[197]Au Mössbauer study of the hydrides of Ni–Au alloys

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Abstract

Hydrides of $Ni_{1-y}Au_y$ alloys with $y = 0.01$, 0.10 and 0.20 were prepared electrolytically or under high pressures of molecular hydrogen and studied by Mössbauer spectroscopy with 77.3 keV γ rays of [197]Au. At a pressure of 7 GPa, hydrogen-to-metal ratios close to unity could be obtained, while using electrochemical loading or at hydrogen pressures around 1 GPa, only interstitial sites without gold neighbours appeared to be occupied, although the ferromagnetism was already completely suppressed. The isomer shifts of the Mössbauer patterns were found to depend on both long range influences of hydrogen and on direct effects of nearest hydrogen neighbours.

1. Introduction

Hydrides of nickel–copper alloys can be obtained easily both electrochemically or under high pressures of molecular hydrogen and have been studied extensively [1–10]. Hydride formation in the $Ni_{1-y}Au_y$ system, however, has so far not been investigated. Homogeneous $Ni_{1-y}Au_y$ alloys are known to remain ferromagnetic up to gold concentrations of about 50 at.% [11–13]. As for Ni–Cu alloys, the incorporation of interstitial hydrogen in the lattices of $Ni_{1-y}Au_y$ alloys is expected to suppress the ferromagnetism by filling the empty electron states in the 3d band of nickel.

A convenient method of studying $Ni_{1-y}Au_y$ hydrides is Mössbauer spectroscopy with the 77.3 keV transition in [197]Au. Compared, for instance, with the use of [57]Fe Mössbauer spectroscopy for studying hydrides of Ni–Cu alloys [10], [197]Au resonance in the present case has the advantage that the gold is an essential component of the lattice rather than a dilute Mössbauer probe whose local environment may be affected by probe–hydrogen interactions. The sensitivity of Mössbauer spectroscopy to the local hydrogen environment of the Mössbauer atoms [10, 14–17] opens up a way of investigating the hydrogen distribution in alloy systems, in addition to yielding

information on magnetic properties. In hydrides of palladium containing 1 at.% [197]Au, for instance, the hydrogen has been shown to avoid interstitial sites with gold neighbours up to hydrogen-to-metal ratios near $x = 0.95$ [14, 15].

Pure $Ni_{1-y}Au_y$ alloys have already been studied by Mössbauer spectroscopy [18–22], which yielded information on the magnetic properties and showed that the isomer shift varies linearly with gold content y between the limiting values for dilute gold in nickel and for pure gold. In this paper we report the first results of a [197]Au Mössbauer study of hydrides of $Ni_{1-y}Au_y$ alloys prepared either electrochemically or under high pressures of molecular hydrogen.

2. Experimental details

Nickel and gold form a continuous series of f.c.c. solid solutions above 815 °C [23, 24]. At lower temperatures, a wide miscibility gap opens, but homogeneous alloys within the two-phase region can be obtained by rapid quenching from above 900 °C [12]. The $Ni_{1-y}Au_y$ alloys with $y = 0.01$, 0.10, and 0.20 used in the present experiments were arc melted in an argon atmosphere and rolled to foils of a thickness between 15 and 40 μm. These foils were sealed in quartz tubes filled with helium gas, annealed between 1000 and 1050 °C for about 24 h and then quenched by dropping the quartz tubes into cold water.

The foils were then loaded with hydrogen electrolytically or under high pressures of molecular hydrogen. The cathodic charging was done at ambient temperature in 0.5 n H_2SO_4 with 0.2 g l^{-1} of thiourea as a promoting agent [25] and at a current density of 20 mA cm^{-2}. After electrolysis, the samples were immediately immersed in liquid N_2. Hydrogen gas pressures up to 1.1 GPa could be reached in a piston-type pressure cell [26–28]. Hydrogenations at 7 GPa were performed in a high pressure cell using manganese hydride as a hydrogen donor [29]. These cells were cooled with liquid N_2 before the pressure was released and the samples were removed. The samples were then stored in liquid N_2 until they were transferred into the Mössbauer cryostat without warming above liquid N_2 temperature. Magnetization and resistance measurements were used to monitor the hydrogen uptake during the cathodic charging and in the piston cell respectively. At all gold concentrations studied at room temperature, ferromagnetism could be suppressed completely by all charging methods used.

