

Neutron scattering studies of γ -CoH

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Received 30 May 2004; received in revised form 3 November 2004; accepted 10 November 2004

Available online 7 July 2005

Abstract

A powder sample of *fcc* (γ) cobalt hydride was synthesised under a pressure of 9 GPa and a temperature of 350 °C and then studied at ambient pressure by neutron diffraction at 95 K and by inelastic neutron scattering (INS) at 5 K in the range of energy transfers 30–380 meV. A profile analysis of the neutron diffraction pattern showed that hydrogen occupies octahedral interstitial sites in the *fcc* metal lattice of γ -CoH with $a = 3.7124(5)$ Å. The INS investigation demonstrated that the fundamental band of optical hydrogen vibrations consists of a strong peak at 102 meV with a broad shoulder towards higher energies. This intensity distribution is typical of *hcp* and *fcc* monohydrides of 3*d*- and 4*d*-metals, and the peak position as a function of the hydrogen–metal distance agrees with the dependence established for those hydrides earlier.

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Keywords: Interstitial alloys; Neutron scattering; Diffraction

1. Introduction

At temperatures of 250–350 °C, the equilibrium solubility of hydrogen in the low-temperature *hcp* (ϵ) modification of cobalt monotonically increases with pressure and reaches an H/Co atomic ratio of $x \approx 0.6$ at 7 GPa [1]. At higher pressures, hydride with $x \approx 1$ is formed on the base of the high-temperature *fcc* (γ) cobalt modification [1]. Both the ϵ solid hydrogen solutions (hydrides) and the stoichiometric γ -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 hydrogen pressure.

Cobalt and its hydrides are ferromagnets. The magnetization measurements showed [2] that magnetic moments in the ϵ hydrides decrease from 1.71 μ_B /atom Co at $x = 0$ to about 1.55 μ_B /atom Co at $x = 0.5$, and decrease to about 1.3 μ_B /atom Co for the γ hydride with $x \approx 1$. A neutron diffraction investigation at ambient pressure and 120 K

showed [3] that hydrogen atoms are randomly distributed over octahedral interstices in the ϵ cobalt hydrides with $x \leq 0.26$ and form layered superstructures in the solutions with $x \geq 0.34$, occupying every third octahedral basal layer at $x = 0.34$ and every second layer at $x \geq 0.38$. So far, the crystal structure of γ cobalt hydride was examined only by X-ray diffraction [1], which provided no information about the type of hydrogen positions in the *fcc* Co lattice.

In the present paper, the full crystal structure of γ -CoH was studied by neutron diffraction and its lattice dynamics by inelastic neutron scattering.

2. Experimental

Plates (0.2 mm thick) of 99.98 wt.% pure polycrystalline cobalt were loaded with hydrogen by a 24 h exposure to a H_2 pressure of 9 GPa at 350 °C and subsequent cooling to 150 K in the high-pressure cell. The hydrogenation method is described in more detail elsewhere [4]. To ensure the homogeneity of the sample, the hydrogenated plates were examined by

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X-ray diffraction ($T = 100$ K, Fe $K\alpha$ radiation) and shown to be single-phase *fcc* hydride, and a few milligrams piece of each plate was analysed for hydrogen content by hot extraction into a calibrated volume at temperatures up to 200°C and shown to contain $x = 1 \pm 0.03$ hydrogen. The plates were brittle. Prior to the neutron scattering experiments, they were ground in an agate mortar under liquid nitrogen to diminish texture effects.

The 400 mg powder sample of γ -CoH thus prepared was studied by neutron diffraction at 95 K with the D20 and D1B diffractometers at the Institute Laue-Langevin in Grenoble using neutrons of a wavelength of $\lambda = 1.29$ and 2.52 Å, respectively. The diffraction data were analysed with a computer program [5] based on the Rietveld profile refinement technique. The inelastic neutron scattering (INS) spectrum from the γ -CoH sample was measured at 5 K with the IN1 BeF spectrometer installed at the hot source of the high-flux reactor at ILL, Grenoble. Cu(200) and Cu(220) monochromators were used to obtain incoming neutrons with energies below and above 120 meV, respectively. Background spectra from empty sample holders were measured separately under the same conditions and then subtracted from the corresponding spectra of the sample.

