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Atomic ordering in the hcp cobalt hydrides and deuterides

V.K. Fedotov^a, V.E. Antonov^a, T.E. Antonova^a, E.L. Bokhenkov^a, B. Dorner^b, G. Grosse^{c,*},
F.E. Wagner^c

^aInstitute of Solid State Physics RAS, 142432 Chernogolovka, Moscow district, Russia

^bInstitute Laue-Langevin, 15X, F-38042 Grenoble Cedex, France

^cPhysik-Department E 15, Technische Universität München, D-85747 Garching, Germany

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Abstract

Cobalt hydrides and deuterides with the hcp metal lattice and H(D)-to-metal atomic ratios $0.18 \leq x \leq 0.5$ were prepared under high pressures of hydrogen or deuterium, respectively, and studied by neutron diffraction in a metastable state at 120 K and ambient pressure. A profile analysis of the spectra showed that in all samples the hydrogen and deuterium atoms occupy octahedral interstitial sites. In the samples with $x \leq 0.26$, the hydrogen and deuterium atoms are randomly distributed over these sites. In the samples with $x \geq 0.34$, they form layered superstructures, occupying every third octahedral base layer at $x = 0.34$ and every second layer at $x = 0.38$ and 0.5. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In the past decades, techniques for compressing gaseous hydrogen to pressures of a few gigapascals made it possible to synthesize hydrides of most transition metals (see [1] and references therein). The metals Cr, Mo, Mn, Tc, Re, Fe and Co were found to form hydrides based on an hcp metal lattice. The hcp hydrides of the group VI metals Cr and Mo have compositions close to MeH. The other hydrides exist in wide composition ranges and can be considered as solid solutions of hydrogen, in which the interstices of the hexagonal metal lattice may either be occupied randomly or in a superstructure order.

The crystal structures of the hcp hydrides of Fe and of the group VII metals Mn, Tc and Re were studied by neutron diffraction, which showed hydrogen to occupy the octahedral interstices. In the TcH_x hydrides, which are stable at $0.39 < x < 0.78$, a layered superstructure of the anti-CdI₂ type, in which hydrogen occupies every second octahedral base layer, was shown to form near $x = 0.5$ [2,3]. In the case of hcp manganese hydrides with a

homogeneity region of $0.65 \leq x < 1$, a few weak peaks in the diffraction pattern of a deuteride with $x = 0.65$ were also interpreted in terms of a partial order into this superstructure with stoichiometry Mn₂H [4]. No hydrogen ordering was observed in hcp ReH_{0.23} [4] and in hcp FeD_{0.42} [5].

At atmospheric pressure, there are two modifications of cobalt: An hcp modification exists at temperatures up to about 450°C, at higher temperatures an fcc modification is stable. In a hydrogen atmosphere at temperatures of 250–350°C, the equilibrium solubility of hydrogen in hcp Co increases monotonically with pressure and reaches $x \approx 0.6$ at 7 GPa [1,6]. A further increase in the hydrogen pressure causes the formation of fcc cobalt hydride with $x \approx 1$ [1,6]. Both the hcp and the fcc cobalt hydride can be retained in a metastable state at atmospheric pressure and low temperatures, if the sample is cooled below about 200 K under high pressure. So far, the crystal structure of cobalt hydrides was studied only by X-ray diffraction, which provided no information about the type of positions occupied by hydrogen and about the possible formation of superstructures in the hcp hydrides at certain hydrogen concentrations.

This paper presents the results of a neutron diffraction investigation of six pressure cooled samples of hcp high-

*Corresponding author. Tel.: +1-610-325-9814; fax: +1-610-325-9823.

E-mail address: ggrosse@ph.tum.de (G. Grosse)

pressure hydrides and deuterides of cobalt with x ranging from 0.18 to 0.5. Samples loaded with both stable hydrogen isotopes were studied in order to increase the reliability of the structure analysis by taking advantage of the marked difference in the neutron scattering amplitudes of H and D. Hydrides and deuterides of cobalt with the same H or D content are expected to have the same crystal structure, since no significant structural difference has ever been observed for any hydride except the very special case of V_2H [7].

