

## **CHAPTER 4**

# **Cobalt-, Rhodium- and Iridium-Hydrogen**

V.N. VERBETSKY and S.V. MITROKHIN

*Chemistry Department, Lomonosov Moscow State University, Moscow  
119899, Russia*

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### Introductory background

The triad of cobalt, rhodium and iridium in the 9th periodic table subgroup belong to a class of metals which do not form hydrides in direct reactions with gaseous hydrogen under lower temperature and pressure conditions. It seems rather important, therefore, to outline a short initial historical survey of experimental studies on syntheses of hydrides of these metals.

For example, "cobalt hydride  $\text{CoH}_2$ ", a black precipitate which is insoluble in water, diethyl ether and ethanol has been obtained [1] in 1926 from the reaction:



Similar experiments [2,3] have permitted preparation of two seemingly analogous hydrides with compositions " $\text{CoH}_2$ " and " $\text{CoH}$ ". Investigation of the thermal stability of these products showed that " $\text{CoH}_2$ " is stable up to 317-318.8K and at higher temperatures decomposes with the formation of " $\text{CoH}$ " which will then desorb hydrogen at 423K. Taking into account the comparative experimental difficulties in such syntheses and the fact that the reaction also terminates in several additional byproducts with limited possibilities of analytical investigation of the products by comparison with current instrumental methods, it seems necessary to consider the results of these pioneer works rather carefully. Thus it seems reasonable to compare and discuss the results of the early cobalt studies from a similar viewpoint to that for assessments of early reports of hydrogen solubility in rhodium and iridium [4-7], where, in particular, the synthesis has been reported in [4] of phases with compositions of " $\text{RhH}_{0.4}$ " and of " $\text{IrH}_{0.4}$ " at room temperature and not very high pressure.

An important advance in the case of this group in the field of preparation of metal hydrides was made by the development of the high gaseous hydrogen pressure apparatus of the two research groups of B. Baranowski and E. Ponyatovsky respectively. The Ponyatovsky group in particular have investigated the  $\text{Co-H}_2$ ,  $\text{Rh-H}_2$  and  $\text{Ir-H}_2$  systems extensively. Further details of these high pressure experiments can be found in reviews [8-11].

**TABLE 1\* Some properties of cobalt, rhodium and iridium**

\*After IUPAC Source Information

Property	Co	Rh	Ir
Atomic number	27	45	77
Number of naturally occurring isotopes	1	1	2
Atomic weight	58.93	102.91	192.22 ( $\pm 0.03$ )
Electronic configuration	[Ar]3d <sup>7</sup> 4s <sup>2</sup>	[Kr]4d <sup>8</sup> 5s <sup>1</sup>	[Xe]4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>
Electronegativity	1.8	2.2	2.2
Metal radius (12-coordinate)/pm	125	134	135.5
MP/ $^{\circ}$ C	1495	1960	2443
BP/ $^{\circ}$ C	3100	3760	4550 ( $\pm 100$ )
Density (20 $^{\circ}$ C)/g cm <sup>-3</sup>	8.9	12.39	22.61
Electrical resistivity (20 $^{\circ}$ C)/ $\mu$ ohm cm	6.24	4.33	4.71

### Adsorption and solubility of hydrogen in the triad of metals

The adsorption data for cobalt is summarised and compared in Table 2 together with calorimetric data and including results of investigation of thermodesorption of hydrogen from single-crystal cobalt and cobalt films. Hydrogen adsorbed on surfaces of cobalt, rhodium and iridium [12-26] appears to be bonded in at least four different forms, differing in desorption activation energy and desorption temperature ranges:  $\alpha$ ,  $\beta_1$ ,  $\beta_2$ ,  $\gamma$  where  $\alpha$  corresponds to the molecular form of hydrogen, and  $\beta_1$ ,  $\beta_2$ ,  $\gamma$  corresponds to one electropositively polarised form  $\beta^+$  and two electronegatively polarised forms  $\beta_s^-$  and  $\beta^-$  with activation energies of 8.8, 41.8 and 79 kJ/mol respectively. Table 3 shows differences in characteristics [26] of hydrogen sorption on the three metal surfaces.

At low temperatures, desorption from the surface of the first and second forms can be described by a first order equation which tends to support either the molecular (I form) or molecular-bridge (II form) types of bonding of the adsorbed hydrogen. The hydrogen desorption activation energies of these two forms lie in the range of 5-17 kJ/mol, with the absolute value decreasing in the sequence Ni >  $\beta$ -Co >  $\alpha$ -Co >  $\alpha$ -Fe > Ir > Rh.

Desorption of the third and fourth adsorption forms has been described by a second order equation and relates to the presence of atomic forms of the adsorbed hydrogen. The hydrogen content of the III atomic form also corresponds to the sequence: Ni >  $\beta$ -Co >  $\alpha$ -Co >

$\alpha$ -Fe > Ir > Rh, while the most firmly bonded IV form of hydrogen is characterised by high values of desorption activation energies of 41-82 kJ/mol for fcc cobalt, 134-167 kJ/mol for rhodium, and 82-125 kJ/mol for iridium.

**TABLE 2** Activation energy and heat of hydrogen adsorption and desorption on cobalt

Surface type	$E_{A_{ads}}$	$E_{A_{des}}$	Desorption		
	kJ/mol	kJ/mol	$-\Delta H_{ads}^*$	order	Reference
Co	5.8	151	145±10	2	22
3% Co/SiO <sub>2</sub>	43				22
10% Co/SiO <sub>2</sub>	18	168	145±7	2	22
10% Co/Al <sub>2</sub> O <sub>3</sub>	39	144	105	2	22
4% Co/TiO <sub>2</sub> (rutile)			88/133		19
Reduced Co (calorimetric)			105		23
Co films (surf. pot./TDP)		42/79			24
Single-crystal Co (0001)		67		2	25

\*Heat of adsorption:  $-\Delta H_{ads} = E_{A_{des}} - E_{A_{ads}}$

**TABLE 3** Parameters of hydrogen sorption on metal surfaces

Metal surface	$E_{ads}$ , kJ/mol	$E_{Me-H}$ , kJ/mol	Phase	Monolayer $s$ (at $T_{crit}$ °K)	Initial sticking coefficient, $S_0$ (T °K)	Frequency factor, $cm^2/at H \cdot s$	Work function at saturation, mV (at $T_{des}$ °K)
Co(1010)			c2x4	0.5 (270)	1.0 (120)		
Rh (111)	78	225				1.21 · 10 <sup>-3</sup>	
Rh (110)	77	225			1.0 (85)		+930 (80)
			2x1-2H	1.0 (290)			
			p1x3	0.33 (~140)			
			p1x2	0.5 (~180)			
			1x3-2H	0.67 (~220)			
			1x2-2H	1.5 (~190)			
			1X1-2H	2.0 (<180)			
Ir (110)	77	225			1.0 ( $\beta_2$ 130)	1.5 · 10 <sup>-2</sup> $\beta_2$	
					0.007 ( $\beta_2$ 30)	2 · 10 <sup>-2</sup> $\beta_1$	

