NEUTRON SCATTERING STUDIES of *fcc* CrH and *hcp* CrH

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Introduction

The solubility of hydrogen in *bcc* chromium metal is small. Chromium hydrides with compositions close to CrH can be produced electrolytically and under high hydrogen pressure [1]. Depending on the electrodeposition conditions, the CrH hydrides can have a *hcp* (ε) or *fcc* (γ) metal lattice [2]. A room-temperature neutron diffraction (ND) investigation of the ε-CrH showed that hydrogen atoms occupy octahedral interstitial positions in the *hcp* chromium lattice and that the hydride is not magnetically ordered [3]. The vibrational spectrum of hydrogen in ε-CrH was studied by inelastic neutron scattering (INS) at 15 K in the range of energy transfers 25–500 meV [4]. The γ-CrH has never been studied by neutron scattering. Experiments on nuclear magnetic resonance and magnetic susceptibility revealed no signs of magnetic order in *fcc* or *hcp* CrH at temperatures down to 3 K [2].

The present paper reports on low-temperature ND and INS investigations of γ-CrH and ε-CrH prepared by electrodeposition. The neutron diffraction (DN-2 diffractometer, JINR, T = 8 K) was used as the most direct means to establish the occurrence or the absence of magnetic ordering in each hydride and to determine the H positions in the *fcc* hydride. The INS investigation (KDSOG-M spectrometer, JINR, T = 10 K) has yielded for the first time the H vibrational spectrum of γ-CrH in a wide energy range from 2 to above 500 meV and also the vibrational spectrum of ε-CrH in the low-energy range ≤ 25 meV.

Results and discussion

The ND investigation showed that hydrogen atoms occupied octahedral interstitial positions in the metal lattice of both *fcc* and *hcp* chromium hydrides and that both hydrides were not magnetically ordered at a temperature as low as 8 K. The absence of any superstructure lines that could be attributed to magnetic ordering in the ND pattern of γ-CrH is illustrated by Fig. 1.

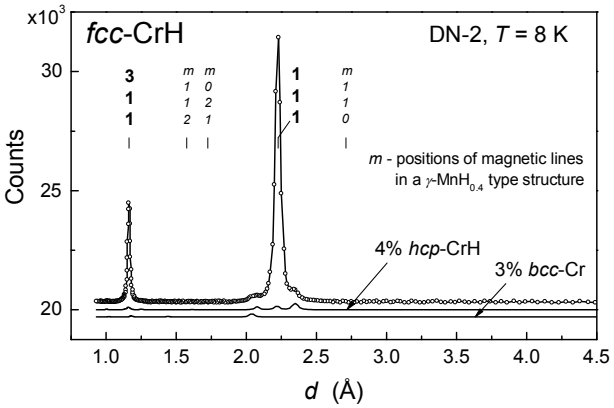

Fig. 1. The ND pattern of a γ-CrH sample containing 4 % ε-CrH and 3% Cr as impurities. The DN-2 time-of –flight diffractometer, JINR, Dubna, T = 8 K.

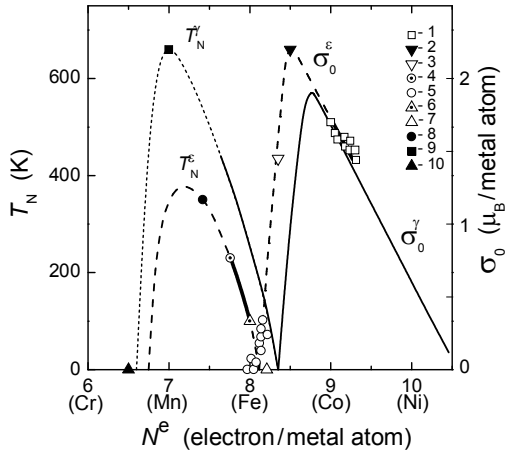

Fig. 2. Slater-Pauling curves for *fcc* (γ) alloys (experiment – thin solid lines) and *hcp* (ε) alloys (experiment – two sections of thick solid lines; an estimation – dashed lines) of 3*d*-metals that are nearest neighbours in the Periodic Table [7]. The symbols show experimental data for hydrides presented as a function of the effective electron concentration, $N^e(x) = N^e(0) + \eta \cdot x$, with η = 0.5 electrons per H atom: 1 – σ_0 of ε-CoH_x solid solutions; 2 – σ_0 of ε′-FeH with a 4*H*-type metal lattice; 3 – σ_0 of $Fe_{0.947}Cr_{0.053}H_{0.92}$ with a 9*R*-type metal lattice; 4 – T_N of ε-Fe; 5 – σ_0 of ε-$FeH_{0.42}$; 6 – T_N of ε-$Fe_{0.776}Mn_{0.224}$; 7 – σ_0 of ε-$Fe_{0.776}Mn_{0.224}H_x$ solid solutions; 8 – T_N of ε-$Mn_{0.83}$; 9 – T_N of γ–Mn;

10 – T_N < 8 K of ε-CrH and γ–CrH. x is the H-to-metal atomic ratio.