2. Sample preparation and experimental details

To prepare the hcp CoH_x and CoD_x samples, 0.2 mm thick plates of 99.98% pure polycrystalline cobalt were loaded with hydrogen (deuterium) by a 24 h exposure to a H_2 (D_2) pressure from 4 to 7 GPa at 325°C and subsequent cooling to 150 K in the high pressure cell. The hydrogenation method is described in more detail elsewhere [1]. Each sample was X-rayed at ambient pressure and 100 K (DRON-2.0 diffractometer, FeK_α radiation) to ensure that it had an hcp metal lattice and was single-phase and homogeneous. The hydrogen (deuterium) content of the samples was determined approximately by hot extraction into a calibrated volume at temperatures up to 200°C using a few milligrams of each sample. The results are in satisfactory agreement with those obtained later more accurately from the neutron diffraction data.

At ambient pressure, cobalt hydrides prepared at high pressure begin to lose hydrogen at temperatures above 230–260 K [6]. When not in use, our samples were therefore stored in liquid nitrogen and were never warmed above 120 K in the course of the measurements. The samples were brittle. Prior to the neutron diffraction experiments, they were ground in an agate mortar under liquid nitrogen to diminish texture effects.

The neutron diffraction experiments were performed at 120 K with neutrons of a wavelength of $\lambda = 1.295 \text{ \AA}$ using the D20 instrument at the ILL, Grenoble. The powder diffraction patterns were recorded in steps of 0.1° in 2θ . The background was determined in a separate empty-can measurement and then subtracted from the measured diffraction patterns. The resulting neutron spectra were analysed using the Rietveld profile refinement technique implemented in the DBWS-9411 computer program [8].

3. Results and discussion

Three hcp CoH_x samples with $x = 0.19, 0.26$ and 0.34 and three hcp CoD_x samples with $x = 0.18, 0.38$ and 0.50 were prepared and measured. The neutron diffraction data and results of their Rietveld profile analysis are illustrated by Figs. 1–3 and summarized in Table 1.

