# <sup>57</sup>Fe Mössbauer study of the hydrides of Ni–Cu alloys

#### B. Zhang and H. J. Bauer

Sektion Physik, Ludwig-Maximilians-Universität, W-8000 München (F.R.G.)

## M. Baier and F. E. Wagner

Physics Department, Technical University of Munich, W-8046 Garching (F.R.G.)

#### V. E. Antonov and T. E. Antonova

Institute of Solid State Physics, Academy of Sciences of the U.S.S.R., Chernogolovka District 142432 (U.S.S.R.)

#### Abstract

Hydrides of Ni<sub>0.70</sub>Cu<sub>0.30</sub> alloys were prepared electrolytically or under high pressures of molecular hydrogen and studied by Mössbauer spectroscopy using dilute substitutional <sup>57</sup>Fe as a probe. At a hydrogen pressure of 7 GPa, a hydrogen-to-metal ratio near x = 0.9 could be reached, while at 1.1 GPa or by cathodic charging hydrogen contents near x = 0.6 were obtained, which are already sufficient to suppress ferromagnetism completely. The hydrogen was found to be repelled by the iron probes, but less effectively than in pure nickel. The temperature dependence of the isomer shift showed that the samples began to lose hydrogen near 200 K. The reappearing magnetic phase had hyperfine parameters practically the same as those of the alloy before hydrogenation.

#### 1. Introduction

Nickel and copper form a continuous series of solid solutions. Both the saturation magnetization and the Curie temperature decrease with increasing copper content of these alloys, which no longer become ferromagnetic even at low temperatures when the copper concentration exceeds about 60 at.% [1]. Ni-Cu alloys with copper contents up to about 50 at.% can be hydrogenated electrolytically or under high pressures of H<sub>2</sub> gas even more easily than pure nickel [2–10], although high hydrogen concentrations are easier to obtain using the latter method. The hydrides retain the f.c.c. structure of the Ni-Cu alloys. At copper concentrations exceeding about 40 at.%, the separation into the  $\alpha$  phase containing only few per cent of hydrogen and the hydrogen-rich  $\beta$  phase disappears [4, 9]. (Alternatively, these two phases have been designated as  $\gamma_1$  and  $\gamma_2$  [9].) As in pure nickel [11], the ferromagnetism of the Ni-Cu alloys is suppressed by hydrogenation [2, 4, 5, 7–10].

Recent Mössbauer studies using <sup>57</sup>Fe as a dilute probe in NiH<sub>x</sub> have shown [12, 13] that the hydrogen is strongly repelled by the iron, such that hydrogen occupies interstitial sites next to iron atoms only at hydrogen-tometal ratios very close to unity. In this context, Mössbauer studies on hydrides such as those of Ni–Cu alloys are of interest since the distribution of hydrogen around the iron probes is expected to be changed by the partial substitution of nickel by another element. Moreover, Mössbauer spectroscopy can yield microscopic information on the magnetic properties of such hydrides as it has done for hydrogen-free Ni–Cu alloys [14, 15].

As first results of an investigation of the  $(Ni_{1-y} Cu_y)H_x$  system by <sup>57</sup>Fe Mössbauer spectroscopy, X-ray diffraction, and magnetic measurements, this paper reports on Mössbauer experiments with hydrides of  $Ni_{0.70}Cu_{0.30}$ .

#### 2. Experimental details

The Mössbauer absorbers were made from an arc-melted Ni<sub>0.70</sub>Cu<sub>0.30</sub> alloy containing 0.15 at.% of isotopically enriched <sup>57</sup>Fe. This was rolled to foils about 15  $\mu$ m thick which were then annealed in a hydrogen atmosphere at 850 °C for several hours and then cooled to room temperature at a cooling rate of about 10 K min<sup>-1</sup>. The foils were loaded with hydrogen electrolytically at ambient temperature in  $0.5 \text{ n } \text{H}_2\text{SO}_4$  with  $0.2 \text{ g } \text{l}^{-1}$  of thiourea as a promoting agent [16] and a current density of 20 mA cm<sup>-2</sup>, or under high pressures of molecular hydrogen. Hydrogen pressures of up to 1.1 GPa were reached in a piston-type pressure cell [8, 17-19], while hydrogenation at 7 GPa was performed in a high pressure cell using  $MnH_x$  as a hydrogen donor [20]. After hydrogenation, the pressure cell was cooled with liquid  $N_2$  before the pressure was released and the sample removed from the cell. The samples were stored in liquid  $N_2$  and later transferred into the Mössbauer cryostat without warming. The hydrogen content was determined by outgassing into a calibrated volume, either after the Mössbauer experiments, or for parts of the samples removed before the transfer into the Mössbauer cryostat. During cathodic charging, the formation of the hydrides was monitored by magnetization measurements. In some cases lattice parameters were measured by X-ray diffraction using Fe K $\alpha$  radiation.