The hydrogen content of the samples was determined after the Mössbauer experiments by outgassing into a calibrated volume. During the transfer into the outgassing apparatus, care was taken to keep the samples at liquid nitrogen temperature in order to avoid premature losses of hydrogen. The accuracy with which the hydrogen-to-metal ratio x could be determined was about 0.02, except for one case ($Ni_{0.80}Au_{0.20}H_{0.8}$) in which the sample was

very small and contaminated with debris from the high pressure cell, from which we estimate an uncertainty of 0.2. For some of the hydrides, the lattice parameters were measured at 100 K by X-ray diffraction using Cu Kα radiation. The X-ray patterns showed that the hydrides were single-phase and had retained the f.c.c. structure.

The Mössbauer measurements were all performed with source and absorber at 4.2 K. The sources were made by irradiating isotopically enriched metallic ^{196}Pt with thermal neutrons in the Munich Research Reactor. In the β^- decay of ^{197}Pt with a half-life of 18 h, the 77.3 keV first excited state of ^{197}Au with spin $\frac{1}{2}^+$ is populated. Under the influence of a magnetic hyperfine interaction, the mixed M1/E2 Mössbauer transition to the $\frac{3}{2}^-$ ground state splits into eight hyperfine lines. Since the nuclear g-factor of the $\frac{1}{2}^+$ state is much larger than that of the $\frac{3}{2}^+$ state, these eight lines form two groups of four lines each [30, 31]. The magnetic hyperfine fields in Ni–Au alloys are too small for the resulting hyperfine patterns to be fully resolved [20]. The spectra of the unhydrogenated alloys therefore appear to consist of two peaks only. In the least square fits of such spectra with appropriate superpositions of eight lorentzian lines, the nuclear parameters derived from the hyperfine splitting of ^{197}Au in iron [30, 31] were used.

3. Results

Some of the Mössbauer spectra of Ni–Au alloys and their hydrides are shown in Fig. 1. A summary of the results is given in Table 1. The hyperfine fields and isomer shifts obtained for the unloaded alloys are in good agreement with previous results [19, 20]. The isomer shifts decrease linearly with increasing gold content y of the alloys. With increasing gold concentration the lines become broader, presumably because there is a distribution of hyperfine fields, isomer shifts, and electric quadrupole interactions.

The hydrogenated samples all exhibit single peaks, albeit with broadened lines, particularly at the higher hydrogen-to-metal ratios (Fig. 1 and Table 1). The absence of magnetic hyperfine splittings shows that the hydrides do not order magnetically even at liquid helium temperature, and that, within the limits of detectability, even the samples loaded electrolytically or at pressures near 1.1 GPa are already single-phase hydrides.