As can be seen from Table 1, in all studied hydrides

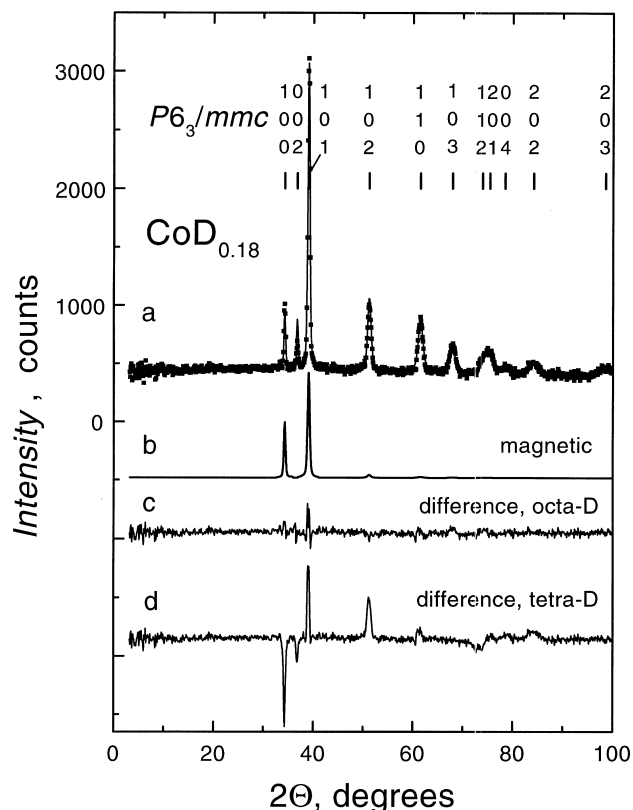


Fig. 1. Neutron powder diffraction pattern of $CoD_{0.18}$ measured at 120 K (dots) and results of its Rietveld analysis (solid lines). Curve (a) is the sum of the magnetic contribution shown by curve (b) and of the nuclear contribution calculated with the structure parameters listed in Table 1. Curve (c) is the difference between the experimental (dots) and calculated (curve a) spectra. Curve (d) is the difference between the experimental spectrum and that calculated for $x = 0.18$ hydrogen atoms randomly occupying tetrahedral interstices in the hcp metal lattice of $CoD_{0.18}$, the other fitting parameters being the same as in Table 1.

hydrogen occupied the octahedral interstitial positions in the hexagonal cobalt lattice and the hydrogen distribution over these sites was random for $x \leq 0.26$ but ordered for $x \geq 0.34$. Fig. 1 illustrates the case of the random distribution of hydrogen while Figs. 2 and 3 show the diffraction patterns for the samples with two different types of hydrogen superstructure.¹

3.1. Ferromagnetism

The hcp modification of Co is a ferromagnet with a Curie temperature of the order of 1400 K and magnetic moments directed along the c -axis and equal to approximately 1.71 Bohr magnetons per Co atom at temperatures below 300 K [9]. According to magnetization measurements with single-crystalline samples [10,11], hcp cobalt hydrides also are ferromagnets with magnetic moments directed along the c -axis. The moments decrease approxi-

¹For brevity, protium and deuterium will henceforth be called hydrogen if what is said refers to both hydrogen isotopes.