#### 3. Results and discussion

# 3.1. Isomer shift as a function of the hydrogen-to-metal ratio

Figure 1 shows the Mössbauer spectra of  $Ni_{0.70}Cu_{0.30}$  and of two hydrides of this alloy. Table 1 summarizes the loading conditions and experimental results. X-ray diffraction at liquid nitrogen temperature showed the sample loaded at 7 GPa to be pure  $\beta$  phase hydride with a unit cell volume 18% larger than that of the unloaded alloy. The sample loaded at 1.1 GPa was not X rayed, but with a hydrogen content of x = 0.59 it is also expected to be pure  $\beta$  phase [3, 4, 9].

This expectation is confirmed by the Mössbauer spectra taken at 4.2 K which, for both hydride samples, do not contain any magnetic fraction. Since



Fig. 1. <sup>57</sup>Fe Mössbauer spectra of  $Ni_{0.70}Cu_{0.30}$ ,  $(Ni_{0.70}Cu_{0.30})H_{0.59}$ , and  $(Ni_{0.70}Cu_{0.30})H_{0.89}$ . In all samples 0.15 at.% of the metal atoms were substituted by enriched <sup>57</sup>Fe. The spectra of the hydrides were measured with both the absorber and the source of <sup>57</sup>Co in rhodium at 4.2 K. The spectrum of the unloaded sample was measured with the absorber at 323 K and the source at 300 K.

#### TABLE 1

Conditions of hydrogenation, lattice parameters, and Mössbauer results for  $(Ni_{0.70}\,Cu_{0.30})H_x$  hydrides

x	a <sub>0</sub> (Å)	S (mm s <sup>-1</sup> )	W (mm s <sup>-1</sup> )	Conditions of hydrogenation
0.0	3.542	$-0.098 \pm 0.005$	$0.41 \pm 0.01$	
0.59		$+0.080 \pm 0.005$	$0.50 \pm 0.01$	1.1 GPa, 25 °C, 117 h
0.89	3.741	$+0.408 \pm 0.005$	$0.41\pm0.01$	7 GPa, 250 °C, 24 h

The lattice constants  $a_0$  were measured at 100 K. The uncertainty of the hydrogen-to-metal ratio x is about 0.02. S is the mean isomer shift with respect to the source of <sup>57</sup>Co in rhodium at 4.2 K, and W the full width at half maximum of the Mössbauer patterns. The isomer shift for the unloaded alloy was determined from the magnetic hyperfine spectrum measured at 4.2 K, while the linewidth was taken from a spectrum measured at 323 K, *i.e.* above the Curie temperature of the alloy.

the hydrogen-free alloy is ferromagnetic at 4.2 K, the spectrum of  $Ni_{0.70}Cu_{0.30}$  shown in Fig. 1 for comparison with the hydride spectra was taken above the Curie temperature. The second-order Doppler shift (see, for example, ref. 21) is nevertheless expected to have practically no influence on the peak positions of the spectra shown in Fig. 1 since the temperature difference between

source and absorber was small in all cases. The centre shifts are therefore representative of the effect of hydrogenation. As in NiH<sub>x</sub> [12, 13] and PdH<sub>x</sub> [22], loading with hydrogen causes an increase in the isomer shift, which corresponds to a decrease in the electron density at the iron nuclei.

