

INVESTIGATION OF THE HYDRIDES OF $\text{Ni}_{0.70}\text{Cu}_{0.30}$ BY ^{57}Fe MÖSSBAUER SPECTROSCOPY AND MAGNETIZATION MEASUREMENTS

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Hydrides of $\text{Ni}_{0.70}\text{Cu}_{0.30}$ prepared both electrolytically and under high pressures of hydrogen gas were studied by Mössbauer spectroscopy on dilute ^{57}Fe probes and by magnetization measurements. At hydrogen-to-metal ratios above $x \approx 0.3$ no ferromagnetism is observed down to 4.2 K. The dependence of the mean change of the isomer shift on the hydrogen content of the samples reveals a repulsive interaction between the hydrogen interstitials and the iron probes. The effect of this interaction is, however, less pronounced than for ^{57}Fe in the hydrides of pure nickel. This difference can be attributed to a competition of the repulsive Fe-H and Cu-H interactions.

1. Introduction

Nickel and copper form a continuous series of solid solutions, whose saturation magnetization and Curie temperature decrease with increasing copper content. Alloys containing more than about 60 at.% Cu do not become ferromagnetic down to 4.2 K [1]. Ni-Cu alloys with copper contents up to about 50 at.% can be loaded with hydrogen electrolytically or under high pressures of H_2 gas [2-11]. The hydrides retain the fcc structure of the Ni-Cu alloys. Like in pure Ni [12], the ferromagnetism is suppressed by hydrogenation [2,4,5,8-11]. At copper concentrations below about 40 at.%, a separation into an α phase containing very little hydrogen and a hydrogen-rich β phase[†] is observed [4,10].

Recently, first results of a Mössbauer study of the hydrides of $\text{Ni}_{0.70}\text{Cu}_{0.30}$ have been reported [13]. The present paper describes a more detailed investigation of the dependence of the isomer shift on the hydrogen content and of the properties of the magnetic α phase containing a few percent of hydrogen only.

[†] Alternatively [10], these two phases have been designated as γ_1 and γ_2 .

2. Experimental Details

As in the previous Mössbauer experiments [13], the absorbers were made from an arc-melted $\text{Ni}_{0.70}\text{Cu}_{0.30}$ alloy containing 0.15 at.% of isotopically enriched ^{57}Fe . Rolled foils of about 15 μm thickness were annealed at 850 °C in H_2 for 2 hours and then loaded with hydrogen either under high pressures of molecular hydrogen or electrolytically at ambient temperature in 0.5 n H_2SO_4 with 0.2 g/l of thiourea as a promoting agent [14] and a current density of about 20 mA/cm². Hydrogen pressures of up to 3 GPa were reached at room temperature in piston-type pressure cells [9,15–17], while the hydrogenation at 7 GPa was performed at 300 °C in a high pressure cell using AlH_3 as a hydrogen donor [18]. After the hydrogenation, the pressure cells were cooled with liquid nitrogen before release of the pressure and removal of the samples. After the hydrogenation, the specimens were stored in liquid nitrogen and transferred into the Mössbauer cryostat without warming. The hydrogen content was determined by outgassing either the whole samples after the Mössbauer measurements or parts removed from the specimens beforehand.

3. Results

The Mössbauer spectra of the hydrides of $\text{Ni}_{0.70}\text{Cu}_{0.30}\text{H}_x$ with hydrogen-to-metal ratios $x \geq 0.3$ are broadened patterns that do not show a magnetic hyperfine splitting [13]. The broadening can be mainly be attributed to the distribution of hydrogens on the six interstitial sites next to the substitutional iron probes. Moreover, the distribution of Ni and Cu atoms in the vicinity of the iron causes some line broadening already at $x = 0$ [13]. In analogy to the model used previously for fitting the spectra of NiH_x [19,20] and PdH_x [21], the spectra were fitted with a superposition of seven equidistant lines corresponding to ^{57}Fe with 0 to 6 nearest hydrogen neighbours. The influence of the distribution of Cu and Ni neighbours was included in the width of these lines. For the isomer shift per hydrogen neighbour a value of $\Delta S = 0.10$ mm/s yielded good fits of the spectra and is in agreement with previous results [13,19–21]. Fig. 1 shows the dependence of the centre shift of the non-magnetic peak on the hydrogen content.

Samples with an average hydrogen content below $x \approx 0.3$ usually are mixtures of the non magnetic β phase and the ferromagnetic α phase containing a few percent of hydrogen. The hydrogen contents of the β phase in such samples were derived using $x = 0.03$ for the the α phase (see below) and taking the relative amounts of the two phases from the areas in the Mössbauer spectra. Samples loaded at a hydrogen pressure of 0.33 GPa at ambient temperature contained no β phase and had hydrogen-to-metal ratios near $x = 0.03$. These small hydrogen contents have no visible influence on the isomer shift or the magnetic hyperfine field of (26.6 ± 0.2) T at 4.2 K. Magnetization measurements in alternating magnetic fields performed as described in Ref. [22], however, show that at $x \approx 0.03$ the Curie temperature is reduced by about 20 K and the saturation magnetization by about 10 % (fig. 2).