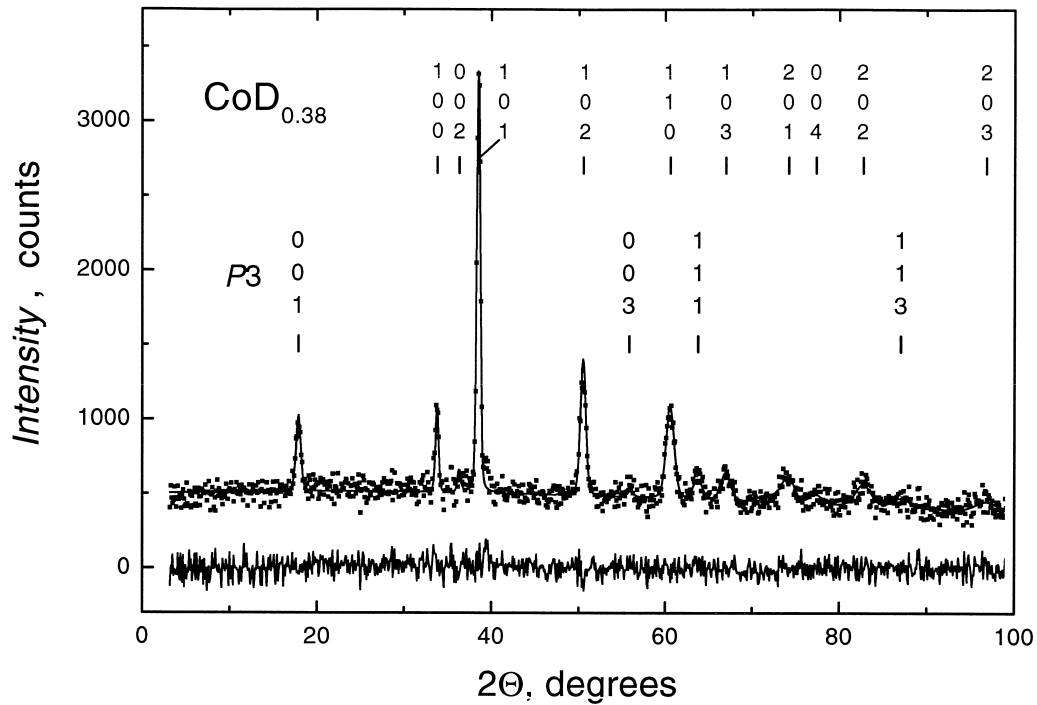


Fig. 2. Neutron powder diffraction pattern of CoD_{0.38} measured at 120 K (dots). Its profile fit shown by the solid line is the sum of the magnetic contribution and of the nuclear contribution calculated with the structure parameters listed in Table 1. The curve at the bottom is the difference between the experimental and calculated spectra. The Miller indices of hcp and superstructure reflections are shown separately in the upper and lower part of the figure, respectively.

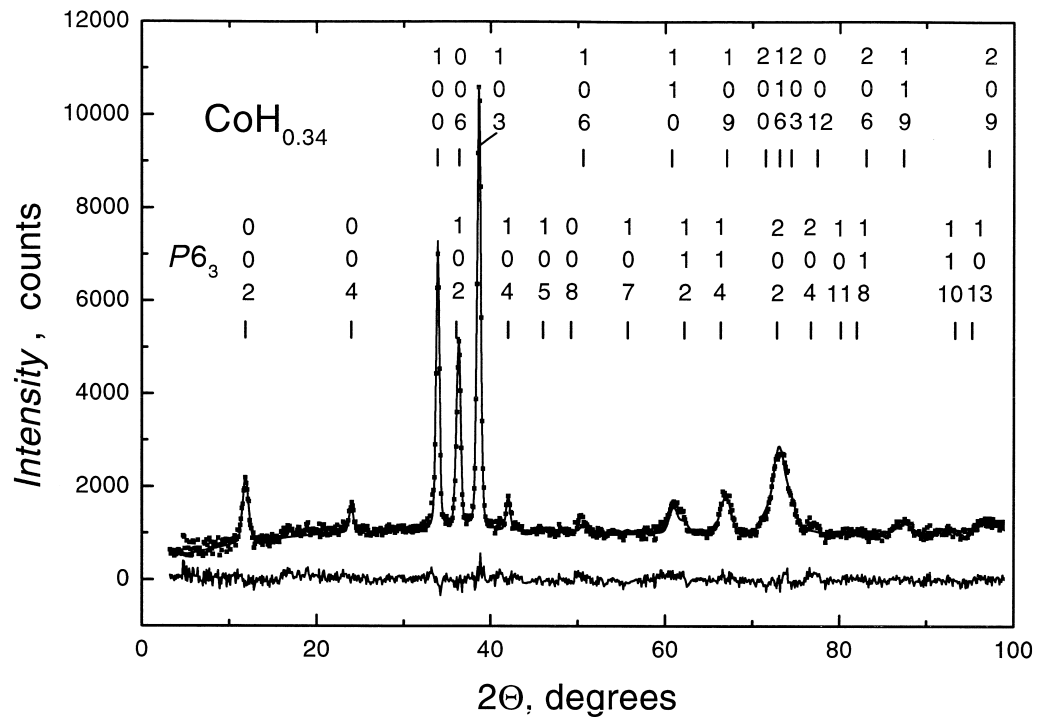


Fig. 3. Neutron powder diffraction pattern of CoH_{0.34} measured at 120 K (dots). Other details are as in Fig. 2. Note that the Miller indices of the hcp reflections refer to the extended unit cell of the superstructure.