### Lattice Solubility

In the early studies of Sieverts [7-8] the pressure  $P_{H_2}$  dependence of hydrogen solubility (C) in cobalt solubility has been described by the equation:

$$C = k\sqrt{P_{H_2}} \quad (1)$$

Negative deviations from Sieverts' law have been observed for values of pressure higher than 15-20 MPa and at temperatures higher than 1473K together with slight deviation at temperatures higher than 1073K, that can be accounted for by reasons of multifold compressions and peculiarities of the molecular-kinetic equilibrium at the gas-metal boundary [27]. The negative deviations are also in keeping with the reported decreases by 3-4 degrees of the melting point of cobalt under pressures higher than 50 MPa [27]. The positive deviations can be accounted for by an influence of hydrogen interaction with crystal structure defects. In addition at the transition of cobalt to the paramagnetic state, it has been found that the heat of hydrogen solution exhibits an increase from 42 to 63.5 kJ/mol and that the solubility simultaneously decreases by an approximate factor of two [27]. Information concerning hydrogen solubility  $S_H$  in cobalt, rhodium and iridium is summarised in Table 4. Comparatively full data on hydrogen solubility and diffusion in the triad metals can also be found in appropriate databooks [29, 45-48]. In one group of studies [30, 49-52] the solubility of hydrogen in cobalt has been investigated under pressures of up to 100 MPa and at temperatures up to 1773K: the corresponding hydrogen solubility isotherms are presented in Fig. 1.

Fig. 2 illustrates a phase diagram of the cobalt-hydrogen system for an approximate pressure of 100 MPa and it may be seen that the melting point of cobalt is decreased by 28K for 100 cm<sup>3</sup> of hydrogen dissolved in 100 g of metal. An increase of hydrogen content in the metal also seems markedly to increase the polymorphous hcp  $\leftrightarrow$  fcc cobalt transition temperature and at 1723K the melt with 1.7 at % of hydrogen transforms to a solid solution of hydrogen in fcc-cobalt.

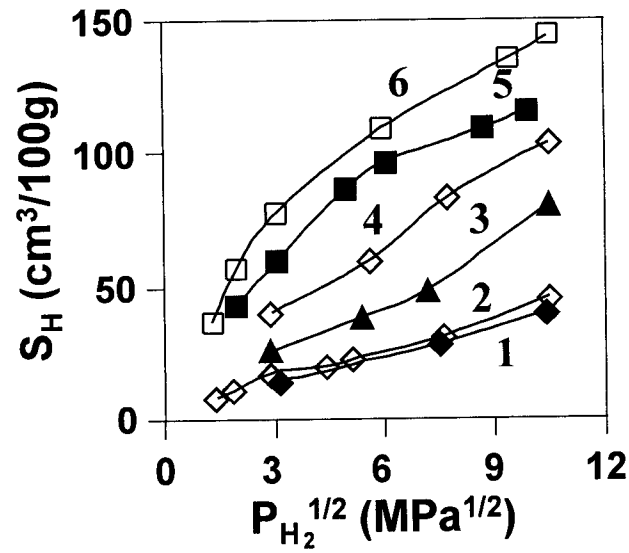


Fig. 1 Influence of hydrogen pressure on hydrogen solubility in cobalt: 1-693, 2-873, 3-1073, 4-1273, 5-1473, 6-1673K [49]

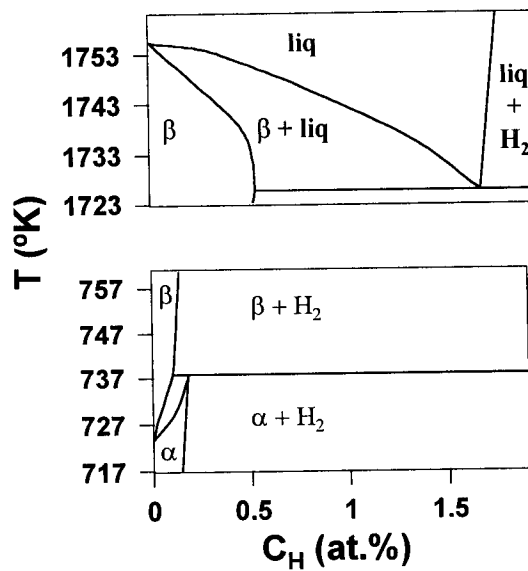


Fig. 2 Phase diagram of the Co- $\text{H}_2$  system with respect to 100 MPa

TABLE 4 Solubility data of hydrogen in cobalt, rhodium and iridium

Metal phase	T °K	A	B	$\psi$	Q	Equation*	Ref.
Co	923-1768	-3.08	-1370			1	37
Co liq	1768-2-73	-2.5	-1670			1	37
Co fcc	1279-1765			0.24	32.6	2	38
Co fcc	1373-1673	1.72	1650	0.166	31.68	2,3	27
Co hcp	573,733	1.73	1120	0.17	21.5	2.3	27
Co	673-1373	1.40	1110	0.079	21.12	2,3	27
Co liq	1765-1973			1.03	41.09	2	38
Co liq	1865-2071	2.70	2890			3	28
Co liq	1833-1973	2.28	2140			3	29
Co liq	1765-1939	2.01	1665			3	30
Co liq	1763-1973	2.004	1625			3	31
Co liq	1873-2133	1.822	1180			3	32,33
Co liq	1773-2133	2.08	1250			3	34,35
Co liq	1823-2023	2.411	1940			3	36
Co fcc	873-1273	1.99	1890			3	40
Co fcc	1363-1765	1.99	1670			3	30
Co fcc	1273-1373	2.52	2425			3	41
Co fcc	873-1473	1.870	1690			3	42
Co fcc	973-1198	1.88	1379			3	43
Co fcc	673-873	0.63	1066			3	44
Co	773-1673	-1.673	795			3	27
Co hcp (D <sub>2</sub> )	673-773	-4.22	-855			1	37
Rh	1073-1873	-3.12	-1394			1	37
Ir	1673-1873	-2.02	-3847			1	37

\* - corresponding equations:

1.  $\log C = 0.5 \log P + A + B/T$ , where C represents at.% H; P is in Pa; T is in °K.
2.  $C = \psi P^{1/2} \exp(-Q/RT)$ , where C is expressed as cm<sup>3</sup>/100g M and P is in Pa;  $\psi$  corresponds to cm<sup>3</sup>/100g Pa<sup>-1/2</sup> and Q is expressed in kJ/mol.
3.  $\log S = A - B/T$ , where solubility S is expressed as % H and T is in °K.

The maximum experimental content of hydrogen attained in liquid cobalt was ~200 cm<sup>3</sup>/100g [50]. Crystallisation of such a melt resulted in the formation of porous ingots of material. Increasing the cooling

rate produced decreases of pore dimensions and increased numbers of pores.

