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Mössbauer experiments with ^{57}Fe and ^{57}Co in palladium hydride: Diffusional relaxation and high hydrogen concentrations

M. Baier[a], G.F. Schneider[a,*], F.E. Wagner[a], I. Dugandžić[b], H.J. Bauer[b], V.E. Antonov[c], T.E. Antonova[c]

[a]Physik-Department, Technische Universität München, D-85747 Garching, Germany
[b]Sektion Physik, Ludwig-Maximilians-Universität, D-80539 München, Germany
[c]Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, District 142432, Russia

Abstract

Palladium hydrides with hydrogen-to-metal ratios close to unity were prepared under hydrogen pressures up to 7 GPa and studied by ^{57}Fe Mössbauer spectroscopy. In highly loaded absorbers the iron probes were found to be practically always surrounded by six hydrogen neighbours despite the repulsive iron–hydrogen interaction. In the emission spectrum of a source of ^{57}Co in PdH_x the diffusional relaxation of the typical hydrogen environment of cobalt to that of iron was observed between 200 and 300 K.

Keywords: Palladium hydrides; Mössbauer spectroscopy; Diffusional relaxation

1. Introduction

Mössbauer studies of absorbers of ^{57}Fe in palladium hydride and of sources of ^{57}Co in this matrix have revealed a repulsive interaction between the dilute substitutional Fe or Co and the interstitial hydrogen [1]. As a consequence, both Co and Fe in PdH_x have fewer than average nearest hydrogen neighbours. By electrolytic hydrogenation it has been impossible to exceed hydrogen-to-metal ratios of $x \approx 0.97$. For this reason, the state where practically all iron probes have the maximum possible number of six nearest hydrogen neighbours could not be reached in the past [1]. By applying a pressure of 7 GPa of molecular hydrogen, such highly loaded samples of palladium hydride have now been obtained.

The repulsive probe–hydrogen interaction is more pronounced for Fe than for Co [1]. At low temperatures, where the hydrogen distribution is virtually static on the timescale of the lifetime of the 14.4 keV state of 140 ns, the emission spectra of sources of ^{57}Co in PdH_x therefore differ from the spectra of ^{57}Fe:PdH_x absorbers. When hydrogen diffusion becomes more rapid at higher temperatures, the hydrogen environment of Co will transform to that of Fe before the emission of the 14.4 keV gamma quanta, and the difference between source and absorber spectra will vanish. The transition between the quasistatic and the fast relaxation regime is expected to occur between 200 and 300 K, where effects of hydrogen diffusion also lead to an anomalous decrease of the Lamb–Mössbauer factor [2]. The relaxation of the iron environment is, however, expected to give rise to a substantial change of the isomer shift only at high hydrogen-to-metal ratios, where the differences between source and absorber spectra are big [1–3]. Hydrogen losses during the Mössbauer experiments therefore prevented the observation of this transition in the past. By exposing the source to a pressure of about 2.4 GPa in a high pressure cell using boron carbide anvils [4,5] during the Mössbauer experiments, hydrogen losses could now be avoided up to ambient temperature. In this way the transition between the two regimes became accessible to observation. Even between 300 and 400 K Mössbauer measurements could be performed despite slow hydrogen losses.

2. Experimental

To obtain a very high hydrogen concentration in PdH_x, a foil of 0.2 at.% ^{57}Fe in Pd was exposed to molecular hydrogen for 24 h at 200 °C and a pressure of 7 GPa in a pressure cell with AlH_3 as a hydrogen donor [5,6]. The cell was cooled with liquid nitrogen before release of the pressure and removal of the sample, which was then continuously kept cold until after the measurement of the

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[*] Corresponding author.

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Mössbauer spectra. The source of ^{57}Co in Pd was hydrogenated in molecular hydrogen in a piston-type pressure cell [7] at ambient temperature and a pressure of 1.0 GPa for 120 h and also cooled before pressure release. It was then transferred into the high pressure cell used for the Mössbauer experiments without being warmed above about 200 K. A single-line absorber of $Pd_{0.995}\,^{57}Fe_{0.005}$ kept near ambient temperature was used to record the emission spectra of this source.

3. Results and discussion

The absorber loaded at 7 GPa yielded a single Mössbauer line at 4.2 K with practically the same width (0.299±0.005 $mm\,s^{-1}$) as before loading and an isomer shift of +0.541±0.005 $mm\,s^{-1}$ with respect to the unloaded absorber. Outgassing into a calibrated volume after the Mössbauer experiments yielded a hydrogen-to-metal ratio of $x=1.04\pm0.02$. The absence of line broadening suggests that this sample contains practically only iron solutes with six nearest hydrogen neighbours. If one assumes that the hydrogen-induced isomer shift, $\Delta S_i=\Delta S_o+i\cdot\Delta S$ [1], where the shift for iron without hydrogen neighbours in the hydride matrix, ΔS_o, is virtually zero [1], the observed isomer shift corresponds to $\Delta S=0.090\pm0.001$ $mm\,s^{-1}$, in excellent agreement with the interpretation of spectra obtained at lower hydrogen contents [1].