Table 1

Positional parameters (x , y , z), thermal factors (B) and site occupancies (ω) for Co–H and Co–D samples according to the Rietveld analysis of the neutron diffraction data collected at 120 K. M is the number of formula units per unit cell, R_p and R_{ex} are the obtained and expected profile factors

Phase		Atom	Site	x	y	z	B (\AA^2)	ω
CoD _{0.18} P6 ₃ /mmc (No.194) $a = 2.529$ \AA $c/a = 1.618$	$m = 1100$ mg	Co	2c	1/3	2/3	1/4	0.4	1.00
	$M = 2$ $c = 4.091$ \AA $R_p/R_{ex} = 4.0/4.7$	D	2a	0	0	0	1.9	0.18
CoH _{0.19} P6 ₃ /mmc (No.194) $a = 2.538$ \AA $c/a = 1.616$	$m = 1300$ mg	Co	2c	1/3	2/3	1/4	0.4	1.00
	$M = 2$ $c = 4.102$ \AA $R_p/R_{ex} = 2.9/4.3$	H	2a	0	0	0	1.9	0.19
CoH _{0.26} P6 ₃ /mmc (No.194) $a = 2.544$ \AA $c/a = 1.618$	$m = 1200$ mg	Co	2c	1/3	2/3	1/4	0.4	1.00
	$M = 2$ $c = 4.116$ \AA $R_p/R_{ex} = 7.0/4.2$	H	2a	0	0	0	1.9	0.26
CoH _{0.34} P6 ₃ (No.173) $a = 2.555$ \AA $c/a = 3 \cdot 1.619$	$m = 1000$ mg	Co	2b	1/3	2/3	1/12	0.4	1.00
	$M = 6$	Co	2b	2/3	1/3	0.245	0.4	1.00
	$c = 12.406$ \AA	Co	2b	1/3	2/3	0.421	0.4	1.00
	$R_p/R_{ex} = 9.0/5.6$	H	2a	0	0	1/6	1.9	0.02
		H	2a	0	0	0	1.9	0.02
		H	2a	0	0	1/3	1.9	0.97
CoD _{0.38} P3m1 (No.164) $a = 2.565$ \AA $c/a = 1.615$	$m = 50$ mg	Co	2d	1/3	2/3	0.257	0.4	1.00
	$M = 2$	D	1a	0	0	0	1.9	0.70
	$c = 4.142$ \AA $R_p/R_{ex} = 6.5/5.6$	D	1b	0	0	1/2	1.9	0.06
CoD _{0.50} P3m1 (No.164) $a = 2.579$ \AA $c/a = 1.614$	$m = 60$ mg	Co	2d	1/3	2/3	0.262	0.4	1.00
	$M = 2$	D	1a	0	0	0	1.9	0.97
	$c = 4.162$ \AA $R_p/R_{ex} = 9.1/6.2$	D	1b	0	0	1/2	1.9	0.04

mately linearly with hydrogen concentration at a rate of $d\sigma/dx = 0.36$ Bohr magnetons per H atom.

With the unpolarized neutron beam used in the experiment, magnetic and nuclear scattering are incoherent with respect to each other and the corresponding intensities are additive. To decrease the number of fit parameters in the structure refinement procedure, the value of the magnetic moment of the Co atoms in each hydride was fixed to a value calculated from the data of Belash et al. [10,11] for the respective hydrogen content. The direction of the moment was assumed to be parallel to the c -axis. In particular, this resulted in zero intensity of the magnetic (002) peak, because the neutron scattering intensity from magnetic planes is proportional to the square of the projection of the magnetic moments onto the planes.

Curve b in Fig. 1 shows the calculated contribution from magnetic scattering to the peak intensities in the neutron diffraction pattern of CoD_{0.18}. Since the values of the magnetic moments of the studied cobalt hydrides do not differ much from each other, the contributions from magnetic scattering to their neutron diffraction spectra are qualitatively the same as in Fig. 1.

3.2. The octahedral coordination of hydrogen

The neutron diffraction pattern of CoD_{0.18} contains no new lines in addition to the lines of the hcp structure. The crystal structure of this phase therefore belongs to the same space group, P6₃/mmc, as the hcp structure of its metal lattice. In the hcp structure, there are two types of highly symmetrical interstitial sites conforming the P6₃/mmc space group, the octahedral and tetrahedral positions. As can be seen from the difference curves c and d in Fig. 1, a model assuming that deuterium randomly occupies octahedral sites gives a satisfactory profile fit of the experimental spectra, while a model with deuterium on tetrahedral sites is qualitatively unacceptable.