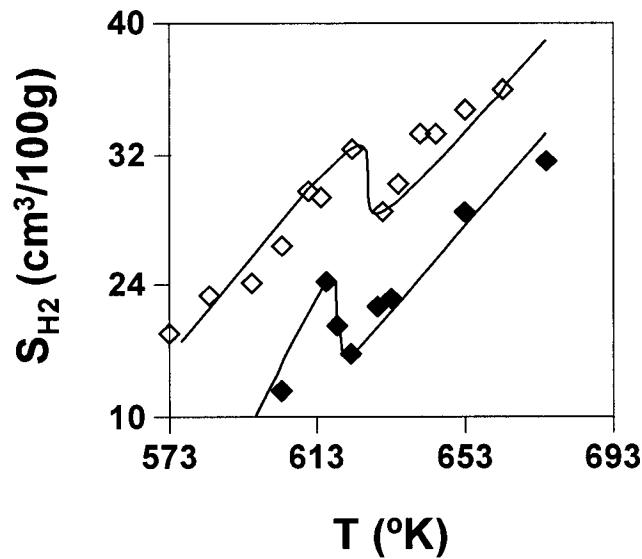


Fig. 3 Hydrogen solubility in two different samples of cobalt near the Curie temperature [52]

A hydrogen solubility anomaly has been found near the Curie temperature as illustrated in Fig. 3, where the hydrogen solubility shows a jumpwise decrease in the narrow (15K) temperature range of the magnetic transition, the minimum of which coincides with the Curie temperature, and the extent of which decreases with increase of hydrogen pressure [52].

### Metal hydrides

A comparison of results of calculations of the main thermodynamical parameters of interaction and of isotherms of hydrogen absorption by cobalt is illustrated in Fig. 4. These calculations have been based on a mean-field lattice gas model and have used the equation of state for liquid hydrogen under high pressure together with the data on solubility under normal pressure [53]. At low pressures an endothermic process of hydrogen solution has been indicated as altering at higher pressures into an exothermic one accompanied by a considerable increase of corresponding solubility and to crossing over of the isotherm patterns. Calculated isothermal data has seemed most reliable for  $x \leq 0.01$  but the degree of



uncertainty has increased with an increasing possibility of phase transformations at higher temperature. Using calculated metal and hydride density states, a self-consistent calculation has been reported [55,56] of the heats of formation of *3d*-, *4d*- and *5d*-metal monohydrides on the basis of local density functional formalism, in terms of the equation:

$$\Delta H = E(\text{MeH}) - E(\text{Me}) - \frac{1}{2}E(\text{H}_2) \quad (2)$$

Calculated and experimental values of the formation heats for hydrides with different compositions are presented in Table 5 and plots with conclusions of other available experimental results are illustrated in Fig. 5. It may be seen from Fig. 5 that for cobalt and rhodium hydrides the heats of formation have negative values while the calculated heat of formation for iridium monohydride is positive, i.e. it seems not to be expected for it to have been formed, which is a possibility in agreement with the absence of related experimental data.

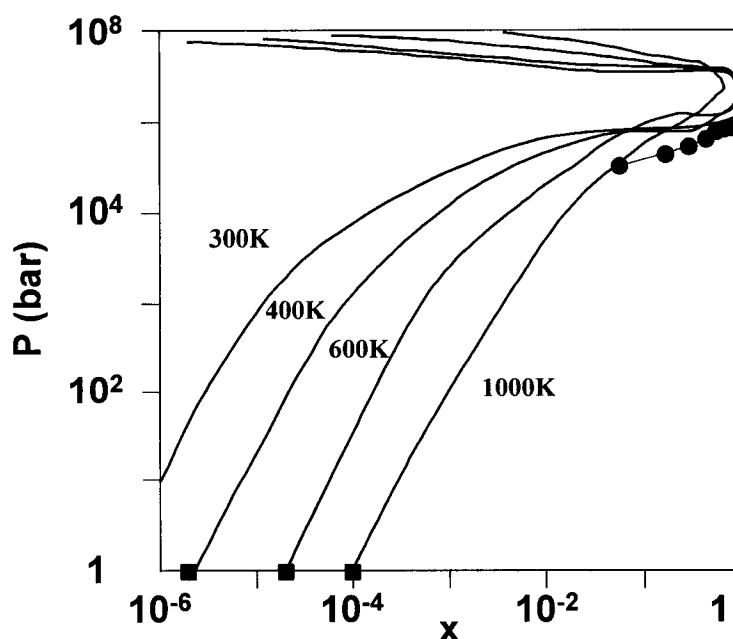


Fig. 4 Metal hydride formation isotherms of Co where full curves represent calculations at  $T = 300\text{K}$ , with  $P_{\text{max}} = 115 \text{ kbar}$  and  $P_{\text{min}} = 45 \text{ kbar}$ ; ■ represents experimental data and ● corresponds to an absorption isotherm at  $623\text{K}$  [54]

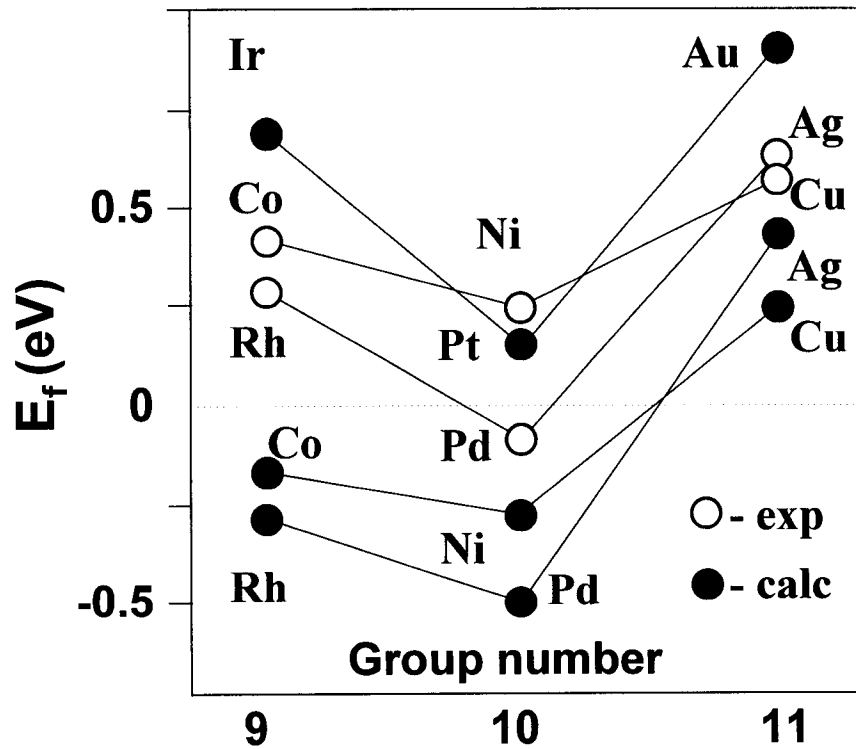


Fig. 5 Calculated and experimental values of heats of formation of monohydrides

TABLE 5 Heats of formation of hydrides

Hydride	$\Delta H_{\text{exp}}$ , kJ/molH <sub>2</sub>	$\Delta H_{\text{calc}}$ , kJ/molH <sub>2</sub>	Reference
CoH <sub>0.5</sub>		+5	57
Co <sub>0.5</sub> H <sub>0.5</sub>	0	+0.2	58
RhH <sub>0.5</sub>		+7	58
Rh <sub>0.5</sub> H <sub>0.5</sub>	6	-0.9	57
Ir <sub>0.5</sub> H <sub>0.5</sub>		+10	59