The isomer shift with respect to the unhydrogenated alloy is  $+0.18 \text{ mm s}^{-1}$  for the hydride with  $x = 0.59 \text{ and } +0.51 \text{ mm s}^{-1}$  for that with x = 0.89. Previous work, particularly for <sup>57</sup>Fe in NiH, [12, 13] and PdH, [22], has shown that in these systems the increase in the isomer shift caused by hydrogenation depends mainly on the number *i* of hydrogen atoms next to the <sup>57</sup>Fe probes, and that the shift is, at least approximately, proportional to this number. For the shift per hydrogen neighbour, values of  $\Delta S = +0.088$  mm s<sup>-1</sup> and  $+0.091 \text{ mm s}^{-1}$  have been derived for <sup>57</sup>Fe in NiH<sub>r</sub> [13] and PdH<sub>r</sub> [22] respectively. If the present results for  $(Ni_{0.70}Cu_{0.30})H_x$  are interpreted in the same manner, the change in isomer shift of +0.51 mm s<sup>-1</sup> caused by hydrogenation to x = 0.89 corresponds to iron with five or six hydrogen neighbours, *i.e.* to a situation where all or nearly all octahedral interstitial sites next to the iron probes are occupied. For the sample with x = 0.59, the shift is only +0.18 mm s<sup>-1</sup>, corresponding to iron with an average of only two neighbours, much less than the average 3.5 neighbours expected for a random occupation of interstitial sites in the f.c.c. lattice at x = 0.59. This shows that the hydrogen has a tendency to avoid sites next to iron, but in  $(Ni_{0.70}Cu_{0.30})H_r$  the influence of the repulsive iron-hydrogen interaction is smaller than in pure NiH $_{x}$  [12, 13], where iron with close to six hydrogen neighbours has not yet been observed even at x values very close to unity, and hydrogen has been found noticeably to populate the sites next to iron probes only when x exceeds about 0.95.

This interpretation of the isomer shifts is supported by the shape and widths of the Mössbauer lines. The shape of the absorption line of pure  $Ni_{0.70}$   $Cu_{0.30}$  above the Curie temperature is already broadened, non-lorentzian, and slightly asymmetric (Fig. 1), presumably because of the distribution of nickel and copper atoms on the 12 metal sites nearest to the iron probes in the f.c.c. lattice. The Mössbauer pattern of  $(Ni_{0.70}Cu_{0.30})H_{0.59}$  differs in shape from that of the unloaded alloy and is substantially broader, indicating a distribution of hydrogen configurations in the vicinity of the Mössbauer atoms. The spectrum of  $(Ni_{0.70}Cu_{0.30})H_{0.89}$  is again narrower than that of  $(Ni_{0.70}Cu_{0.30})H_{0.59}$ , but still broader than that of the unloaded alloy. Together with the large isomer shift, this indicates that in this case mainly iron with five and six hydrogen neighbours is present.

## 3.2. Temperature dependence of the spectra of $Ni_{0.70}Cu_{0.30}$ and its hydride

The temperature dependences of the Mössbauer spectra were measured for the unloaded  $Ni_{0.70}Cu_{0.30}$  alloy and for a sample of  $(Ni_{0.70}Cu_{0.30})H_{0.66}$ prepared electrochemically. The spectra of the unloaded sample (Fig. 2) exhibit a magnetic hyperfine splitting with lines that are moderately broadened by a distribution of hyperfine fields. The mean hyperfine fields and centre shifts are shown in Fig. 3 as a function of temperature. The magnetic



Fig. 2. <sup>57</sup>Fe Mössbauer spectra of the hydrogen-free Ni<sub>0.70</sub>Cu<sub>0.30</sub> alloy measured at different temperatures with the source of <sup>57</sup>Co in rhodium at 300 K.

hyperfine splitting collapses near 300 K, in good agreement with magnetic measurements [1, 5]. The temperature dependence of the centre shift could be fitted by a Debye model curve for the second-order Doppler shift [21] with a Debye temperature of  $\theta_{\rm D} = 428$  K. Relative to dilute <sup>57</sup>Fe in pure nickel, the resonance in Ni<sub>0.70</sub>Cu<sub>0.30</sub> is shifted by 0.02 mm s<sup>-1</sup> towards higher velocities. This result is in good agreement with the shifts observed by Window *et al.* [14] for Ni–Cu alloys. The mean hyperfine fields at low temperatures and the width of the distribution of hyperfine fields are also in good agreement with the results obtained by these authors for Ni<sub>0.70</sub> Cu<sub>0.30</sub> containing 1 at.% Fe.