A similar analysis of the respective diffraction patterns showed that hydrogen is randomly distributed over the octahedral sites also in CoH_{0.19} and CoH_{0.26}. To determine the positions of the hydrogen atoms in the atomically ordered hydrides with $x \geq 0.34$, the structural (hcp) lines in the neutron diffraction spectra were fitted alone assuming a disordered arrangement of hydrogen in octahedral and tetrahedral interstices, respectively. The neglect of the

hydrogen superstructure is possible in this context, because the intensities of these lines change only weakly with hydrogen ordering. The tetrahedral model again did not even give a qualitative agreement with experiment and it was concluded that hydrogen occupies octahedral interstices.

The octahedral hydrogen coordination in hcp cobalt hydrides agrees with the empirical rule [7,4] that hydrogen occupies octahedral interstices in close packed metal lattices of hydrides of transition metals right of the vanadium group in the periodic table. So far no exceptions have been observed to this rule, which has clear physical grounds: The atomic radii of the transition metals and, correspondingly, the size of the interstices decrease from left to right in the periodic table. Therefore, for the metals on the right of a certain element, hydrogen atoms fit only on the octahedral interstices, which are larger than the tetrahedral interstices.

3.3. The superstructure at $0.38 \leq x \leq 0.5$

Fig. 2 shows the neutron diffraction pattern of $\text{CoD}_{0.38}$; the spectrum of $\text{CoD}_{0.50}$ looks similar. The spectrum shown in Fig. 2 contains at least 3 lines which are forbidden for an hcp lattice and can be indexed as (001), (003) and (111) based on the same hexagonal cell. The appearance of (00 l) superstructure reflections with odd l indicates the absence of the $c/2$ translation along the z -axis which links the base layers of the hydrogen sublattice in the disordered cobalt hydrides. This translation is absent also in the anti- CdI_2 type superstructure, space group $\text{P}\bar{3}\text{m}1$, observed earlier in hcp technetium hydrides with $x \approx 0.5$ [2,3]. In this superstructure, hydrogen occupies every second base layer of octahedral sites in the hexagonal metal lattice.

As can be seen from Table 1 and Fig. 2, the anti- CdI_2 model allows a satisfactory profile fit of the spectra of the samples $\text{CoD}_{0.38}$ and $\text{CoD}_{0.50}$. From the refined values of the fitting parameters one can also draw the following conclusions, which appear sound on physical grounds:

Firstly, the analysis shows that the ordering of both deuterides is not complete and deuterium atoms partly occupy layers which should be empty in the ideal anti- CdI_2 type structure. The occupation ratio of the two types of layers is $0.04/0.97 \approx 0.04$ in the case of the deuteride with nearly stoichiometric composition $\text{CoD}_{0.50}$ and increases to $0.06/0.70 \approx 0.09$ for the deuteride with $x = 0.38$.

Secondly, the cobalt atoms are displaced from the hcp positions (1/3, 2/3, 1/4) so that the metal layers separated by hydrogen atoms move apart while those containing nearly no hydrogen between them move closer together. In the stoichiometric deuteride, $\text{CoD}_{0.50}$, the displacements, $\delta z = 0.262 - 1/4 = 0.012$ (0.05 Å), are noticeably larger than in the case of the deuteride with $x = 0.38$, where

$\delta z = 0.257 - 1/4 = 0.007$ (0.03 Å). Similar displacements of the metal atoms, $\delta z \approx 0.01$ (0.04 Å), were observed for a nearly stoichiometric technetium hydride with the anti- CdI_2 type structure and a hydrogen content of $x = 0.45$ [2,3].