### Cobalt hydride

An investigation of the Co-H<sub>2</sub> system has been reported [60,61] at hydrogen pressures up to the high value of 90 kbar, and the corresponding pressure dependences of hydrogen absorption in cobalt are shown in Fig. 6. At 523K it may be seen that the solubility in hcp-Co increases monotonously up to compositions in the range of CoH<sub>0.5</sub>-CoH<sub>0.6</sub>. At the higher (623K) temperature of investigation the range of

existence of an hcp-phase has become extended, although isobaric solubilities would seem to have exhibited decreases. This allows the

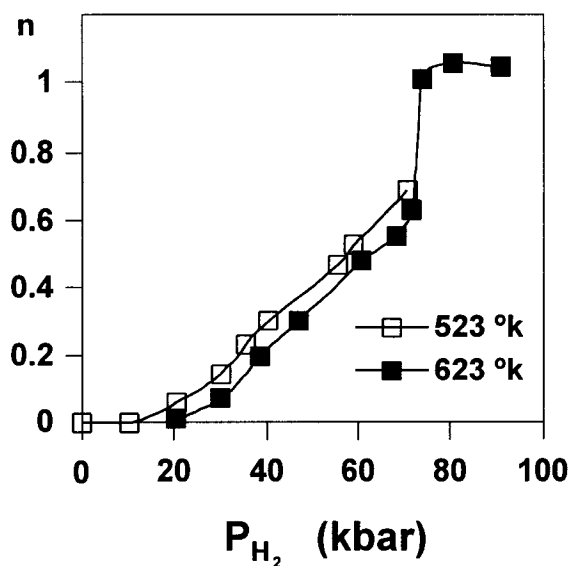


Fig. 6 Pressure dependent absorption of hydrogen in cobalt

possibility of assuming that in the region of high hydrogen pressure concentrations in the metal, the heat of absorption changes sign as is found for the Ni-H<sub>2</sub> system [62]. Fig. 6 has also shown that at 623K the trend of hydrogen solubility dependence at pressures below 70 kbar is analogous to that for 523K while at higher pressures the solubility increases jumpwise up to a value corresponding to a suggested formation of a monohydride CoH phase.

Quenched samples of cobalt hydrides are relatively unstable at ambient pressure and begin to decompose at temperatures higher than 223K. Concentrational dependences of lattice parameters of samples saturated with hydrogen under high pressure and then quenched by immersion in liquid nitrogen are shown in Fig. 7. CoH<sub>0.6</sub> is a single-phase structure based on that of hcp-cobalt while the CoH hydride is formed on a basis of the fcc-cobalt structure. Samples with intermediate compositions appear to correspond to two-phase structures containing the above-mentioned hydrides. CoH is characterised by a lattice parameter of  $a = 3.722 \text{ \AA}$  and its formation is accompanied by a volume increase of  $\sim 1.8 \text{ \AA}^3/\text{Co}$ , which is a comparable behaviour to levels of expansion produced in cases of other transition metals [8-11].

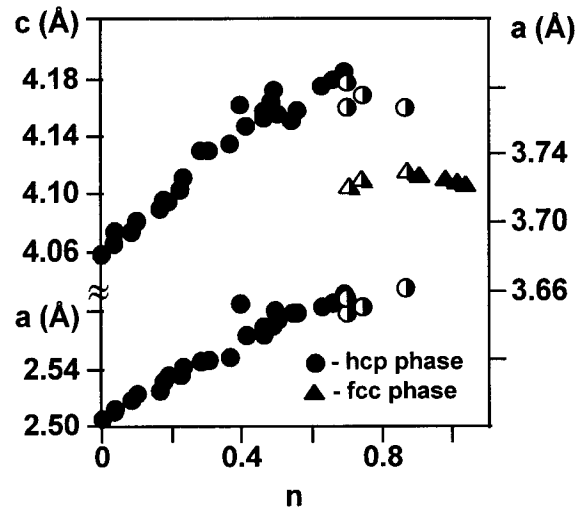


Fig. 7 Concentrational dependence of lattice parameters for the Co-H<sub>2</sub> system at 463K and atmospheric pressure. Half-filled symbols correspond to two-phase samples

Results of Mössbauer analyses of the hydrides are presented in Table 6 [63]. On hydriding in the range of compositions  $0 \leq x \leq 0.6$  there is a 6% decrease of the hyperfine field that is approximately one half of the value of the relative decrease of the spontaneous magnetisation in the same range which could be accounted for as a consequence of filling of the  $3d$ -band. In the concentration range of  $0.6 \leq x \leq 0.9$  the Mössbauer spectrum consists of two components which can be assigned to hcp- and fcc-CoH<sub>x</sub> respectively. The isomer shift increases linearly with hydrogen content without noticeable discontinuity between the hcp and fcc phases. The hyperfine field in the fcc- hydride phase is somewhat higher than in the hcp-hydride phase (by a value of  $\sim 1$ T) and that is very similar to the case of pure cobalt where the hyperfine field in the fcc-modification is also larger than in the hcp-modification.

Investigations have been carried out of the magnetic properties of cobalt hydrides synthesised under high pressure [64,65]. Dependencies of spontaneous magnetisation for samples with different hydrogen content at 80-200K are shown in Fig. 8. As can be seen the magnetisation decreases monotonously with increasing hydrogen concentration up to H/Co  $\approx 0.35$  and then slightly increases. No anomaly was found for either the hcp-type or fcc-type region hydride. Phases containing hydrogen synthesised from polycrystal and single-crystal samples of different plane orientations are seemingly

characterised by the same value of spontaneous magnetisation for the same hydrogen content.

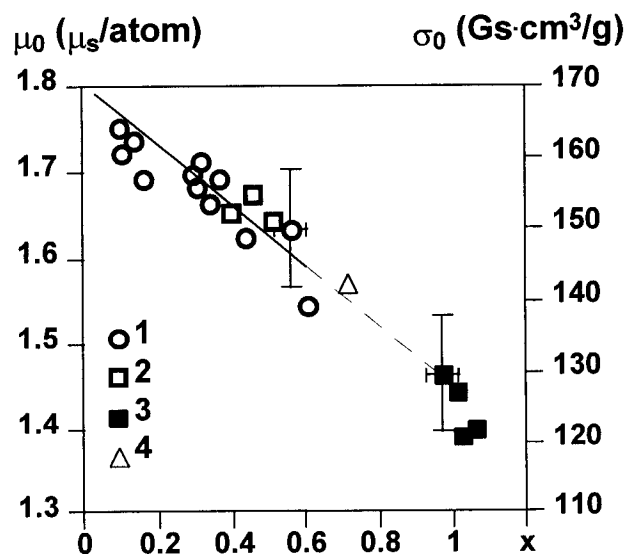


Fig. 8 Spontaneous magnetisation versus hydrogen concentration for the Co-H<sub>2</sub> system:  
 1 - polycrystal samples; 2 - single-crystal hcp solution; 3 - single-crystal fcc-hydride;  
 4 - two-phase sample.