3. Results and discussion

3.1. Neutron diffraction

The neutron diffraction patterns of the γ -CoH sample and the results of their profile analysis are presented in Figs. 1 and 2. The statistics of the spectra and the signal-to-noise ratio were rather poor due to a few unfavourable factors acting together: the relatively small mass of the sample, the low coherent neutron cross-section of Co and H atoms, the large neutron absorption by Co atoms and the large incoherent neutron scattering from H atoms. Nevertheless, the profile analysis gave a decisive conclusion concerning the type of interstitial sites that hydrogen atoms occupy in the *fcc* metal lattice of γ -CoH.

To reduce the number of fitting parameters, the magnetic contribution to the scattering intensity (curve b in Fig. 1) was calculated using a value of $1.3 \mu_B/\text{atom Co}$ from reference [2]. The hydrogen content $x = 1$ of the hydride was also fixed.

As seen from Fig. 2, the neutron diffraction pattern of γ -CoH contains no new lines in addition to the lines of the *fcc* structure. The crystal structure of this hydride therefore belongs to the same space group, $Fm\bar{3}m$, as the *fcc* structure of its metal lattice. In the *fcc* structure, there are two types of highly symmetrical interstitial sites conforming the $Fm\bar{3}m$ 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 hydrogen occupies every octahedral site gives a satisfactory profile fit of the experimental spectra, while a model with hydrogen randomly distributed over the tetrahedral sites (which are twice as many as the metal sites) is

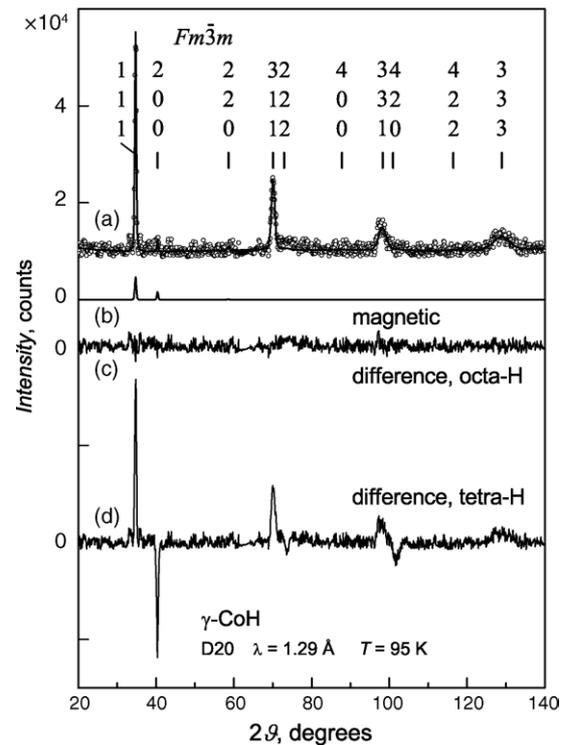


Fig. 1. Neutron powder diffraction pattern of γ -CoH measured at 95 K with the D20 diffractometer at ILL, Grenoble, using neutrons with a wavelength of $\lambda = 1.29$ Å (open circles) and results of its Rietveld analysis (solid lines). Curve (a) is the sum of the magnetic contribution shown by curve (b) and of the nuclear contribution calculated for the $Fm\bar{3}m$ structure of the NaCl type with hydrogen atoms occupying every octahedral site in the *fcc* Co lattice with $a = 3.7124(5)$ Å. Curve (c) is the difference between the experimental (circles) and calculated (curve a) spectra. Curve (d) is the difference between the experimental spectrum and that calculated for $x = 1$ hydrogen atoms randomly occupying one half of the tetrahedral interstices, the other fitting parameters being the same as for curve (c).