The octahedral co-ordination of H atoms in chromium hydrides is typical of hydrides of the group VI-VIII transition metals [5]. The absence of magnetic ordering in *fcc* CrH suggests a very steep decrease in the Néel temperature T_N of (metastable) *fcc* alloys of 3*d*-metals with the decrease in the effective electron concentration N^e from 7 el./atom for *fcc* Mn (an antiferromagnet with T_N = 660 K) to about 6.5 el./atom for *fcc* CrH with T_N < 8 K. A similar steep decrease in the Curie temperature of ferromagnetic *fcc* alloys of 3*d*-metals occurs with N^e decreasing in the invar range 8.8–8.4 el./atom (see Fig. 2)

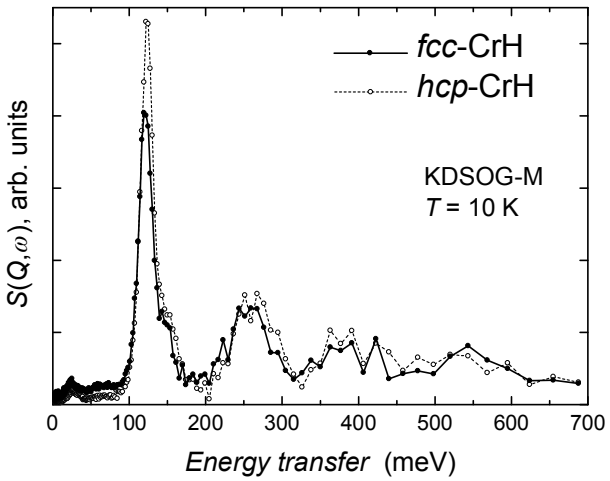

Fig. 3. INS spectra of γ-CrH and ε-CrH measured with the KDSOG-M time-of–flight spectrometer at JINR, Dubna. T = 10 K.

The INS spectra of γ-CrH and ε-CrH are shown in Fig. 3. The spectra are much alike and look similar to the INS spectra of hydrides of all other 3*d*- and 4*d*-metals of groups VI–VIII studied so far. The first, fundamental band of optical H vibrations consists of a strong peak (centred at $\hbar\omega_0$ = 120 and 122 meV for γ-CrH and ε-CrH, respectively) with a broad shoulder towards higher energies. Based on results for palladium deuteride [6], the main peak is usually ascribed to nearly nondispersive transverse optical modes, while the shoulder is assumed to arise from longitudinal optical modes, which show significant dispersion due to long-range H–H interactions.

The second and third optical H bands have a smoother intensity distribution and appear at energies approximately two and three times the energy of the fundamental band, respectively. As a function of the hydrogen–metal distance R, the values of $\hbar\omega_0$ for γ-CrH and ε-CrH agree well with the approximately linear dependence $\hbar\omega_0(R)$ for γ- and ε-hydrides of 3*d*-metals (Fig. 4).

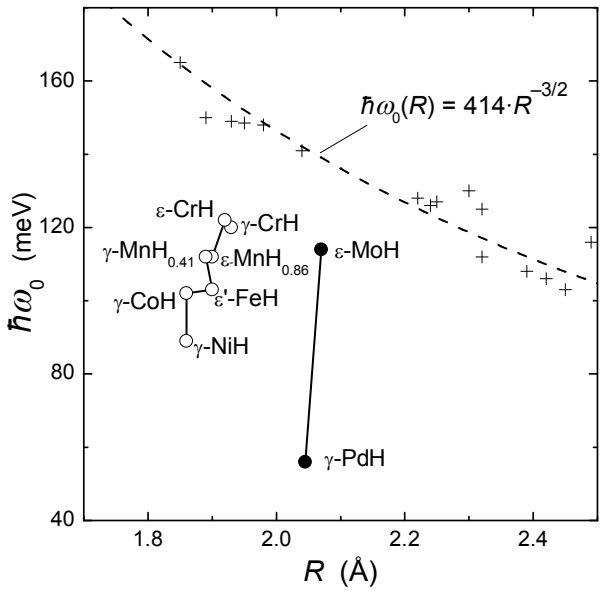

Fig. 4. Energy of the main optical hydrogen peak, $\hbar\omega_0$, versus the shortest hydrogen–metal distance R for various dihydrides with a fluorite-type structure (crosses) [8] and for monohydrides of 3*d*-metals (open circles) and 4*d*-metals (solid circles) with octahedral co-ordination of hydrogen (see [9,10] and references therein).

References

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