices are partially occupied, then the composition $x = \text{H/Mo}$ can be estimated as $x = 1.35$ (10).

Several metals were earlier observed to form nonstoichiometric compounds when saturated with hydrogen: ReH_{0.85} [3], CuH_{0.5} [26,27], TcH_{0.8} [17] and WH_{1.3} [2]. The reason why these metals do not form higher stoichiometric hydrides when the hydrogen pressure is further increased is unclear. In the case of the Mo-H system a possible explanation of why MoH₂ do not form can be given taking into account a blocking effect, as originally proposed by Switendick [28]. It was found that the hydrogen-hydrogen interatomic distance in all dihydrides is higher than 2.14 Å, which is a manifestation of a short-range H-H repulsion. There are very few metal hydrides which violate this empirical rule [29].

The shortest H-H distance of 2.15 Å in the hypothetical MoH₂ is realized between the octa and tetra sites, according to the first principle calculations [15]. It should be noted that the GGA-PBE calculation method used in Ref. [15] typically overestimates interatomic distances by about ~0.5%, and MoH₂ should be close to the violation of the shortest H-H distance criterion.

Since the X-ray diffraction studies done in this work are not sensitive to the hydrogen positions in the crystal structure of MoH_{1.35}, the shortest H-H interatomic distance in this compound can hardly be estimated. The lattice parameters of MoH_{1.35} are smaller than these of the hypothetical MoH₂, and hydrogen atoms

Table 1
Comparison of the equation of state parameters for Mo and saturated MoH_x.

Substance	V_0 , Å ³ per Mo atom	B_0 , GPa
bcc Mo	15.55 (10)	273 (15) [22]
hcp MoH _x above 15 GPa	18.5 (2)	340 (30)

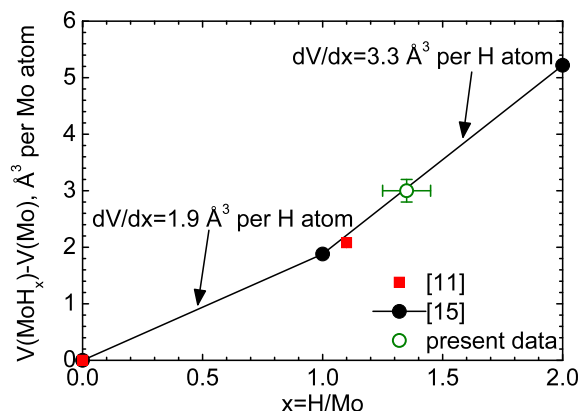


Fig. 4. Volume expansion of molybdenum hydrides, caused by hydrogen. The results of ab-initio calculations [15] are shown by the black filled circles, the experimental results of Ref. [11] are shown by the red squares, and the green open circle is present data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

can displace from the ideal positions at the centers of their sites to relax the H-H repulsion. At present it is not clear which effect dominates, thus, further theoretical and experimental work is needed to understand why the saturation composition of hydrogen in molybdenum is non-stoichiometric.

4. Conclusions

To summarize, we have studied the crystal structure and the lattice parameters of molybdenum under high hydrogen pressure up to 30 GPa. The composition H/Mo of molybdenum hydride is shown to increase continuously with pressure increase, instead of being constant or undergo discontinuities. At the pressure of about 15 GPa the composition H/Mo saturates at about 1.35 (10), and there are no further hydrogen absorption steps up to the maximal reached pressure, contrary to the ab-initio predictions. Our results show the importance of high pressure technique as an instrument for the synthesis of new compounds with unexpected stoichiometries, and, particularly, for new hydrogen-rich materials.

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