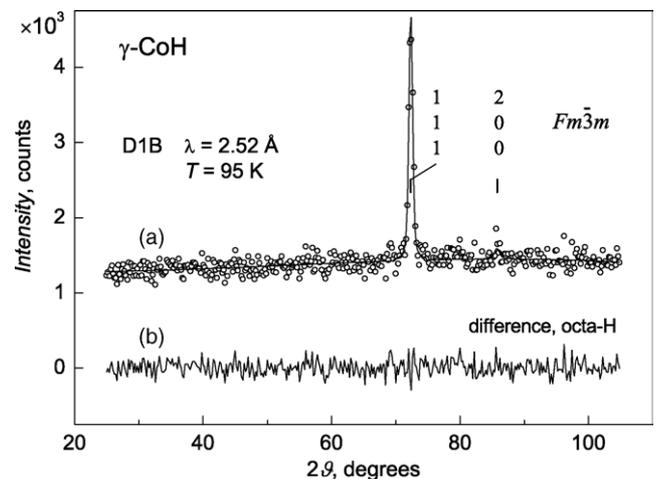


Fig. 2. Neutron powder diffraction pattern of γ -CoH measured at 95 K with the D1B diffractometer at ILL, Grenoble, using neutrons with a wavelength of $\lambda = 2.52$ Å (open circles). Its profile fit shown by solid line (a) is the sum of the magnetic contribution and of the nuclear contribution calculated for the $Fm\bar{3}m$ structure with hydrogen atoms on octahedral sites in the *fcc* Co lattice. Curve (b) is the difference between the experimental and calculated spectra.

qualitatively unacceptable. Correspondingly, any admixture of tetrahedral hydrogen makes the agreement between the calculation and experiment worse, and the model allowing partial occupancy of sites of both types converges to 100% occupancy of the octahedral ones.

The octahedral hydrogen coordination established for γ -CoH is characteristic of all hydrides with close packed metal lattices that are formed by transition metals of groups VI–VIII [6]. The difference about 1.8 \AA^3 per metal atom per H atom between the atomic volumes of γ -CoH and Co [1] as well as the interatomic distances $R(\text{Co-H}) = 1.856 \text{ \AA}$ and $R(\text{Co-Co}) = R(\text{H-H}) = 2.625 \text{ \AA}$ in γ -CoH are typical of monohydrides of 3d-metals of these groups.

3.2. Inelastic neutron scattering

The INS spectrum of γ -CoH is shown in Fig. 3 and looks similar to the spectra of monohydrides of all other 3d- and

