

# Neutron-diffraction investigation of structures of the hydrides of molybdenum, rhodium, and nickel

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## INTRODUCTION

The development of a technique for compressing hydrogen to high pressures has enabled us to synthesize and investigate the hydrides of a number of transition metals (Mn, Fe, Co, Mo, Tc, Rh, Re) which were previously thought not to form hydrides.<sup>1,2</sup> X-ray investigation revealed that these hydrides are based on closest packings of atoms of the metal - hcp or fcc. As concerns the positions of the hydrogen atoms, in view of the relatively small amounts of substance synthesized at high pressures (a few tens of milligrams), the possibility of making neutron-diffraction investigations appeared only after the construction of the DISK high-transmission multidetector neutron diffractometer.<sup>3</sup> The results of neutron-diffraction investigation of the structures of the hydrides of technetium<sup>4</sup> and rhenium<sup>5</sup> supplemented the previously discovered<sup>6,7</sup> correlation between the type of interstices occupied by hydrogen atoms in the metal lattice and the radius of the metal atoms. According to Refs. 4-7, in metals with large atomic radius the tetrahedra are preferred by hydrogen, but in metals with small atomic radius the octahedra are preferred, and the change in the coordination occurs at some critical atomic radius of the metal  $r_{cr} \approx 1.34-1.40 \text{ \AA}$ . The results in Refs. 4 and 5 contain an indication that for the d-metals of different periods the critical radius is not the same. To make this fact more precise, we need data on the structure of the hydrides of molybdenum and rhodium, which lie in the 4d period and have atomic radii close to the critical value ( $r_{Mo} = 1.39 \text{ \AA}$ ,  $r_{Rh} = 1.34 \text{ \AA}$ ). Moreover, in Refs. 8 and 9 on the basis of a study of the concentration dependence of bulk effects with the solution of hydrogen in nickel, the hypotheses were advanced that the tetrahedral interstices in the lattice become filled with hydrogen at concentrations  $H/Ni \geq 1$ , while the atomic radius of nickel is less than the critical value ( $r_{Ni} = 1.24 \text{ \AA}$ ) and in  $NiH_{0.6}$  Zhebelev et al.<sup>10</sup> have established the octahedral coordination of the hydrogen atoms.

In our work, with the aid of neutron diffraction we have studied the structure of molybdenum and rhodium hydrides, and also of nickel hydride of limitingly high composition.

## SPECIMENS AND EXPERIMENTAL METHOD

To prepare the specimens we used molybdenum foil about 0.05 mm thick made from molybdenum purified by zone melting, electrolytic nickel, and rhodium powder (40 mesh, 99.998% Rh). The metals were saturated with hydrogen by keeping them for 8 h at fixed temperatures and hydrogen pressures in the region of formation of the corresponding hydrides, according to the T-PH<sub>2</sub> diagrams, followed by quenching under pressure to about 100 K (Ref. 2). In normal conditions the hydrides obtained were unstable relative to decomposition

to metal and hydrogen; marked emission of hydrogen from molybdenum hydride at atmospheric pressure began at T = 220 K, and from the hydrides of nickel and rhodium at T = 250 and 180 K. To prevent loss of hydrogen the specimens were kept in liquid nitrogen. To avoid the influence of texture on the intensities of the diffraction maxima, the molybdenum and nickel hydride specimens before neutron diffraction were pulverized in a porcelain mortar at liquid nitrogen temperature. Neutron diffraction patterns were recorded at T = 120 K with a special nitrogen cryostat, designed to permit transfer of the specimens for 1-2 min without warming above 120 K. All the specimens of molybdenum and rhodium hydrides weighed about 30 mg, and those of nickel hydride weighed about 150 mg. The duration of exposure was 15-30 h; the mean statistical error did not exceed 4-5%.

The hydrogen content of the specimen was determined to an accuracy of  $H/Me = \pm 0.03$  by measuring the gas volume separated by thermal decomposition of the hydride.

## EXPERIMENTAL RESULTS

1. Molybdenum hydride. The hydride  $MoH_x$  was synthesized at T = 598 K and  $P_{H_2} = 7 \text{ GPa}$ ; according to volumetric analysis  $x = 1.19$ . In the neutron diffraction pattern (Fig. 1a) we observe lines indexed in the hcp cell with parameters  $a = 2.937 \pm 0.005 \text{ \AA}$ ,  $c = 4.758 \pm 0.007 \text{ \AA}$ , agreeing with the x-ray data.<sup>11</sup> Consequently  $MoH_x$  is an interstitial solid solution based on the hcp lattice of the metal.

