

Hydrogen Uptake of Palladium-Gold Alloys Studied by ^{197}Au Mössbauer Spectroscopy*

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Hydrides of $\text{Pd}_{0.99}\text{Au}_{0.01}$ and $\text{Pd}_{0.90}\text{Au}_{0.10}$ alloys were prepared electrolytically or under pressures of hydrogen gas up to 7.2 GPa and studied by Mössbauer spectroscopy with the 77 keV γ -rays of ^{197}Au . The observed isomer shifts show that in $\text{Pd}_{0.99}\text{Au}_{0.01}\text{H}_x$ the interstitial sites next to the gold atoms become occupied by hydrogen only at $x \gtrsim 0.95$. The isomer shifts observed at $x \lesssim 0.95$ are attributed to volume expansion and long range electronic effects. This interpretation is supported by the volume dependence of the ^{197}Au isomer shift in $\text{Pd}_{0.99}\text{Au}_{0.01}\text{H}_x$ measured at pressures up to 6 GPa. In $\text{Pd}_{0.90}\text{Au}_{0.10}\text{H}_x$, hydrogenation at temperatures around 325°C was found to cause the formation of gold-rich zones.

1. Introduction

Mössbauer spectroscopy with the 77 keV gamma rays of ^{197}Au was used in the past [1, 2] to study the hydrogen distribution near substitutional gold and platinum atoms in PdH_x . The dependence of the isomer shift on the hydrogen content showed that gold repels hydrogen from its nearest neighbour interstitial sites up to hydrogen-to-metal ratios of $x \cong 0.92$, the highest that could be reached by electrolytic loading. As a consequence, the isomer shift hardly changes within the β phase region for $0.65 \lesssim x \lesssim 0.92$. Platinum solutes in palladium hydride were studied in ^{197}Au Mössbauer experiments using sources of ^{197}Pt in PdH_x [1, 2]. These experiments

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showed that Pt in PdH_x still has virtually no nearest hydrogen neighbours at $x \approx 0.65$, while for $x \gtrsim 0.7$ the occupancy of sites next to Pt rapidly increases with x . As x approaches unity, hydrogen is expected to occupy also sites next to gold atoms. Such high hydrogen contents were now obtained under pressures of H_2 gas up to 7.2 GPa. Moreover, the Mössbauer studies have been extended to gold concentrations of 10 at.%, since recent experiments with $\text{Ni}_{1-y}\text{Au}_y\text{H}_x$ had shown that in this system the occupancy of interstitial sites next to gold also depends critically on the gold concentration y [3].

The isomer shifts observed for gold without nearest hydrogen neighbours have been attributed mainly to the hydrogen-induced volume expansion [1–3]. To substantiate this view, the volume dependence of the isomer shift of ^{197}Au in $\beta\text{-PdH}_x$ at constant hydrogen content was now determined by measurements at quasihydrostatic pressures up to about 6 GPa.

2. Experimental details

$\text{Pd}_{1-y}\text{Au}_y$ alloys were arc melted and rolled to foils of 10 to 200 μm thickness. These were loaded with hydrogen either electrolytically as described previously [1, 2] or under high pressures of hydrogen gas. For the gas phase loading two different techniques were used: Hydrogen pressures up to 2.7 GPa were reached in piston-type pressure cells [4, 5]. Pressures up to 7.2 GPa were obtained in high pressure cells containing AlH_3 as a hydrogen donor [6]. The donor hydride was allowed to decompose at 230°C and 1.7 GPa for five minutes. Then the loading temperature was set and the pressure was raised to the chosen value. The loading temperature was 325°C in most of these loadings. Alternatively, the cell was rapidly cooled to 100°C before the pressure was raised to the final value. In all cases, the cells were cooled with liquid N_2 before the pressure was released and the samples were removed and stored in liquid N_2 until they were transferred into the Mössbauer cryostat without intermediate warming. All Mössbauer experiments were performed at 4.2 K with sources made by neutron irradiation of metallic ^{196}Pt . After the Mössbauer measurements, the hydrogen content was determined by outgassing with an accuracy ranging between about 1 and 3%, depending on the size of the samples. Thereafter Mössbauer spectra were again taken to reveal any metallurgical changes induced by the hydrogenation. In most cases, the lattice constants and superconducting transition temperatures of the samples were also measured. They were found to be in good agreement with previous results [7].

