^{1}H NMR spectra and echoes in Pd–H and Pd–Ag–H alloys

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Abstract

The paper presents the experimental results of rigid-lattice proton magnetic resonance spectra and second moments in Pd–H, $Pd_{0.90}Ag_{0.10}$–H, $Pd_{0.80}Ag_{0.20}$–H, $Pd_{0.75}Ag_{0.25}$–H, and $Pd_{0.65}Ag_{0.35}$–H alloys at $T = 2.4$ K in a wide hydrogen concentration range. Free induction decay (FID), solid and inhomogeneous echoes were detected and interpreted. The interpretation based on dipole–dipole interaction of homogeneously distributed proton spin system is satisfactory at high hydrogen concentration, but an inhomogeneous field of paramagnetic origin (most probably coming from Fe impurities) plays the dominant role at small hydrogen content. An unexpected correlation was found between the macroscopic magnetic susceptibility and the second moment coming from the inhomogeneous internal field.
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1. Introduction

Our goal is to survey the hydrogen location in Pd–H and Pd–Ag–H systems and its dependence on the hydrogen and silver concentration. We used ^{1}H NMR spectroscopy to get information on the hydrogen occupancy of the octahedral interstitial lattice sites. We carried out the NMR line-shape measurements at a temperature low enough to reach the rigid-lattice state in order to avoid the effects of hydrogen diffusion.

To fulfill our goal set above, we made ^{1}H NMR experiments on Pd–H and Pd–Ag–H systems at temperatures as low as 2.4 K and varied H/M ratios from 0.04 to maximum H/M using our technology for hydrogen introduction [1].

No rigid-lattice proton NMR results have been reported to make it possible to determine the hydrogen occupation in Pd–H system and this is especially true for H/M values lower than 0.2. The lowest temperature of the published measurements was 4.2 K [2]. To our knowledge, no proton NMR line-shape investigations have been published on Pd–Ag–H systems in the literature.

We report here our results on the mentioned metal–hydrogen systems based on ^{1}H NMR free induction decay (FID) and echo

measurements made in a wide range of H/M (minimum = 0.04 and maximum = 0.6) at temperature $T = 2.4$ K.

1.1. Palladium and palladium–hydrogen systems

Palladium–hydrogen was the first and probably is the most frequently investigated metal–hydrogen system. The results concern the occupation [3,4], the motion, the electronic structure [5], etc. of hydrogen in the metallic lattice and the macroscopic properties of Pd and Pd–H alloys. As far as the magnetic results are concerned, palladium is a strongly enhanced itinerant paramagnet, the measured static spin susceptibility of which exceeds the Pauli susceptibility χ by an order of magnitude [6] with a maximum at around 80 K [7–10]. The χ of the Pd matrix depends strongly on the temperature [11].

The local magnetic field measured by NMR Knight shift at the sites of ^{105}Pd nuclei in Pd metal at a fixed frequency [12,13] shows a correlation with the Pd magnetic susceptibility [7] in the temperature range of 4.2–300 °K. The susceptibility of Pd is extremely sensitive to iron impurities [9] (raising the iron concentration from 1 to 3 ppm causes a marked rise of χ below 10 K). The value of local magnetic moment of electronic origin is estimated to be of 11.3 μ_B (Bohr magneton) in a Pd alloy containing 1% Fe at 100 K [11,14]. The magnetic moments associated with iron impurities are local according to Mössbauer experiments on very dilute solution of ^{57}Fe in palladium at $T < 4.2$ K [15].

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The effective magnetic moment of ^{57}Fe was found to be about 12.6 μ_B and its spin is 13/2. It appears evident that the spin of the iron impurity polarizes the palladium matrix in its vicinity to give an enhanced local moment.

1.2. Introduction of hydrogen

Hydrogen absorbed in palladium occupies octahedral sites of the face centered cubic (fcc) metal lattice [3,4]. The interstitial hydrogen produces a 4.4 eV wide electronic band centered 1 eV below the bottom of palladium-derived d bands in the Pd–H system [5]. The electrons added by the interstitial hydrogen fill the d-band holes at E_F as well as extra s-p band states that are pulled down below E_F [5]. This latter result also explains why the number of added electrons (0.6) in Pd–H exceeds the number of d-band holes (0.36) in palladium [16].