All hydrides exhibit smaller isomer shifts than the respective unhydrogenated alloys. Hydrogenation thus reduces the electron density at the gold nuclei, as has been observed for gold in all metal–hydrogen systems studied so far [14, 15, 32, 33]. In Fig. 2 the hydrogen-induced changes in the isomer shift, *i.e.* the differences between the shifts of the hydrides and the shift of the respective unhydrogenated alloy, are plotted as a function of the hydrogen-to-metal ratio.
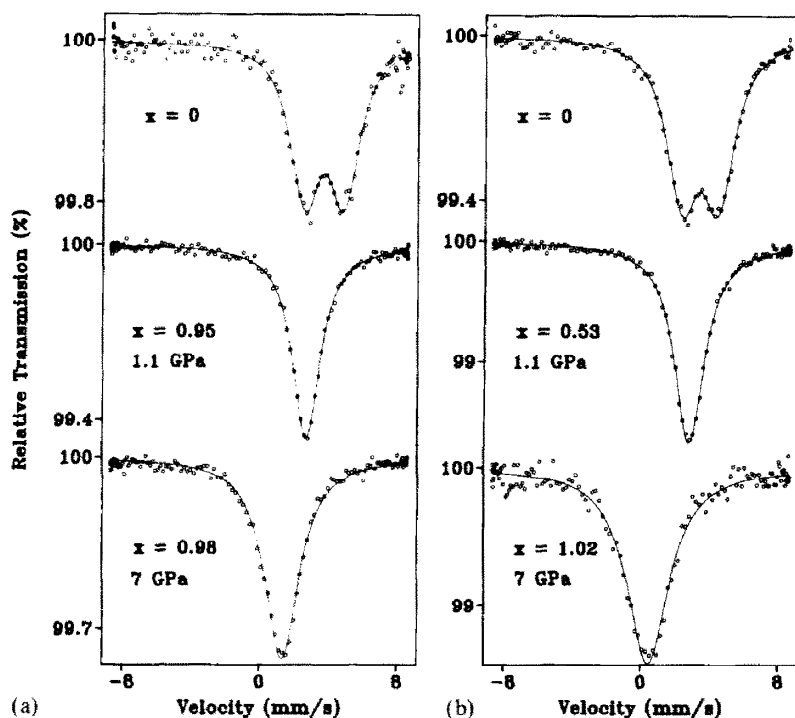
Fig. 1. ^{197}Au Mössbauer spectra of hydrides of (a) $Ni_{0.99}Au_{0.01}$ and (b) $Ni_{0.90}Au_{0.10}$ with different hydrogen-to-metal ratios x measured at 4.2 K with a source of ^{197}Pt in ^{196}Pt metal.

TABLE 1

Summary of results obtained on hydrides of $Ni_{1-y}Au_y$ alloys with different hydrogen-to-metal ratios x

y	x	a_0 (Å)	S (mm s^{-1})	B_{hf} (T)	W (mm s^{-1})	Conditions of hydrogenation
0.001	0	3.526	$+3.74 \pm 0.02$	26.9 ± 0.4	1.93 ± 0.07	
	0.95		$+2.72 \pm 0.01$	—	1.96 ± 0.03	1.1 GPa, 25 °C, 170 h
	0.98	3.742	$+1.34 \pm 0.01$	—	2.41 ± 0.04	7 GPa, 250 °C, 24 h
0.10	0.0	3.596	$+3.38 \pm 0.01$	24.9 ± 0.3	2.07 ± 0.04	
	0.53		$+2.81 \pm 0.01$	—	2.17 ± 0.04	electrolysis, 10 h
	0.53		$+2.82 \pm 0.01$	—	2.21 ± 0.05	1.1 GPa, 25 °C, 170 h
	1.02	3.763	$+0.45 \pm 0.03$	-	2.94 ± 0.09	7 GPa, 250 °C, 24 h
0.20	0	3.653	$+2.79 \pm 0.01$	18.5 ± 0.3	2.30 ± 0.03	
	0.24		$+2.58 \pm 0.01$	-	2.38 ± 0.01	0.8 GPa, 25 °C, 170 h
	0.25		$+2.60 \pm 0.01$	—	2.31 ± 0.01	1.1 GPa, 25 °C, 170 h
	0.8	3.794	$+0.26 \pm 0.01$	—	3.02 ± 0.05	7 GPa, 250 °C, 24 h

The lattice parameters a_0 were measured at 100 K. S is the isomer shift with respect to the platinum metal source, B_{hf} the magnetic hyperfine field, and W the full width at half maximum of the Mössbauer lines.
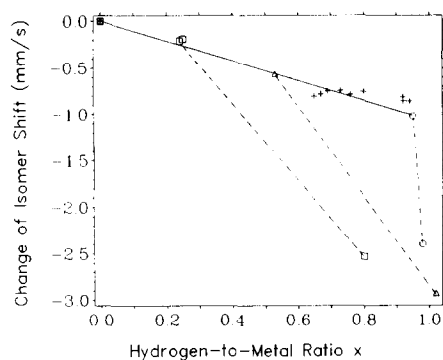
Fig. 2. Change in the isomer shift of the [197]Au Mössbauer resonance caused by hydrogenation of $Ni_{1-y}Au_y$ alloys with $y = 0.01$ ($\bigcirc$), 0.10 ($\triangle$) and 0.20 ($\square$). For comparison, the changes in the [197]Au isomer shifts caused by hydrogenation of $Pd_{0.99}Au_{0.01}$ alloys [14, 15] are also shown (+). The fully drawn straight line is considered as describing the isomer shift for gold atoms without hydrogen neighbours, the deviations from this line at high hydrogen contents (– – –) are ascribed to the direct interaction between gold atoms and their nearest hydrogen neighbours.