3.4. The superstructure at $x = 0.34$

The superstructure lines in the neutron diffraction pattern of the $\text{CoH}_{0.34}$ sample (Fig. 3) differ significantly from those of the samples with higher hydrogen contents, $x = 0.38$ and 0.50 (Fig. 2). A new hexagonal unit cell with a lattice parameter c three times larger than that of the other hydrides is necessary to index the reflections of $\text{CoH}_{0.34}$ with integral Miller indices. Of the (00 l) reflections, only those with even l are present in the spectrum (Fig. 3). This suggests that the c -axis of the enlarged unit cell is a screw axis with a $c/2$ translation along it.

Among the three-fold and six-fold screw axes concomitant with a hexagonal unit cell, only the 6_3 axis includes the $c/2$ translation. In the hydrogen sublattice of $\text{CoH}_{0.34}$, the 6_3 operation reduces to a simple $c/2$ translation, since the hydrogen positions are located on the screw axis. The length of this translation is three times the distance between the nearest octahedral base layers.

The composition of the sample $\text{CoH}_{0.34}$ is close to the stoichiometry Co_3H . Assuming a layered superstructure, this suggests that hydrogen occupies a third of all octahedral base layers. With the $c/2$ translation linking every third layer, only a superstructure in which hydrogen occupies every third layer is therefore possible.

As no other symmetry elements but the 6_3 screw axis were evident from the qualitative analysis of the neutron diffraction data, the refinement of the crystal structure of $\text{CoH}_{0.34}$ was carried out in the framework of the space group $\text{P}6_3$. The model of a superstructure with hydrogen occupying every third base layer of octahedral interstices in the hexagonal cobalt lattice provided a satisfactory profile fit of the $\text{CoH}_{0.34}$ spectrum (Table 1 and Fig. 3). To decrease the number of fit parameters in the refinement procedure, the z coordinates of nearly empty octahedral layers were fixed to the positions in the disordered structure (at $z = 0$ and $z = 1/6$ in the notation of Table 1) and their occupancies were set equal to each other.

As one can see from Table 1, like in $\text{CoD}_{0.38}$ and $\text{CoD}_{0.50}$, the hydrogen ordering in $\text{CoH}_{0.34}$ is not complete. Some hydrogen occupies the layers at $z = 0$ and $1/6$, which should be empty in the ideal structure. The ratio of the occupancies of the two types of layers is $(0.02 + 0.02)/0.97 \approx 0.04$. The metal layers at $z = 0.245$ and 0.421 , which are separated by the hydrogen layer at $z = 1/3$, move apart. The displacement $\delta z = 1/4 - 0.245 \approx 0.005$ (0.06 Å) is of the same magnitude as in $\text{CoD}_{0.38}$ and $\text{CoD}_{0.50}$.