TABLE 6 Mössbauer results for cobalt hydrides

		a, Å	c, Å	S, mm/s	$\Delta E_Q$ mm/s	$B_{hf}$ T	W, mm/s	I, %	Structure
0.00		2.503	4.064	-0.101(5)	-0.054(5)	32.4(1)	0.33(1)	100	hcpCo
0.22(2)	4.0	2.538	4.104	-0.018(5)	-0.074(5)	31.6(1)	0.46(1)	100	CoH <sub>x</sub>
0.48(2)	5.0	2.575	4.164	+0.108(5)	-0.077(5)	30.7(1)	0.37(1)	100	CoH <sub>x</sub>
0.56(2)	6.0	2.590	4.183	+0.123(5)	-0.065(5)	30.7(1)	0.36(1)	100	CoH <sub>x</sub>
0.67(3)	9.0	2.594	4.184	+0.17(5)	-0.065(5)	30.6(1)	0.36(1)	629(2)	CoH <sub>0.6</sub>
	*								)
			3.723	+0.206(5)	-0.018(5)	31.8(1)	0.29(1)	31(2)	CoH <sub>0.8</sub>
0.84(2)	8.1	3.72		+0.215(5)	-0.041(5)	31.5(1)	0.54(1)	100	CoH <sub>x</sub>
0.90(4)	9.0	3.722		+0.245(5)	-0.038(5)	31.5(1)	0.46(1)	100	CoH <sub>x</sub>

\* The samples were loaded at a hydrogen pressure  $P_{H_2}$  and 623K(598K when there is an asterisk behind the P value) for 24 h. The mean hydrogen-to-metal ratios  $x$  were determined by outgassing after Mössbauer experiments;  $a$  and  $c$  are lattice parameters determined at 100K.  $S$  is the isomer shift with respect to the source of <sup>37</sup>Co in rhodium at 4.2K.  $\Delta E_Q$  is the effective quadrupole interaction.  $B_{hf}$  is the magnetic component in the Mössbauer spectrum. Experimental uncertainties are given in parentheses.

Magnetisation curves for single-crystal cobalt and a  $\text{CoH}_{0.525}$  hcp-hydride specimens are shown in Fig. 9. In the magnetic field parallel to the basal plane the curve shape points to the fact that in the hcp-hydride case, the effective field of magnetocrystal anisotropy for  $\text{CoH}_{0.525}$  is 14.5 kOe compared to 12.5 kOe for cobalt. The saturation magnetisation of the hydride phase is  $146 \text{ Gs} \cdot \text{cm}^3/\text{g}$ . These results have suggested that introduction of hydrogen into the cobalt lattice increases the effective anisotropy field and decreases the spontaneous magnetisation. These changes seem due to the co-operative influence of two factors: (a) lattice volume increases on formation of the hydride phase and (b) alteration of the number of magnetic moment carriers due to transfer of part of the hydrogen electrons to the cobalt energy band.

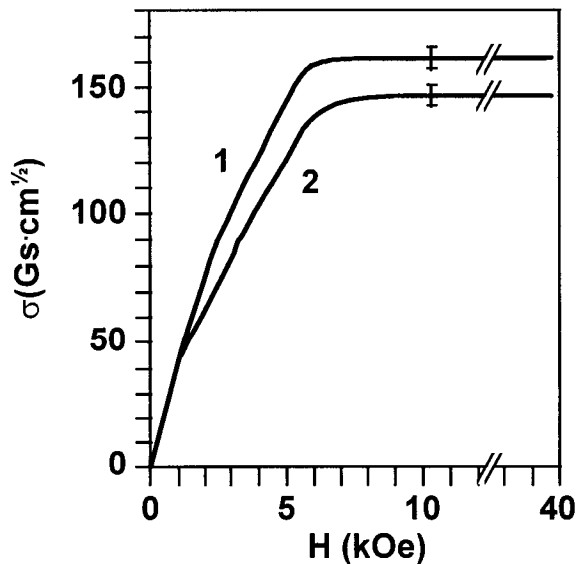


Fig. 9 Magnetisation curves for single-crystal samples of Co and Co-H in the basal plane at 90K: 1 - cobalt; 2 - hcp-solid solution  $\text{CoH}_{0.525}$

### Rhodium hydride

The investigation of the Rh-H system under high pressure conditions have shown that at  $\approx 40$  kbar and 523K there is a jumpwise increase of hydrogen solubility with the formation of a hydride phase [66]. Results of X-ray analyses of samples with a composition  $\text{RhH}_{0.4}$ - $\text{RhH}_{0.5}$ , quenched in liquid nitrogen at 83K have confirmed the

presence of two phases: the starting fcc-rhodium and a new hydride phase also based on the structural form of rhodium, but with a lattice parameter  $a = 4.02 \text{ \AA}$ , i.e.  $\approx 6\%$  greater than that for pure rhodium ( $a = 3.803 \text{ \AA}$ ). One could expect that in specimens under high pressures, the hydrogen/rhodium content would be still larger than in the quenched samples since under atmospheric pressure hydrogen-saturated samples rapidly decompose even at temperatures  $< 173\text{K}$ .

The phase diagram of the Rh-H system [67,68] is based on results of electroresistance experiments shown in Fig. 10 where  $\gamma_1$  and  $\gamma_2$  phases are correspondingly the hydrogen poor and hydrogen enriched interstitial solid solutions on the basis of the fcc-rhodium lattice. The dependence of the isomorphous  $\gamma_1 \Leftrightarrow \gamma_2$  phase transition pressure can be interpolated by a line with a slope corresponding to:

$$dT/dP \approx 27 \cdot \text{kbar}^{-1} \quad (3)$$

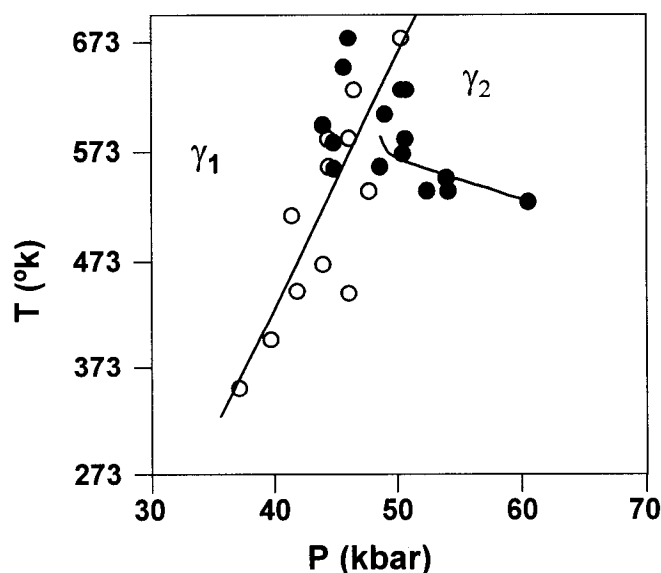


Fig. 10 Temperature-hydrogen pressure phase diagram of the rhodium-hydrogen system:

- pressure of hydride formation transition  $\gamma$  (hyd. poor)  $\gamma_2$ (hyd.enriched);
- pressure of the hydride decomposition transition  $\gamma_2 \rightarrow \gamma_1$

begins to increase rapidly and at 473K the formation of hydride only takes place under a pressure of 67 kbar. It has also been suggested that the critical temperature, which is not represented in the phase diagram, has a value higher than 673K.

Neutronographical investigation of the approximately  $\text{RhH}_{1.0}$  rhodium hydride composition, synthesised under a pressure of 7 GPa and at 623K, has indicated that it has the NaCl structure (Fig. 11). Also, since the reflections with odd indices have considerably stronger intensity than those with even indices, it seems likely that the hydrogen is situated in the octahedral interstitial sites of the fcc rhodium lattice [69,70] which is characteristic of interstitial hydrogen locations in other fcc metals such as nickel and palladium [8]. It was also of interest that this hydride sample did not give any evidence of a superconductivity transition at temperatures higher than 0.3K [71].