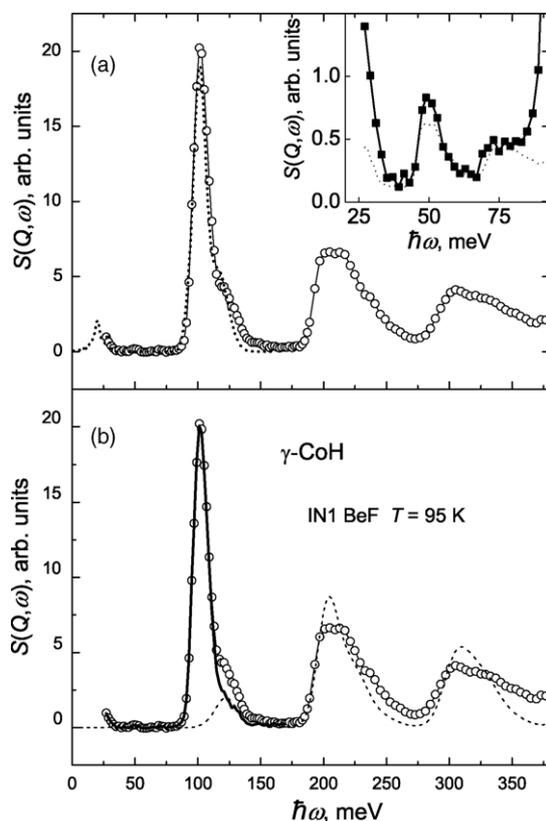


Fig. 3. The dynamical structure factor $S(Q, \omega)$ of γ -CoH as a function of the energy loss $\hbar\omega$ of the inelastically scattered neutrons. The open circles connected by a solid line represent the spectrum of the γ -CoH powder sample measured at 5 K with the IN1 BeF spectrometer at ILL, Grenoble, and corrected for the presence of neutrons of half the wavelength in the monochromated incoming beam. The inset in (a) shows the low-energy portion of the raw INS spectrum subject to the corrections (solid squares) and the calculated contribution from the $\lambda/2$ neutrons (dashed curve). The dashed curve in (a) shows results of the lattice dynamics calculations carried out to estimate the spectrum of ‘acoustic’ vibrations in γ -CoH at energies below 30 meV. The dashed curve in (b) is the calculated multiphonon contribution and the thick solid curve is the one-phonon spectrum of γ -CoH.

4d-metals of groups VI–VIII studied so far (see [7] and references therein). The first fundamental band of optical H vibrations consists of a strong peak centred at $\hbar\omega_0 = 102 \text{ meV}$ with a shoulder towards higher energies extending up to about 140 meV. The second and the third optical H band resulting from multiphonon neutron scattering have a smoother intensity distribution and appear at energies approximately two and three times the energy of the fundamental band, respectively.

The lattice part of the INS spectrum of γ -CoH at energies below 30 meV was calculated using the force constants from the Born-von-Kármán fit (dashed curve in Fig. 3a) to the fundamental optical peak. The longitudinal (L) and transverse (T) force constants were: $L(\text{Co-Co}) = 25 \text{ N/m}$, $L(\text{Co-H}) = 18.7 \text{ N/m}$, $L(\text{H-H}) = 2.5 \text{ N/m}$, $T(\text{H-H}) = -1.5 \text{ N/m}$ for the nearest neighbours, and $L(\text{H-H}) = 2.5 \text{ N/m}$, $T(\text{H-H}) = 0.8 \text{ N/m}$ for the second nearest neighbours.

Using the estimated low-energy lattice part of the vibrational spectrum of γ -CoH, the contribution from multiphonon neutron scattering was calculated in an isotropic and harmonic approximation using an iterative technique [8]. As one can see from Fig. 3b, the calculated dashed curve rather well describes the main features of the multiphonon part of the experimental spectrum at energies above 150 meV.

The one-phonon spectrum of γ -CoH obtained by subtracting the calculated multiphonon spectrum from the experimental data is shown in Fig. 3b by the thick solid curve. A high-energy shoulder of the main optical peak is still clearly seen in this spectrum. Such a shoulder is characteristic of the vibrational spectra of all hydrides of the VI–VIII group transition metals studied so far. Based on results for palladium deuteride [9], its occurrence is usually ascribed to the

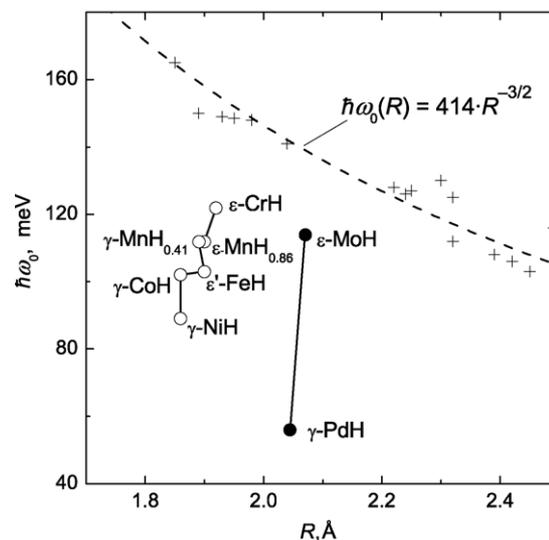


Fig. 4. Energy of the main optical hydrogen peak, $\hbar\omega_0$, vs. the shortest hydrogen–metal distance R for various dihydrides with a fluorite-type structure (crosses) [13] and for monohydrides of 3d-metals (open circles) and 4d-metals (solid circles) (see [7] for references and discussion). The dashed curve is a least-squares fit to the data for the dihydrides.

dispersion of longitudinal optical phonon modes caused by long-range repulsive H–H interactions.