4. Discussion

The hydrogen-induced centre shifts for ^{57}Fe in $\text{Ni}_{0.70}\text{Cu}_{0.30}\text{H}_x$ show a strongly non-linear dependence on the hydrogen content but are generally higher than those for ^{57}Fe in hydrides of pure nickel (fig. 1), where below room temperature the β phase exists only with hydrogen

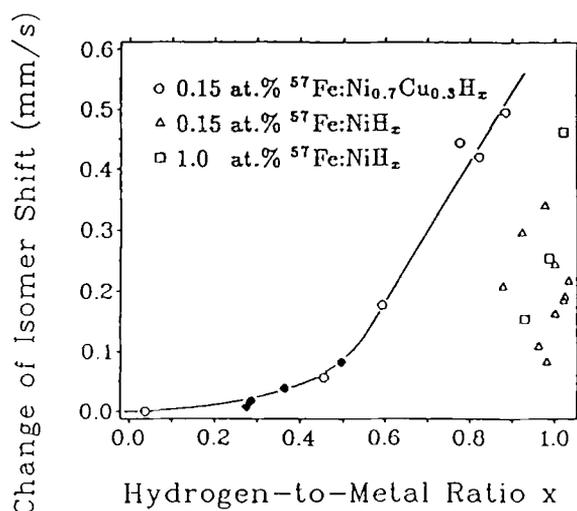


Fig. 1: Isomer shifts of ^{57}Fe in $Ni_{0.70}Cu_{0.30}H_x$ hydrides as a function of the hydrogen content. Open circles represent data from single-phase, filled circles data from two-phase specimens. The shifts were measured at 100 K and are given relative to hydrogen-free $Ni_{0.70}Cu_{0.30}$ at the same temperature. Shifts for dilute ^{57}Fe in NiH_x hydrides [19,20] with respect to unloaded nickel are shown for comparison (triangles and squares).[†]

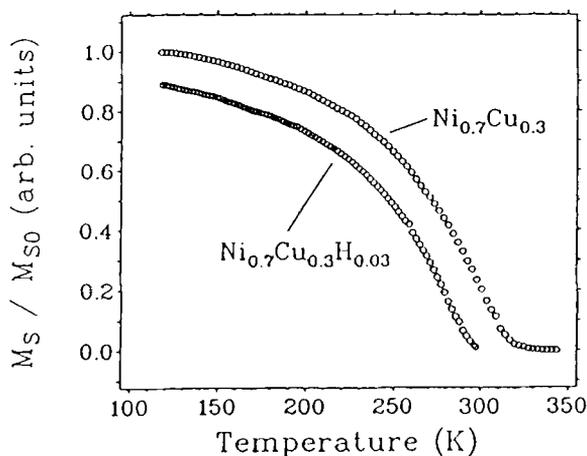


Fig. 2: Temperature dependence of the saturation magnetization of $Ni_{0.70}Cu_{0.30}H_{0.03}$ and of the same alloy after complete outgassing.

contents $x \gtrsim 0.9$ [7]. The shifts for β - NiH_x show no correlation with the hydrogen content (fig. 1), presumably because the accuracy of the determination of the hydrogen content is insufficient to resolve the steep increase of the shift with increasing hydrogen content for $x \gtrsim 0.9$. Such a steep increase is expected if there is a strongly repulsive interaction between the hydrogen and the iron probes [19–21], which largely prevents hydrogen from occupying sites next to iron at except at hydrogen contents close to $x = 1$.

For the $Ni_{0.70}Cu_{0.30}$ alloys the increase of the isomer shift with the hydrogen concentration

is smoother, showing that hydrogen penetrates into the vicinity of the iron probes already at lower hydrogen concentrations. This can be explained by a distribution of interstitial site energies in the disordered Ni-Cu alloys, where interstitial sites with many Cu neighbours will be less favourable for hydrogen occupation than sites with fewer or none, in a similar manner as has been proposed for hydrides of amorphous alloys [23,24]. Hydrogen sites with an iron neighbour will be distributed within the range of site energies and therefore become filled gradually together with other sites with comparable energy. Model calculations based on the model of a site energy distribution [23,24], whose description would exceed the scope of this paper, can indeed explain the dependence of the centre shift on the hydrogen content and on temperature [13] with reasonable values of the model parameters.

The lack of sensitivity of the ^{57}Fe for probing the influence of the dissolved hydrogen in the α phase can also be understood in this way, since for small x the interstitial sites next to the iron will not be occupied even in Ni-Cu alloys. The magnetic properties, i. e. the Curie temperature and the saturation magnetization, however, are strongly affected, as is suggested by the rigid band model, since the incorporation of hydrogen fills the empty d states in Ni or Ni-Cu alloys.

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