To locate the hydrogen atoms we used the ratios of the intensities of the lines (100), (002), (101) which depend on the type of interstices occupied by hydrogen: For the composition  $MoH_{1.0}$  for the tetrahedral model they are 0.5:10:30, and for the octahedral model 15.4:10:17.4. The experimental ratio 16.9:10:20.5 (Table I) indicates the preferential placing of hydrogen atoms in octahedra, which is also confirmed by calculation of the full diffraction pattern; minimization of the uncertainty factor  $R = \sum |I_e - I_p| / \sum I_e$  from the hydrogen concentration gives the composition of the hydride  $x = 0.95 \pm 0.05$  (Table I). Since in the hcp lattice to each metal atom there belongs only one octahedron, exceeding the equiatomic composition in the hydride,  $MoH_{1.19}$  can be realized either on account of partial filling of the tetrahedral gaps with hydrogen, or on account of the formation of vacancies in the sublattice of metal atoms. Both these possibilities were considered, but led to a marked deterioration of the agreement between theory and experiment. Thus according to the neutron diffraction data, molybdenum hydride has a structure based on a hcp lattice with completely filled octahedral interstices - a structure of the NIAs type.

TABLE I. Experimental and Theoretical Intensities of Diffraction Lines

HKL	MoH			HKL	RhH			NiH		
	$d_0, \text{\AA}$	$I_0$	$I_p$		$d_0, \text{\AA}$	$I_0$	$I_p$	$d_0, \text{\AA}$	$I_0$	$I_p$
100	2.54	56.6	56.7	111	2.32	102.0	100.4	2.17	96.4	93.9
002	2.38	33.5	36.7	200	2.01	5.4	5.0	1.87	13.8	13.3
101	2.25	68.8	63.7	220	1.42	7.6	6.2	1.323	15.9	16.0
102	-	<1.5	0.2	311	1.207	86.6	88.1	1.127	95.5	96.6
110	1.47	6.7	5.0	222	-	$\leq 3.0$	3.3	1.080	7.5	9.2
103	1.34	21.6	24.9	400	-	$\leq 3.0$	2.5			
200				331	0.918	72.5	74.5			$R=2.6\%$
112	1.243	100.0	99.5	420						
201							$R=2.5\%$			
004	-	<1.5	1.3							
202	-	<1.5	0.0							
104	1.070	19.2	21.4							
203	0.984	18.3	16.6							
210	0.941	51.9	50.7							
211										$R=5\%$

Note. In the calculations we used the Debye-Waller factors ( $B, \text{\AA}^2$ ): 0.2 for Rh, 0.3 for Mo and Ni, 1.2 for H.

2. Rhodium hydride. The hydride  $\text{RhH}_{1.0}$  was synthesized at  $T = 623 \text{ K}$  and  $P_{\text{H}_2} = 7 \text{ GPa}$ . In the neutron diffraction pattern (Fig. 1b) we see lines indexed in the fcc cell with parameter  $a = 4.01 \pm 0.01 \text{ \AA}$ , satisfactorily agreeing with the x-ray data<sup>12</sup> and increased in comparison with the parameter of the fcc cell of the original metal ( $a = 3.803 \text{ \AA}$ ). Consequently, rhodium hydride is an interstitial solid solution of hydrogen on the basis of the fcc lattice of the metal.

From Fig. 1b and Table I we see that the lines with odd indices HKL are ten times more intensive than the lines with even indices. Just this intensity ratio must be expected in the case of filling of the octahedral interstices in the fcc lattice of rhodium with hydrogen, since the amplitudes of coherent scattering of neutrons by Rh and H atoms are opposite in sign and similar in absolute value ( $b_{\text{Rh}} = 0.58 \cdot 10^{-12} \text{ cm}$ ,  $b_{\text{H}} = -0.374 \cdot 10^{-12} \text{ cm}$ ). The intensities of the diffraction maxima calculated in the octahedral model agree with the experimental values (Table I); minimization of the R index gives the composition  $\text{RhH}_{0.95 \pm 0.05}$ . Rhodium hydride has the NaCl structure.

3. Nickel hydride. The hydride  $\text{NiH}_x$  was synthesized at  $T = 523 \text{ K}$  and  $P_{\text{H}_2} = 2 \text{ GPa}$ ; according to volumetric analysis  $x = 1.11$ . The lines in the neutron diffraction pattern (Fig. 1c) were indexed in the fcc cell with  $a = 3.740 \pm 0.005 \text{ \AA}$ . The experimental values of the structure factors  $|F_{\text{HKL}}|$  are the same (within the Debye-Waller factor) for all reflections with even and odd HKL. This means that, as also in the case of rhodium hydride, the diffraction pattern is described in all by two types of structure factors:  $b_{\text{Ni}} + x \cdot b_{\text{H}}$  for the even HKL and  $b_{\text{Ni}} - x \cdot b_{\text{H}}$  for the odd HKL, i.e., the structure is of the NaCl type. Better agreement with experiment in this structure was obtained for the equiatomic composition NiH (Table I). Introduction into the calculation of hydrogen-filled tetrahedra or vacancies in the metal sublattice (which would correspond to excess over the equiatomic composition) led to disagreement with experiment. According to the neutron diffraction data, hydrogen is

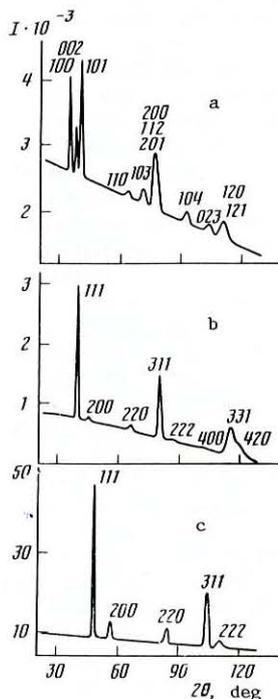


FIG. 1. Neutron diffraction patterns of hydrides of molybdenum (a), rhodium (b), and nickel (c),  $T = 120 \text{ K}$ ,  $\lambda = 1.548 \text{ \AA}$  (a, b),  $1.760 \text{ \AA}$  (c).

found in nickel hydride only in octahedra, and the hydride has the NaCl structure.