Fig. 1 shows emission spectra of the $^{57}Co{:}PdH_{0.94}$ source kept in the Mössbauer high pressure cell. Between 100 and 200 K the increasing temperature causes the hydrogen to overcome the repulsive interaction with the Co. This gives rise to the shoulder growing at the low velocity side of the pattern. Between 200 and 300 K, the transition from the hydrogen environment of Co to that of Fe becomes so fast that at 300 K one observes largely the hydrogen environment typical for iron, with fewer hydrogen neighbours than for Co and a consequent increase in the mean isomer shift[1]. The fast hydrogen diffusion also leads to a motional averaging of the number of nearest hydrogen neighbours around the individual probe atoms and hence to a line narrowing. The mean centre shifts observed during the series of experiments with the source in the high pressure cell are shown in Fig. 2. Above 300 K one expects the centre shifts to decrease again, because the repulsive iron–hydrogen interaction is overcome thermally. This is, however, difficult to observe because slow

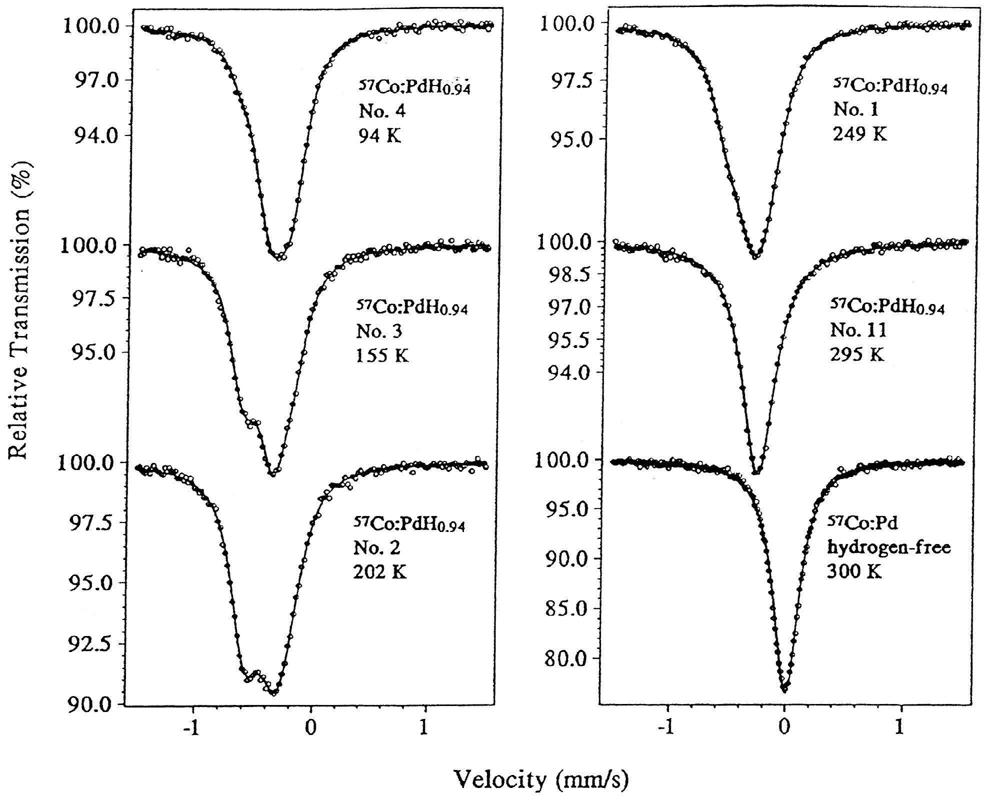

Fig. 1. Mössbauer spectra measured with the source of ^{57}Co in $PdH_{0.94}$ at different temperatures. The single-line absorber of ^{57}Fe in Pd was always kept close to ambient temperature. For comparison a spectrum of the hydrogen-free ^{57}Co:Pd source is also shown. The numbers of the spectra refer to the numbers of the data points in Fig. 2.

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[1] Note that for source experiments increasing isomer shifts correspond to an increasing electron density at the nucleus and hence to a smaller number of hydrogen neighbours, since hydrogen neighbours lower the electron density at the iron nucleus [1–3].

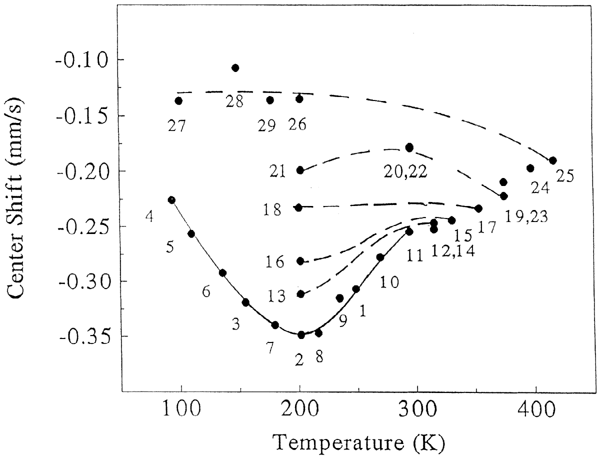

Fig. 2. Mean hydrogen-induced centre shifts observed for sources of ^{57}Co in PdH$_x$ with an initial hydrogen to metal ratio of $x=0.94$. At the data points the consecutive numbers of the Mössbauer experiments are given. The recording of each spectrum took about three days. The full line represents the temperature dependence of the centre shift for $x=0.94$. During the measurements above 300 K the source slowly lost hydrogen. The dashed curves therefore represent the approximate temperature dependence of the centre shift at lower hydrogen contents prompted by the few data points presently available. The hydrogen content of the sample at the end of the experiments (data points 26 to 29) can be estimated from the isomer shifts to be $x\approx0.80$ [1–3].

hydrogen losses occur during the several days required to record a Mössbauer spectrum. These hydrogen losses manifest themselves by increased centre shifts when the temperature is again lowered after the absorber was kept above 300 K for some time (Fig. 2). The individual dashed curves in Fig. 2 therefore represent the temperature dependence of the centre shifts at consecutively lower hydrogen concentrations. For a better definition of these temperature dependencies, more data points need to be measured in future experiments.

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