As a function of the hydrogen–metal distance R , the position $h\omega_0 = 102$ meV of the main optical peak in the spectrum of γ -CoH agrees with the approximately linear dependence $h\omega_0(R)$ for hydrides of 3d-metals (Fig. 4).

4. Conclusions

The γ -hydride of cobalt is a typical representative of hydrides of the group VI–VIII transition metals. The octahedral coordination of hydrogen atoms in γ -CoH meets the criterion [10] to say that hydrogen can occupy only octahedral interstitial sites in 3d-metals positioned to the right of vanadium in the periodic table because the size of tetrahedral sites in these metals becomes too small due to the monotonic decrease in their atomic radii with increasing atomic number. The position $h\omega_0 = 102$ meV of the main optical peak in the vibrational spectrum of γ -CoH agrees with the results of first-principles calculations [11,12] predicting a monotonic increase in the steepness of the potential well for interstitial hydrogen in transition metals from right to left in the periodic table due to a less efficient screening of the ionic core charges by the decreasing number of valence electrons.

Acknowledgements

This work was supported by grant No. 02-02-16859 from the Russian Foundation for Basic Research and by the Pro-

gram “Physics and Mechanics of Strongly Compressed Matter” of the Russian Academy of Sciences.

References

- [1] V.E. Antonov, I.T. Belash, V.Yu. Malyshev, E.G. Ponyatovskii, Dokl. Akad. Nauk SSSR 272 (1983) 1147 (in Russian).
- [2] I.T. Belash, V.Yu. Malyshev, B.K. Ponomarev, E.G. Ponyatovskii, A.Yu. Sokolov, Fiz. Tverd. Tela 28 (1986) 1317 [Engl. Trans. Sov. Phys. Solid State 28 (1986) 741].
- [3] V.K. Fedotov, V.E. Antonov, T.E. Antonova, E.L. Bokhenkov, B. Dorner, G. Grosse, F.E. Wagner, J. Alloys Comp. 291 (1999) 1.
- [4] V.E. Antonov, T.E. Antonova, N.A. Chirin, E.G. Ponyatovsky, M. Baier, F.E. Wagner, Scripta Mater. 34 (1996) 1331.
- [5] R.A. Young, A. Sakthivel, T.S. Moss, C.O. Paiva-Santos, DBWS9411 User's Guide, Georgia Institute of Technology, Atlanta, 1995.
- [6] V.E. Antonov, J. Alloys Comp. 330–332 (2002) 110.
- [7] V.E. Antonov, K. Cornell, B. Dorner, V.K. Fedotov, G. Grosse, A.I. Kolesnikov, F.E. Wagner, H. Wipf, Solid State Commun. 113 (2000) 569.
- [8] A.I. Kolesnikov, I. Natkaniec, V.E. Antonov, I.T. Belash, V.K. Fedotov, J. Krawczyk, J. Mayer, E.G. Ponyatovsky, Physica B 174 (1991) 257.
- [9] J.M. Rowe, J.J. Rush, H.G. Smith, M. Mostoller, H.E. Flotow, Phys. Rev. Lett. 33 (1974) 1297.
- [10] V.A. Somenkov, V.P. Glazkov, Z. Phys. Chem. N.F. 117 (1979) 125.
- [11] C. Elsässer, H. Krimmel, M. Fähnle, S.G. Louie, C.T. Chan, J. Phys.: Condens. Matter 10 (1998) 5131.
- [12] C. Elsässer, Ab-initio-Elektronentheorie für Übergangsmetall-Wasserstoff-Verbindungen, Universität Stuttgart, Habilitationsschrift, 1994.
- [13] D.K. Ross, P.F. Martin, W.A. Oates, R. Khoda Bakhsh, Z. Phys. Chem. N. F. 114 (1979) 221.