The change of isomer shift as a function of pressure was measured at 4.2 K using hydrides made electrolytically and a high pressure cell with boron carbide or alumina anvils [8]. The pressures within these cells were determined with a superconducting lead manometer [9].

3. Results and discussion

3.1. Concentration dependence of the isomer shifts in $\text{Pd}_{0.99}\text{Au}_{0.01}\text{H}_x$

The results for $\text{Pd}_{0.99}\text{Au}_{0.01}\text{H}_x$ are summarized in Table 1. In Fig. 1 the hydrogen-induced changes of the isomer shift, $\Delta S(x) = S(x) - S(0)$, are

Table 1. Summary of results obtained on hydrides of Pd_{1-y}Au_y with different hydrogen-to-metal ratios *x*.

<i>x</i>	<i>a</i> ₀ (Å)	<i>S</i> (<i>x</i>) (mm/s)	<i>S</i> (0) (mm/s)	<i>W</i> (<i>x</i>) (mm/s)	<i>W</i> (0) (mm/s)	<i>T</i> _c (K)	Conditions of hydrogenation
<i>Hydrides of Pd_{0.99}Au_{0.01} alloys</i>							
0.00	3.887	1.02 (1)	—	2.05 (4)	—	<1.5	before hydrogenation
0.74	4.044	0.21 (4)	0.95 (2)	2.08 (25)	2.01 (12)	<1.5	0.5 GPa, 325° C, 24 h
0.90	4.068	0.15 (2)	0.96 (1)	2.03 (10)	2.02 (8)	4.8	1.0 GPa, 325° C, 24 h
0.94		0.16 (2)	0.99 (2)	1.94 (9)	1.99 (9)		0.5 GPa, RT, 160 h
0.94		0.07 (2)	0.99 (1)	1.94 (13)	2.04 (8)		2.7 GPa, RT, 22 h
0.95	4.084	−0.01 (2)	0.94 (1)	2.15 (6)	1.99 (7)	6.7	2.1 GPa, 325° C, 24 h
0.95		−0.03 (1)	0.98 (3)	2.16 (7)	1.91 (16)		1.0 GPa, RT, 48 h
0.97		−0.09 (2)	0.98 (1)	2.09 (13)	1.97 (6)		1.7 GPa, RT, 48 h
0.98	4.090	−0.30 (2)	0.90 (2)	2.33 (9)	2.06 (10)	8.5	4.1 GPa, 325° C, 24 h
1.00	4.099	−1.10 (1)	0.86 (2)	2.19 (6)	2.21 (13)	9.0	7.0 GPa, 325° C, 24 h
<i>Hydrides of Pd_{0.90}Au_{0.10} alloys</i>							
0.00	3.899	0.74 (1)	—	2.12 (2)	—	<1.5	before hydrogenation
0.58	4.04	0.01 (1)	0.55 (1)	2.44 (4)	2.55 (6)	<1.5	0.5 GPa, 325° C, 24 h
0.68		−0.24 (1)	0.78 (1)	2.17 (8)	2.18 (4)		2.7 GPa, RT, 22 h
0.69		−0.29 (1)	0.77 (1)	2.18 (7)	2.12 (5)		1.7 GPa, RT, 48 h
0.72		−0.40 (1)	0.78 (1)	2.15 (8)	2.03 (5)		0.5 GPa, RT, 160 h
0.73		−0.54 (1)	0.75 (1)	2.14 (8)	2.02 (8)		1.0 GPa, RT, 48 h
0.74	4.059	−0.38 (1)	0.49 (1)	2.40 (4)	2.54 (4)	<1.5	1.0 GPa, 325° C, 24 h
0.77	4.072	−0.52 (1)	0.41 (1)	2.43 (2)	2.69 (5)	2.0	2.1 GPa, 325° C, 24 h
0.86	4.086	−0.76 (1)	−0.18 (1)	2.43 (4)	2.90 (2)	5.3	4.1 GPa, 325° C, 24 h
0.87	4.083	−0.98 (1)	0.63 (1)	2.34 (4)	2.22 (8)	4.6	4.1 GPa, 100° C, 24 h
0.88	4.095	−0.89 (1)	−0.17 (1)	2.45 (4)	3.11 (7)	6.2	7.2 GPa, 325° C, 24 h