### Iridium hydride

The iridium electroresistance behaviour in a high pressure hydrogen atmosphere has been found to differ little from that for the pure metal in an inert atmosphere [68], indicating that the concentration of hydrogen in iridium under a pressure of 90 kbar and at 523K is only about 0.005 H/M. After returning the system to ambient conditions this small content of hydrogen appears fully to desorb as is consistent with calculated estimates [53].

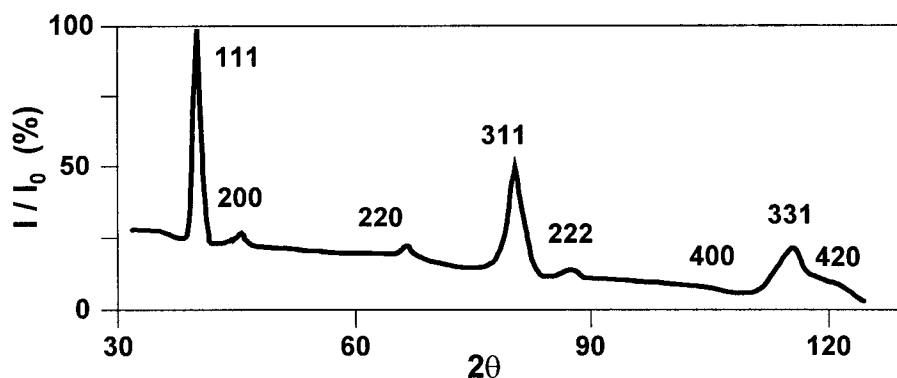


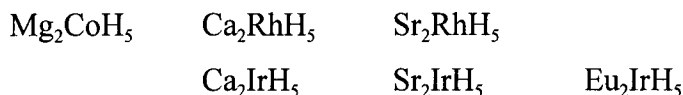
Fig. 11 Neutronographical pattern of rhodium hydride at  $T = 120\text{K}$ ,  $\lambda = 1.548$

### Complex hydrides

Although any direct reactions of the triad metals with hydrogen are involved with high hydrogen pressure, as a rule formations of more complex hydride compounds take place at pressures of near to atmospheric. Of these, the group  $\text{M}_2\text{TH}_x$ , where M is an alkaline-earth metal or europium, has been studied more or less in full, and the



synthesis, structure and physico-chemical properties of these compounds have been reviewed [72-84]. The series

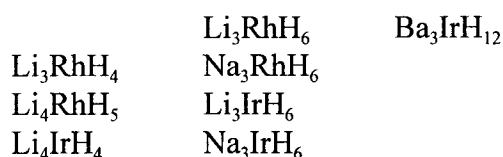


has to be considered as a table of co-ordination-type compounds rather than as a group of metallic interstitial hydrides and their structures described as consisting of two-valent cations  $\text{M}^{2+}$  and complex anions  $\text{Rt}_5^{4-}$ , obeying the 18-electron rule. In comparison with behaviour of complex hydrides of other transition metal subgroups, when the level of valence electron concentration increases, the complementary hydrogen content decreases, and the configuration position of hydrogen atoms relative to neighbouring transition metals changes from octahedral (Fe, Ru, Os) via square-pyramidal (Co, Rh, Ir) to square-planar (Pd, Pt) or tetrahedral (Ni). It has been found [74,79,80] in all corresponding deuterides, studied by neutron diffraction, that the t-H distances are shorter than the M-D distance, indicating a covalent nature of the transition metal-hydrogen bonding. The existence of high-temperature (cubic) and low-temperature (tetragonal) modifications has been recorded for such compound hydrides and the corresponding phase transition has been studied in detail for  $\text{Sr}_2\text{RhH}_5$  [74] which exists at room temperature in a cubic structural form ( $a = 7.646 \text{ \AA}$ , space group  $\text{Fm}\bar{3}\text{m}$ ), which at 200-140K undergoes a transformation to a tetragonal structure with cell parameters  $a = 5.32 \text{ \AA}$ ,  $c = 7.796 \text{ \AA}$ , and space group  $\text{I4}/\text{mmm}$ . Square-pyramidal complexes  $[\text{IrD}_5]^{4-}$  are present in both structures, possessing a six-variant disorder for the cubic modification and a two-variant one for the tetragonal modification where, in both cases, the iridium atoms are in a planar configuration bonding with four deuterium atoms.

Europium, the close analogue of alkaline-earth metals, forms a hydride  $\text{Eu}_2\text{IrH}_5$  in conjunction with iridium which is isostructural with  $\text{Sr}_2\text{IrH}_5$  [82-84], but does not exhibit a phase transition to a tetragonal structure.  $\text{Eu}_2\text{IrH}_5$  is paramagnetic at high temperature with an effective magnetic moment of 7.0-7.4  $\mu\text{B}$  that corresponds to a two-valent europium and a single-valent iridium arrangement. Besides the complex hydride with iridium, europium also forms a compound hydride with rhodium,  $\text{Eu}_2\text{RhH}_5$  in which europium again has a two-valent co-ordination, contrary to the case of  $\text{EuRh}_2$  where the europium-ion has a three-valent coordination [85].

The existence of a  $\text{Mg}_6\text{Co}_2\text{H}_{11}$  hydride and a cubic  $\delta$ -phase structure in the Mg-Co-H system have been claimed [86-88] besides the better-known  $\text{Mg}_2\text{CoH}_5$ . According to the structural analysis data [86]  $\text{Mg}_6\text{Co}_2\text{H}_{11}$  has a cubic structure with cell parameters  $a = 8.1 \text{ \AA}$ ,  $c = 10.0643 \text{ \AA}$ , and a space group Pnma. This structure is composed of 14 crystallographically independent deuterium atoms, of which 9 are co-ordinated with cobalt atoms in saddle-like  $[\text{Co}_{(1)}\text{D}^4]^{5-}$  and tetragonal-pyramidal  $[\text{Co}_{(2)}\text{D}_5]^{4-}$  complexes with 5 atoms connected only with magnesium atoms. This compound also corresponds with the 18-electron rule and constitutes an example of a complex hydride characterised by the presence of two types of transition metal ligands.

The existence of another group of structurally-related compounds of rhodium and iridium has also been listed [89-95] as tabled below:



The structure of these compounds can be described as a grouping of isolated polyhedra  $[\text{MH}_4]^{3-}$  or  $[\text{MH}_6]^{3-}$  divided by ions of the active metal. An existence of  $\text{MgRhH}_{-1}$  and  $\text{Mg}_2\text{RhH}_{1,1}$  hydrides, which can be considered as pertaining to a metal hydride type, has also been quoted [96,97].

$\text{MgRhH}_{-1}$  has a tetragonal-distorted structure of the CsCl type in which the hydrogen atoms form square rings  $[\text{Rh}_4\text{H}_4]$ . The structure of  $\text{Mg}_2\text{RhH}_{1,1}$  is similar to that of  $\text{Ti}_2\text{Ni}$  and increases of temperature can lead to formation of another hydride with a  $\text{Ti}_2\text{Pd}$  type structure, where the hydrogen atoms occupy octahedral sites, with the magnesium atoms located in the apices.