As also in molybdenum hydride, in nickel hydride the composition obtained from neutron diffraction data differs from the composition determined by volumetric analysis. It is not ruled out that this discrepancy may be due to impurities of unknown finely disperse or amorphous hydrides with  $\text{H/Me} > 1$ , which make a small contribution to the general pattern of neutron scattering. This question requires further investigation.

## DISCUSSION OF RESULTS

The results of our investigation of the crystal structures of rhodium, nickel, and molybdenum hydrides agree with the general scheme of structure of hydrides.<sup>6</sup> On the basis of fcc metals with hydrogen in the octahedra one would expect the formation of interstitial solid solutions up to the composition MeH (NaCl type structure). This structure is realized in the hydrides of rhodium and nickel. For solid solutions based on bcc metals with octahedral positioning of the hydrogen atoms we predicted rearrangement of the lattice and formation of a hexagonal interstitial phase with structure of the NiAs type. This is indeed the structure of molybdenum hydride.

Data on the coordination of hydrogen in molybdenum and rhodium hydrides, in combination with those obtained earlier for the hydrides of rhenium and technetium,<sup>4,5</sup> enable us to refine the "critical" atomic radius of the metal, at which there is a change in the coordination of the hydrogen atoms from octahedral to tetrahedral:  $r_{CR} = 1.34 \text{ \AA}$  for 3d metals,  $r_{CR} = 1.39\text{--}1.40 \text{ \AA}$  for 4d and 5d metals. The fact that the change in coordination occurs in a narrow range of atomic radii of the metal indicates relative constancy of the effective dimension of the hydrogen atom in different metallic lattices,  $r_H = 0.55\text{--}0.57 \text{ \AA}$ . Some difference in the "critical" radii for the 3d and 4d, 5d metals is evidence that the causes of change of the coordination of hydrogen may have an electronic nature.

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## Structure of 8-ethyl-9-methyladenine

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Investigation of the structures of bases of nucleic acids, their alkyl derivatives, and their crystal hydrates yields information on the geometric characteristics of water-base hydrogen bonds, and allows us to estimate the influence of hydrophobic substituents on hydration of the bases. Of the crystal hydrates of the bases the least studied are the crystal hydrates of adenine and its derivatives; only one structure is known, namely adenine trihydrate.<sup>1</sup> The most closely studied derivative of adenine, 9-methyladenine, does not form a crystal hydrate. Some interest is occasioned by the ethyl derivatives of adenine. An ethyl group reduces the packing factor of such plane molecules as adenine. Water tends to fill the gaps which arise, forming crystal hydrates. The conformational freedom of the ethyl group may lead to a phase transition associated with ordering.

We obtained crystals of 8-ethyl-9-methyladenine and its dihydrate. In this article we give a complete x-ray structural investigation of the crystals of anhydrous 8-ethyl-9-methyladenine. The structure of its dihydrate will be published separately.

Single crystals suitable for a diffraction experiment were grown by sublimation in vacuum at about 100 °C onto a glass substrate. Even with slow cooling of the crystals from about 70 °C (the substrate temperature) to room temperature we observe their cracking and peeling from the substrate. This may be due to a phase transition accompanied by a sudden change in volume. The crystals grow in the form of hollow needles, easily twinned.

The experiment was made in a Syntex P2<sub>1</sub> automatic diffractometer. The crystals of 8-ethyl-9-methyladenine, C<sub>8</sub>H<sub>5</sub>H<sub>11</sub>, are triclinic, space group P $\bar{1}$ ,  $a = 7.025(2) \text{ \AA}$ ,  $b = 7.358(1) \text{ \AA}$ ,  $c = 8.392(2) \text{ \AA}$ ,  $\alpha = 87.19(2)^\circ$ ,  $\beta = 101.56(2)^\circ$ ,  $\gamma = 92.24(2)^\circ$ ,  $V = 424.2(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $d_{calc} = 1.39 \text{ g/cm}^3$ ,  $\mu(\text{Mo K}\alpha) = 1 \text{ cm}^{-1}$ . The unit-cell parameters were determined by the method of least squares for 15 reflections with  $24^\circ \geq 2\theta \geq 38^\circ$ . The set of reflections was obtained by  $\theta/2\theta$  scanning at variable rate of 2-29 deg/min in Mo K $\alpha$  radiation (graphite monochromator) to  $2\theta \leq 55^\circ$ . Of 1955 independent