The lattice parameters *a*₀ were measured at 100 K. *S*(*x*) and *S*(0) are the isomer shifts with respect to a Pt metal source for the hydrogenated and for the outgassed samples, respectively. *W*(*x*) and *W*(0) are the corresponding full widths at half maximum of the Mössbauer lines, and *T*_c is the superconducting transition temperature. Errors are given in parentheses.

shown together with data obtained previously with electrolytically loaded samples [1, 2]. The isomer shift for absorbers of Pd_{0.99}Au_{0.01}H_{*x*} is nearly independent of the hydrogen content within the β phase region up to *x* = 0.95. Above this concentration, a steep decrease of the isomer shift sets in. Smaller isomer shifts of the ¹⁹⁷Au Mössbauer resonance correspond to smaller *s* electron densities at the gold nuclei. In all transition elements studied so far as solutes in PdH_{*x*} as well as the isostructural NiH_{*x*}, hydrogen neighbours have been found to cause a decrease of the electron density at the probe nuclei [1–3, 10–12], since *s* electrons are withdrawn from the metal atoms towards the hydrogen neighbours [13, 14]. The Mössbauer results show that virtually no hydrogen occupies sites next to Au in PdH_{*x*} as long as interstitial sites having only Pd neighbours are available. At a gold concentration of *y* = 0.01, about 6% of the interstitial sites have at

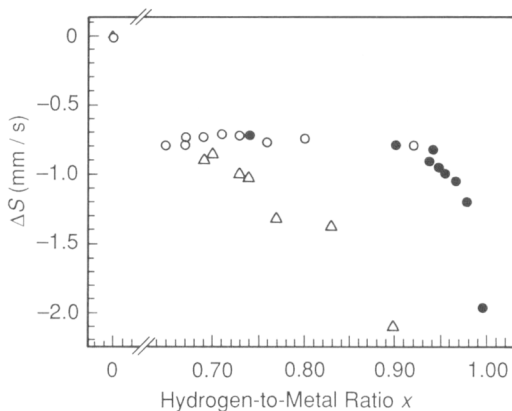


Fig. 1. Hydrogen-induced changes of the Mössbauer isomer shifts of absorbers of $\text{Pd}_{0.99}\text{Au}_{0.01}\text{H}_x$ (circles) and of sources of $\text{Pd}_{0.98}\text{Pt}_{0.02}\text{H}_x$ (triangles). Open symbols represent previous measurements [1, 2], filled ones results obtained in this work. The isomer shift scale has been chosen in such a way that for both source and absorber experiments decreasing shifts correspond to decreasing electron density at the gold nuclei.

least one nearest gold neighbour. Thus hydrogen cannot but occupy sites next to gold for $x \gtrsim 0.94$, causing the observed steep decrease of the electron density at the Au nuclei. Because of the uncertainty of about 2% in the determination of x , it is not certain that the lowest isomer shift value observed, $S = -1.10$ mm/s at nominally $x = 1.00$ (Table 1), corresponds to gold with six nearest hydrogen neighbours, but presumably it comes close to this limit. This view is supported by ^{197}Au Mössbauer measurements [1, 2] with sources of ^{197}Pt in PdH_x , which yield information on the hydrogen environment of Pt in PdH_x , since at 4.2 K the hydrogen distribution does not rearrange before the Mössbauer γ rays are emitted within about 2 ns after the nuclear transformation of ^{197}Pt to ^{197}Au . The isomer shifts observed in the source experiments show (Fig. 1) that the electron density at Au nuclei with the hydrogen environment typical for Pt in PdH_x decreases monotonically with x above $x \approx 0.7$. At $x = 0.9$ it already reaches about the value (Fig. 1) observed in the absorber experiments at nominally $x = 1.00$. This shows that Pt repels hydrogen less strongly than gold, and supports the expectation that the source and absorber experiments should yield the same isomer shifts when all sites around the gold atoms become occupied.