## References

1. T. Weichselfelder and B. Thiede, *Ann.*, **447** (1926) 64.
2. R.C. Ray and B.B.N. Sahai, *J. Indian Chem. Soc.*, **23** (1946) 61.
3. B. Sarry, *Z. Anorg. Chem.*, **286** (1956) 211.
4. I.I. Zhukov, *Izv. Sfkh*, **3** (1926) 600.
5. F. Wilm, *Berichte*, **14** (1881) 629.
6. H. Hoppl and F. Seuler, *Berichte*, **16** (1883) 117.
7. J.W. Döberiner, *Ann.Chim.Phys.*, **24** (1823) 91.
8. B. Baranowski, in *Metal Hydrides*. Ed. G. Bambakidis, Plenum Press, New York, London, 1981, 193.

9. E.G. Ponyatovsky, V.E. Antonov and I.T. Belash, *Usp. fiz. nauk.* **137** (1982) 663.
10. V.N. Verbetsky, S.P. Malyshenko, S.V. Mitrokhin, V.V. Solovei and Yu.F. Shmal'ko, *Int. J. Hydrogen Energy*, **22**, (1998) 1165.
11. S. Filipek and B. Baranowski, *Proc. 6th Int. Symp. High-Purity Materials Science and Technology, Dresden*, 1985, 90.
12. N.M. Popova, L.V. Babenka and G.A. Saveljeva, *Adsorbicija i vzaimodeistvie prosteishikh gazov s metallami VIII gruppy. Adsorption and interaction of the simplest gases with VIII group metals.* Alma-Ata. 1979.
13. R.B. McLellan and W.A. Oates, *Acta metall.*, **21** (1973) 181.
14. V.K. Solnyshlova, L.V. Babenkova, H.M. Popova and D.V. Sokol'sky. Dokl. Akad. Nauk SSSR, **230** (1976) 377.
15. V.I. Mi L.V. Babenkova, H.M. Popova, D.V. Sokol'sky and R.S. Hanses, *J. Chem. Phys.*, **45** (1966) 2240.
16. Yu.G. Kul'evskaya, L.V. Babenkova, H.M. Popova and D.V. Sokol'sky, Dokl. Akad. Nauk SSSR, **242** (1978) 969.
17. I.N. Blagoveshchenskaya, L.V. Babenkova, H.M. Popova and D.V. Sokol'sky, Dokl. Akad. Nauk SSSR, **243** (1978) 955.
18. G. Padberg and J.M. Smith, *J. Catal.*, **18** (1970) 1.
19. J. Dollimore and B.H. Harrison, *J. Catal.*, **28** (1973) 275.
20. J.C. Adrian and J.M. Smith, *J. Catal.*, **18** (1970) 57.
21. C.H. Bartholomew, in *Hydrogen Eff.Catal.: Fundam. and Pract. Appl.*, New York, Basel, 1988, 139.
22. J.M. Zowtiak and C.H. Bartholomew, *J. Catal.*, **83** (1983) 107.
23. R. Rudman and F.S. Stone, *Trans. Faraday Soc.*, **54** (1958) 421.
24. R. Dus and W. Lisowski, *Surf. Sci.*, **61** (1976) 635.
25. M.F. Bridge, C.M. Comrie and R.M. Lambert, *J. Catal.*, **58** (1979) 28.
26. K.R. Christmann, in *Hydrogen Eff.Catal.: Fundam.and Pract. Appl.*, New York, Basel, 1988, 3.
27. N.P. Serdyuk and A.A. Chuprin. *Zhur. Fiz. Khim.*, **54** (1980) 2822.
28. M. Weinstein and J.F. Elliot, *Trans. Met. Soc. AIME*, **227** (1963) 382.
29. F.E. Walley and R.D. Penske, *Trans. Met. Soc. AIME*, **232** (1965) 1455.
30. H. Schenk and K.W. Lange, *Ber. Bunsenges. phys. Chem.*, **70** (1966) 485.
31. H. Schenk and K.W. Lange, *Arch. Eisenhüttenw.*, **37** (1966) 739.
32. M.S. Petrushevskii, P.V. Gel'd and B.A. Baum, *Izv. VUZ'ov Metally*, **5** (1971) 28.
33. E.S. Levin, T.K. Kostina and M.S. Petrushevskii, *Izv. VUZ'ov Cvetnaya metall.*, **1** (1973) 31.
34. M.S. Petrushevskii, P.V. Gel'd and L.E. Abramycheva, *Izv. VUZ'ov Chyornaya metall.*, **10** (1977) 5.
35. M.S. Petrushevskii, P.V. Gel'd and L.E. Abramycheva, Dokl. Akad. Nauk SSSR, **227** (1976) 337.
36. S. Baya, T. Fuwa and K. Ono, *J. Iron and Steel Inst. Japan*, **53** (1967) 101.
37. E. Fromm and H. Jehn, *Bull. Alloy Phase Diagrams*, **5**, (1984), 324.
38. E. Fromm and E. Gebhardt, *Gasy i uglerod v metallakh. Gases and carbon in metals.* Moscow, Metallurgiya, 1980.
39. A. Sieverts and H. Hagen, *Z. Phys. Chem.*, **169A** (1934) 237.
40. A. Sieverts, G. Zapf and H. Moritz, *Z. Phys. Chem.*, **183A** (1938) 19.