4. Discussion

The hydrogen uptake of the alloys during electrolytic charging or at hydrogen pressures around 1 GPa was found to decrease rapidly with increasing gold content but nevertheless was sufficient to suppress the ferromagnetism in all cases. The hydrogen-to-metal ratios reached under these conditions suggest that only those octahedral interstitial sites in the f.c.c. lattice are occupied which do not have any gold among the six nearest metal atoms: In the absence of short-range order, 94% of the interstitial sites are expected to meet this requirement in $Ni_{0.99}Au_{0.01}$, compared with 53% in $Ni_{0.90}Au_{0.10}$ and 26% in $Ni_{0.80}Au_{0.20}$. If only these sites are occupied, one thus expects values of x of 0.94, 0.53 and 0.26, in excellent agreement with the hydrogen-to-metal ratios actually observed (Table 1).

The changes in the isomer shift brought about by hydrogenation at moderate pressures or by electrolysis support such a view. They decrease linearly with increasing hydrogen content (Fig. 2) by about -1.0 mm s^{-1} between $x = 0$ and $x = 0.95$. In hydrides of $Pd_{0.99}Au_{0.01}$ alloys a similar behaviour was observed [14, 15], as can be seen from Fig. 2, which also shows the results for the Pd–H system. The interpretation given to the results for gold in PdH_x has been [14, 15] that the observed changes are brought about by long-range effects only, while hydrogen does not occupy interstices next to gold atoms owing to a strongly repulsive interaction with the gold. In palladium hydride this situation persists up to the highest hydrogen-to-metal ratios ($x \approx 0.95$) that could be obtained by cathodic charging [14, 15]. The same explanation now appears appropriate for the hydrides of $Ni_{1-y}Au_y$ alloys. Figure 2 shows that the long-range effect depends linearly on the hydrogen-to-metal ratio and has practically the same magnitude as in PdH_x,

but it is difficult to say to what extent it arises from lattice expansion and to what extent it is due to intrinsic changes in the electronic structure.

At the high hydrogen contents achieved by loading at 7 GPa, interstitial sites with gold neighbours must be occupied. One therefore expects that direct interactions between the gold and its hydrogen neighbours contribute to the isomer shift. The steep decrease in the isomer shift at high hydrogen contents can be explained in this way. It is most drastic in $(Ni_{0.99}Au_{0.01})H_x$, where going from $x = 0.95$ to $x = 1.00$ causes a change that is larger than the change caused by going from $x = 0$ to $x = 0.95$ (Fig. 2). When hydrogen can occupy sites next to gold atoms, a distribution of different numbers of nearest hydrogen neighbours is expected, with the electron density and isomer shift the smaller the more hydrogen atoms there are next to a gold atom. This distribution explains the relatively large linewidths at the high hydrogen-to-metal ratios, while the lines remain rather narrow at the lower hydrogen contents (Table 1). It should be noted that for ^{197}Au in PdH_x, such effects of nearest neighbours have also been observed, but only when sources of ^{197}Pt in PdH_x were studied. In these experiments, the hydrogen can occupy sites next to platinum atoms and will remain there when the ^{197}Pt decays to ^{197}Au at 4.2 K. It is difficult to tell how many nearest hydrogen neighbours the gold atoms in the $(Ni_{1-y}Au_y)H_x$ samples loaded at 7 GPa have on average, but the linewidth argument indicates that the gold atoms still have incompletely filled nearest neighbour hydrogen shells even at the highest hydrogen contents attained so far.

Acknowledgments

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