3.2. Pressure dependence of the isomer shift in $\text{Pd}_{0.99}\text{Au}_{0.01}\text{H}_x$

The isomer shift of about -0.7 mm/s between ^{197}Au in PdH_x at the lower limit of β phase at $x \approx 0.6$ and ^{197}Au in hydrogen-free Pd has been attributed [1, 2] to the decrease of s electron density going along with volume

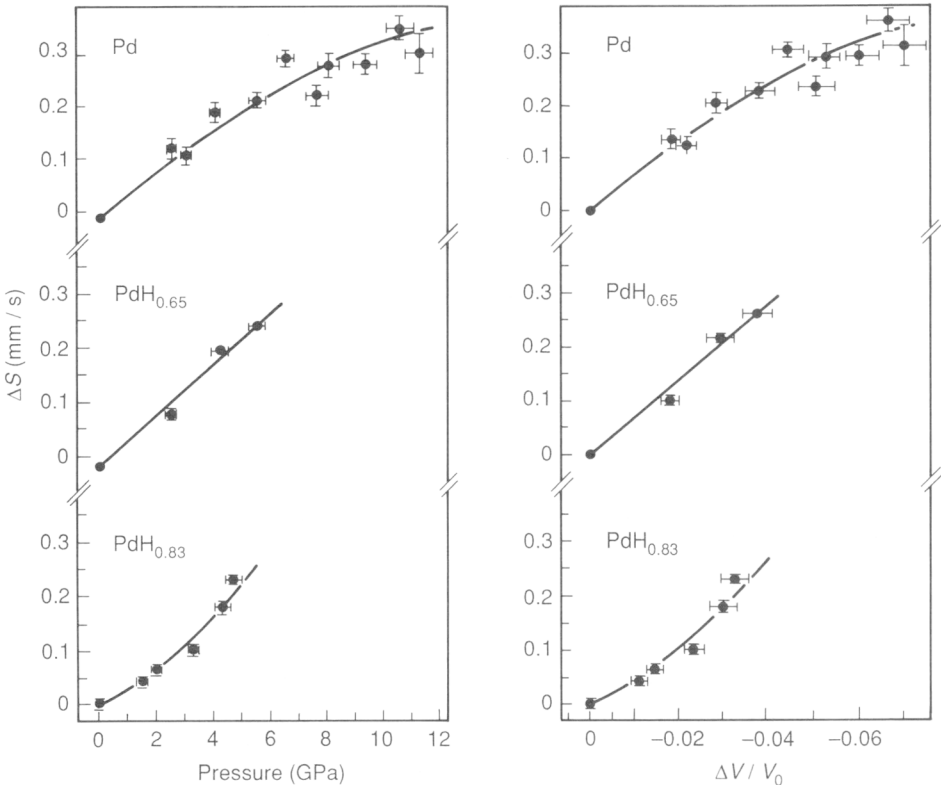


Fig. 2. Increase of the Mössbauer isomer shifts of ^{197}Au in $\text{Pd}_{0.99}\text{Au}_{0.01}$, $\text{Pd}_{0.99}\text{Au}_{0.01}\text{H}_{0.65}$ and $\text{Pd}_{0.99}\text{Au}_{0.01}\text{H}_{0.83}$ under pressure and as a function of the corresponding volume reduction. The results for Au in pure Pd are in good agreement with previous data [1, 2].

expansion and to long-range electronic effects. Surprisingly, however, the hydrogen-induced volume expansion within the β phase leaves the isomer shift practically unchanged (Fig. 1). In this context, it was of interest to measure the volume dependence of the isomer shift of Au in $\beta\text{-PdH}_x$ by applying high pressure. The increase of the isomer shift (Fig. 2) and hence the electron density at the gold nuclei under pressure was found to be reversible, somewhat nonlinear in pure Pd and $\text{PdH}_{0.83}$, but generally of similar magnitude in pure Pd and in PdH_x . The pressure dependence of the isomer shifts was converted into the volume dependence using the Birch-Murnaghan equation of state [15] with the coefficients for palladium and palladium hydride given by Tkacz *et al.* [16]. Although the nonlinearity of the dependence of the isomer shift on the volume change (Fig. 2) renders an extrapolation from the pressure induced compression to the hydrogen-