41. A. Mapo-Oka, S. Savada and T. Mori, in *Vzaimodeistvie metallov s gazami. Interaction of metals with gases*, Moscow, Nauka, (1973), 159.
42. N.A. Galaktionova, *Vodorod v metallakh, Hydrogen in metals*, Moscow, Metallurgiya, 1967.
43. T.G. Jones and R.D. Pelke, *Met. Trans.*, **2** (1971) 2655.
44. W. Wiegelin and K.H. Lieser, *Z. Electrochem.*, **61** (1957) 359.
45. B.A. Kolachev, A.A. Il'in, V.A. Lavrenko and Yu.V. Levinskii. *Gidridnye sistemy. Spravochnik. Hydride systems. Databook*, Moscow, Metallurgiya, 1992.
46. *Vzaimodeistvie vodoroda s metallami. Interaction of hydrogen with metals*, ed. A.P. Zakharov, Moscow, Nauka, 1987.
47. P.V. Gel'd, R.A. Ryabov and L.P. Mokhrachova. *Vodorod i fizicheskie svoystva metallov I splavov (Gidridy perekhodnykh metallov). Hydrogen and the physical properties of metals and alloys (Transition metal hydrides)*, Moscow, Nauka, 1985.
48. P.V. Gel'd, R.A. Ryabov and E.S. Khodes, *Vodorod i nesovershenstva struktury metallov. Hydrogen and the imperfections of metal structure*, Moscow, Metallurgiya, 1979.
49. V.I. Shapovalov and N.P. Serdyuk. *Zhur. fiz. khim.*, **53** (1979) 2187.
50. V.I. Shapovalov. *Zhur. fiz. khim.*, **54** (1980) 2899.
51. V.Yu. Karpov and V.I. Shapovalov, *Zhur. fiz. khim.*, **54** (1979) 2858.
52. V.I. Shapovalov and LV. Boiko, *Izv. VUZ'ov Chyornaya metall.*, **8** (1984) 122.
53. A. Driessen, P. Sanger, H. Hemmes and R. Giessen, *J. Phys.: Condens. Matter*, **2** (1990) 9797.
54. E.G. Ponyatovsky, V.E. Antonov and I.T. Belash, in *Problemy fiziki tverdogo tela. Problems in solid state physics*, ed. A.M. Prokhorov and A.S. Prokhorov, Mir, Moscow, 1984.
55. A.R. Williams, J. Kubler and C.D. Gelatt Jr., *Phys. Rev.*, **B19** (1979) 6094.
56. M. Metfessel and J. Kubler, *J. Phys.: Met. Phys.*, **12** (1982) 141.
57. A. Driessen, H. Hemmes and R. Griessen, *Z. phys. Chem.*, **F143** (1985) 145.
58. I.B. Wang and D.O. Northwood, *J. Less-Common Met.*, **135** (1987) 239.
59. P.C.P. Boten and A.R. Miedema, *J. Less-Common Met.*, **71** (1980) 147.
60. I.T. Belash, V.E. Antonov and E.G. Ponyatovsky, *Dokl. Akad. Nauk SSSR*, **235** (1977) 128; V.E. Antonov, I.T. Belash, V.Yu. Malyshev and E.G. Ponyatovsky, *Dokl. Akad. Nauk SSSR*, **272** (1983) 1147.
61. V.E. Antonov, T.E. Antonova, M. Baier, G. Grosse and F.W. Wagner, *J. Less-Common Met.*, **239** (1996) 198.
62. I. Czarnota and B. Baranowski, *Bull. Acad Polon.Sci.*, **14** (1966) 191.
63. G. Schneider, M. Baier, R. Wordel, F.E. Wagner, V.E. Antonov, E.G. Ponyatovsky, Yu. Kopilovskii and E. Makarov, *J. Less-Common Met.*, **172-174** (1991) 333.
64. I.T. Belash, V.Yu. Malyshev, B.K. Ponomarev, E.G. Ponyatovsky and A.Yu.Sokolov, *Fizika tverdogo tela (Leningrad)*, **28** (1986) 1317.
65. V.G. Thiessen, V.E. Antonov, I.T. Belash, B.K. Ponomarev and E.G. Ponyatovsky, *Phys. stat. sol.*, **A48** (1978) K185.
66. V.E. Antonov, I.T. Belash, V.F. Degtyareva and E.G. Ponyatovsky, *Dokl. Akad. Nauk SSSR*, **239** (1978) 342.
67. V.E. Antonov, I.T. Belash, V.I. Koltygin and E.G. Ponyatovsky, *Dokl. Akad. Nauk SSSR*, **248** (2979) 131.

68. V.E. Antonov, I.T. Belash, V.Yu. Malyshev and E.G. Ponyatovsky, *Int. J. Hydrogen Energy*, **11** (1986) 193.
69. A.V. Irodova, V.P. Glazkov, V.A. Somenkov, S.Sh.Shilstein, V.E. Antonov and E.G. Ponyatovsky, *Kristallografiya*, **33** (1988) 769.
70. V.A. Somenkov, V.P. Glazkov, A.V. Irodova and S.Sh.Shilstein, *J. Less-Common Met.*, **129** (1987) 171.
71. V.E. Antonov, I.T. Belash, O.V. Zharikov and A.V. Palnichenko, *Phys. stat. sol.*, **B142** (1987) K155.
72. R.O. Moyer, R. Ward, G. Katz and J. Tanaka, *Inorg. Chem.*, **8** (1969) 1010.
73. R.O. Moyer, C. Stanitski, J. Tanaka, M.I. Kay and R. Kleinberg, *J. Solid State Chem.*, **3** (1971) 541.
74. I. Laxis, R. Bichot, E. Valdis and P. Wachter, *Mater. Res. Bull.*, **18** (1983) 1555.
75. C.E. Messer, J.C. Eastman, R.G. Mers and A.J. Maeland, *Inorg. Chem.*, **3** (1964) 776.
76. E. Belin, M. Gupta, P. Zolliker and K. Yvon, *J. Less-Common Met.*, **13** (1987) 267.
77. S.G. Porutsky, E.A. Zhurakovsky, S.A. Mogilevsky, V.N. Verbetsky and O.S. Bakuma, *Solid State Commun.*, **74** (1990) 551.
78. N.V. Kandalova and V.N. Verbetsky, *Vestnik MGU, Khim.*, **32** (1991) 419.
79. K. Kojima, T. Imni, K. Hiraoka and T. Hihara, *J. Less-Common Met.*, **130** (1987) 105.
80. K. Nomura, Y. Ishido and S. Ono, *J. Ceram. Soc. Japan*, **86** (1978) 67.
81. P. Zolliker, K. Yvon, P. Fischer and J. Schefer, *Inorg. Chem.*, **24** (1985) 4177.
82. R.O. Moyer and R. Lindsay, *J. Less-Common Met.*, **70** (1980) 57.
83. J. Zhuang, W. Kunman, L.M. Corless, J. Hastings and R.O. Moyer, *J. Solid State Chem.*, **48** (1983) 117.
84. Z.M. Stadnik and R.O. Moyer, *J. Less-Common Met.*, **98** (1984) 159.
85. K.H.J. Buschow, R.L. Cohen and K.W. West, *J. Appl. Phys.*, **48** (1977) 2589.
86. R. Cerny, F. Bonhomme, K. Yvon, P. Fischer, P. Zolliker, D.E. Cox and A. Hewat, *J. Alloys Compds.*, **187** (1992) 233.
87. G. Konstanchuck, E. Ivanov, A. Stepanov and T. Samsonova, *Izv. Akad. Nauk SSSR, Khim. Nauki*, **3** (1989) 93-98.
88. M. Yoshida, F. Bonhomme, K. Yvon and P. Fischer, *J. Alloys and Compds.*, **190** (1993), L45.
89. J.D. Farr, *J. Inorg. Nucl. Chem.*, **14** (1960) 202.
90. A.F. Graefe and R.K. Rabeson, *J. Inorg. Nucl. Chem.*, **29** (1967) 2917.
91. S.K. Karma, F.C. Chang and C.B. Magee, *J. Less-Common Met.*, **60** (1978) 47.
92. L.B. Lundberg, D.T. Cromer and C.B. Magee, *Inorg. Chem.*, **11** (1972) 400.
93. W. Bronger, P. Müller, J. Kowalczyk and G. Auffermann, *J. Alloys and Compds.*, **176** (1991) 263.
94. W. Bronger, P. Müller, J. Kowalczyk and G. Auffermann, *J. Alloys and Compds.*, **176** (1991) 263.
95. K. Kadir and D. Noréus, *J. Alloys and Compds.*, **209** (1994) 213.
96. F. Bonhomme, K. Yvon and P. Fischer, *J. Alloys and Compds.*, **186** (1992) 209.
97. F. Bonhomme, P. Selvam, M. Yoshida, K. Yvon and P. Fischer, *J. Alloys and Compds.*, **178** (1992) 167.



## **Hydrogen Metal Systems II**

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## **Cobalt-, Rhodium- and Iridium-Hydrogen**

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