The mean centre shift of  $(Ni_{0.70}Cu_{0.30})H_{0.66}$  is more positive by about 0.14 mm s<sup>-1</sup> than that of the unloaded alloy. Up to 200 K its temperature dependence can be explained by the second-order Doppler shift (Fig. 4). Above 200 K, the centre shift begins to decrease more rapidly, showing that the sample begins to lose hydrogen within the timespan of one or a few days required to measure a Mössbauer spectrum. Consequently, this decrease in the isomer shift is irreversible and the shift remains reduced in spectra measured subsequently at 100 K (Fig. 4). The magnetic  $\alpha$  phase first reappeared, with an intensity of 18% of the area, in a spectrum measured at 100 K after the sample had been at 240 K for a day. The isomer shift of the reappearing magnetic pattern is practically the same as before hydrogenation,



Fig. 3. Temperature dependence of the mean magnetic hyperfine fields  $\bar{B}_{hf}$  and the mean centre shifts S with respect to the source of <sup>57</sup>Co in rhodium at 300 K for hydrogen-free Ni<sub>0.70</sub>Cu<sub>0.30</sub>. The curve fitted to the centre shifts corresponds to the Debye model with  $\theta_D = 428$  K. Triangles represent the hyperfine field and the centre shift of the  $\alpha$  phase after its reappearance on keeping the hydride at 240 K for a day.



Fig. 4. Centre shifts of  $(Ni_{0.70}Cu_{0.30})H_x$  with an initial hydrogen content of x = 0.66, measured with a source of <sup>57</sup>Co in rhodium at 300 K ( $\bigcirc$ );  $\bullet$  centre shift measured at 100 K after the sample had lost some hydrogen during the preceding measurement above 200 K; the respective data points are connected by dashed lines. The fully drawn curve represents the centre shift for the unloaded alloy (see Fig. 3).

and the same is true for the magnetic hyperfine field (Fig. 3). The small amount of hydrogen that is expected to be dissolved in the  $\alpha$  phase [4, 9] thus has no noticeable influence on the Mössbauer pattern. The remaining isomer shift for the iron in the non-magnetic  $\beta$  phase (+0.02 mm s<sup>-1</sup> with respect to the unloaded alloy at 100 K) is also very small. Outgassing yielded a mean hydrogen content of  $\tilde{x} = 0.21$  for this sample, which means that x should be somewhat larger in the non-magnetic  $\beta$  phase, the exact value depending on the hydrogen content of the  $\alpha$  phase fraction. The small shift observed for the  $\beta$  phase at this concentration again reflects the repulsive interaction between the iron and the hydrogen, which at this low hydrogen concentration virtually prevents hydrogen from occupying sites next to the iron.

# 4. Conclusions

The results of this work show that iron probes in hydrides of Ni-Cu alloys have a repulsive interaction with the hydrogen, but the iron becomes surrounded with hydrogen more easily than in the hydrides of pure nickel. In interpreting these findings, one should bear in mind that there is a tendency for short-range order in Ni-Cu alloys [14], which results in the formation of nickel-rich microclusters. The iron is expected to behave much like nickel and will therefore preferentially be surrounded by nickel atoms. At low and moderate hydrogen concentrations, the hydrogen is expected to prefer interstitial sites that have predominantly nickel neighbours and avoid sites with many copper neighbours as well as sites next to iron. At higher hydrogen contents, the interstitials appear to prefer sites with an iron neighbour to sites with several copper neighbours, with the result that in hydrides of Ni-Cu alloys the iron probes have more hydrogen neighbours than in pure nickel hydride at equal overall hydrogen-to-metal ratios. Details of this behaviour should also depend on the degree of short-range order in the Ni-Cu alloys, and hence on the cooling rate of these,

Mössbauer spectroscopy can thus be used as a sensitive tool to study details of the microstructure of the hydrides of Ni-Cu alloys. A systematic investigation, in which both the copper concentration and the hydrogen content are varied, is expected to yield a better understanding of the hydrogen distribution in these systems.

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