induced lattice expansion somewhat uncertain, one concludes that the 10% volume expansion between α -Pd and β -PdH_{0.6} [17] can explain the corresponding decrease of the isomer shift by 0.7 mm/s. The further 6% volume increase in β -PdH_x between $x = 0.06$ and $x = 1.0$ would suggest a further decrease of the isomer shift by about 0.4 mm/s, while actually the isomer shift within the β phase remains practically constant until hydrogen begins to occupy sites next to gold at $x \gtrsim 0.95$ (Fig. 1). This suggests that within the β phase the effect of volume expansion is compensated by an increase of the electron density at the gold nuclei due to long-range electronic effects presumably caused by the filling of the *s* band with increasing hydrogen content. This effect is expected to be stronger within the β phase, where the *d* states are already filled, than at lower hydrogen contents, where both empty *d* and *s* states are still available.

3.3 The system Pd_{0.90}Au_{0.10}H_x

While the samples of Pd_{0.99}Au_{0.01}H_x on loading and outgassing always exhibited at least to a good approximation the same isomer shifts as before loading (Table 1), Pd_{0.90}Au_{0.10} alloys hydrogenated at 325°C always yielded a substantially decreased isomer shift after outgassing. Assuming a roughly linear dependence of the isomer shift in Pd_{1-y}Au_y alloys on *y*, the isomer shift of about -0.2 mm/s (Table 1) found for samples outgassed after loading at pressures above 4 GPa and 325°C shows that the gold in the outgassed specimens is in an environment with a mean composition of Pd_{0.5}Au_{0.5}. Such unmixing does not occur in samples hydrogenated at room temperature (Table 1). It was also not observed when the alloy was heated under pressure to 325°C in a nitrogen atmosphere. Hydrogenation at 100°C and 4.1 GPa was found to give rise to minor unmixing only (Table 1). The unmixing thus is induced by the hydrogen, but only at elevated temperatures. The formation of the gold-rich zones goes along with a substantial broadening of the Mössbauer lines (Table 1), presumably because the gold atoms experience a wider spread of nearest neighbour Au and Pd atoms than in the homogeneous Pd_{0.90}Au_{0.10} alloys. The hydrides typically have smaller linewidths than the outgassed samples, presumably since zones with higher gold enrichment, which yield smaller isomer shifts owing to the high gold content, contain less hydrogen [18] and therefore exhibit a smaller hydrogen-induced decrease of the isomer shift compared to zones poorer in gold, which take up more hydrogen.

The present Mössbauer data do not reveal whether the gold-rich zones are incoherent precipitates or whether they form coherently. Coherent zones appear probable since X-ray diffraction did not reveal the presence of a second phase in the loaded samples. In a previous study of the hydrides of Pd_{1-y}Au_y alloys [7], neither the formation of gold-rich precipitates nor hydrogen-induced atomic ordering like in the Pd-Cu-H and Pd-Ag-H

systems [19, 20] has been observed. Whether or how the unmixing observed now is related to the short-range order and superstructure ordering reported for the Pd-Au system [21–23], should be clarified in future work.

In $\text{Pd}_{0.90}\text{Au}_{0.10}\text{H}_x$ specimens loaded at ambient temperature to $x \approx 0.7$, one observes larger hydrogen-induced changes of the isomer shift than in $\text{Pd}_{0.99}\text{Au}_{0.01}\text{H}_x$ at the same hydrogen content (Table 1), presumably because the higher gold concentration requires that hydrogen occupies interstitial sites with gold neighbours already at relatively low hydrogen-to-metal ratios. Thus in a homogeneous $\text{Pd}_{0.90}\text{Au}_{0.10}$ alloy one expects the interstitial sites with only Pd neighbours to accommodate hydrogen only up to $x = 0.53$. It is interesting to note that hydrogen contents sufficient to enforce occupation of sites with gold neighbours can be reached easier at higher gold concentrations than at lower ones. A similar behaviour was previously observed in the $\text{Ni}_{1-y}\text{Au}_y\text{H}_x$ system [3].

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