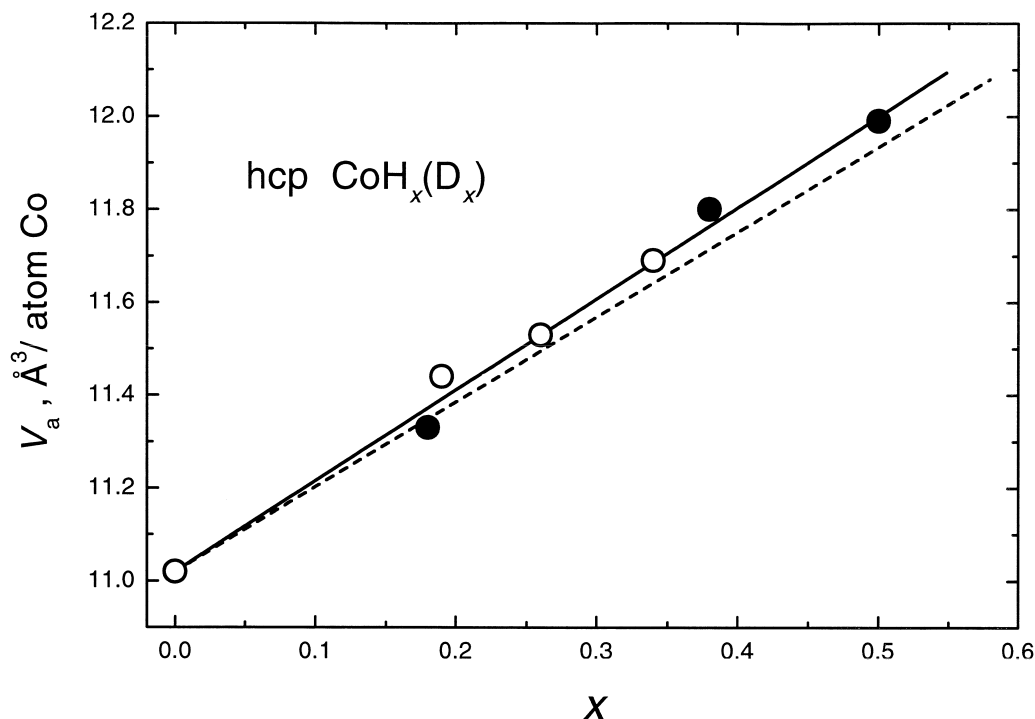


Fig. 4. Volume per Co atom, V_a , as a function of the H(D)-to-metal atomic ratio, x , for hcp cobalt hydrides (open circles) and deuterides (solid circles) at atmospheric pressure and 120 K according to the neutron diffraction data of the present work. The dashed line shows the $V_a(x)$ dependence for hcp cobalt hydrides from Ref. [6].

The hydrogen content of the hcp cobalt hydrides studied in this work could be determined from the neutron diffraction data. Fig. 4 shows that the resulting dependence of the atomic volume, V_a , on the hydrogen content is approximately linear, $\partial V_a / \partial x \approx 2 \text{ \AA}^3$ per H atom. This dependence is close to that obtained earlier by X-ray diffraction [6] (dashed line, $\partial V_a / \partial x \approx 1.8 \text{ \AA}^3$ per H atom). There the hydrogen contents had been obtained by hot extraction, which yields the mean hydrogen content of the samples. The neutron data appear more reliable because they give the hydrogen content of the hcp phase alone. The mean hydrogen content might, for example, be systematically higher in the samples with $x \approx 0.5$ – 0.6 , because these were synthesized under P – T conditions in the vicinity of the hcp \rightarrow fcc transformation and might therefore contain a certain amount of the fcc phase with $x \approx 1$.

4. Conclusions

The neutron diffraction investigation of cobalt hydrides with hydrogen-to-metal atomic ratios x between 0.18 and 0.50 showed that at $T = 120$ K hydrogen occupies octahedral interstices in the hcp metal lattices. Hydrogen was found to be randomly distributed over these sites at $x \leq 0.26$ and to form layered superstructures at $x \geq 0.34$. A superstructure corresponding to the Co_3H stoichiometry

with hydrogen occupying every third octahedral base layer is observed at $x = 0.34$. This superstructure is formed within a rather narrow concentration range, which does not exceed $0.26 < x < 0.38$. At $x \geq 0.38$, the anti- CdI_2 type superstructure is formed, which corresponds to the stoichiometry Co_2H and where hydrogen occupies every second octahedral layer.

The ordering in both superstructures is not complete and hydrogen partly occupies layers which should be empty in the ideal case. With increasing hydrogen content, the space group of the hydride structures changes from the highly symmetrical $\text{P6}_3/\text{mmc}$ for the hydrides with a disordered arrangement of hydrogen to P6_3 for the Co_3H superstructure and to $\text{P}\bar{3}\text{m1}$ for the Co_2H superstructure. Hydrogen ordering also lowers the symmetry of the metal lattice by causing displacements of the metal atoms from the hcp positions, the metal layers separated by hydrogen atoms moving apart from one another.

Acknowledgements

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