The theoretical calculation of the rigid-lattice proton dipolar second and fourth moments (M_2 and M_4) of the ^{1}H NMR line for fcc lattice is given for instance in [17]. The rigid-lattice dipolar M_2 of Pd–H system gives $M_2 = 10.75 \times 10^{-8}$ T^2 for $H/M = 1$, with contributions of the resonant and nonresonant nuclei and the lattice expansion caused by the introduced hydrogen taken into account.

The ^{1}H NMR experimental results on Pd–H system are published in papers [2,18–21]. The only analysis of line shape for polycrystalline Pd (foil samples, $H/M = 0.70$–0.81) appeared in the paper of Avram and Armstrong [2]. They used the solid echo pulse sequence to escape the recovery time problem and found that the characteristic echo shape can be represented by an empirical function of $f(t) = f(0) \exp(-a^2 t^2) J_{3/2}(bt)/(bt)^{3/2}$, where $J_{3/2}(bt)$ is a Bessel function of the first kind, a and b are adjustable parameters and $f(0)$ is normalization constant (later we will refer to $f(t)$ as Avram–Armstrong empirical function). The authors assumed that proton–proton dipolar contribution to spectrum shape is dominant. Their theoretical calculations showed that the calculated M_2 and M_4 were higher than measured even at $T = 40$ K. They ascribed the effect to phonon-assisted tunneling of hydrogen atoms and found the acceptable agreement between calculated and measured M_2 and M_4 values at temperatures around 4 °K.

1.3. The effect of silver alloying-addition

The Pd–Ag alloys are probably the simplest and consequently the best representatives of the chemically disordered alloys; they were subjects of widespread experimental and theoretical investigations. The atom radii of the two alloying elements are nearly the same in this system. Pd and Ag form homogeneous solid solution of fcc structure in the whole concentration range of the alloying addition silver. The hydrogen solubility for the pure metals differs by many orders of magnitude, so the (probably binomial) local distribution of the constituents exerts strong effect on the microscopic physical properties too. The hydrogen solubility in Pd–Ag alloys decreases with increasing silver concentration. The magnetic susceptibility of pure Pd is reduced by both silver and hydrogen addition and demonstrates the change in electronic structure. Starting with the pure palladium, the paramagnetic susceptibility of the nonordered solution decreases with increasing silver content and reaches zero at about 60 at.% Ag. At higher silver content, the susceptibility is slightly negative (see [22,23] and references therein).

No data on the chemical impurity content, especially that of the transition metal impurities of the investigated samples (except in [21]), are given in the literature.

2. Experimental

2.1. Sample parameters and preparation

Lumps of palladium were used (purity 99.95 wt%, Goodfellow) with main quoted impurities Ag: 50, Pt: 40, Rh and Si: 20, Fe, Cu, and Pb: 10, Al, Ca, Mn, and Na: 1 ppm. The alloys were prepared with silver (purity 99.99 wt%, Goodfellow) of main quoted impurities Bi, Mg: 1, Fe: 2, Au: 5, Pb: 10, and Cu: 20 ppm.

The samples were mixed and alloyed by induction melting under reduced argon pressure of 8×10^4 Pa. To reach homogeneity, the ingots were re-melted three times. Binary Pd–Ag alloys of 10, 20, and 35 at.% Ag content were produced and cold-rolled in five to seven steps to a thickness of 15–20 μm. The steps of cold rolling were separated by surface cleaning in 6M HCl and annealing at 700 °C also in the case of pure palladium sample.

The palladium silver foil Pd$_{0.75}$Ag$_{0.25}$, 0.025 mm thick (with purity of Pd: 74.99% and Ag: 24.93%, Johnson Matthey GmbH) had main quoted impurities Pt: 454, Ir: 34, Fe: 142, and Cu: 22 ppm.

Sandwich-type samples consisting of a few foils were made with Teflon spacers for the NMR measurements.

2.2. Hydrogen introduction

A complementary unit to the spectrometer was constructed to produce in situ hydrogen charging or discharging. The Pd and Pd–Ag samples contained in a glass tube and inserted into the probe coil of the pulse spectrometer were connected with vacuum and high-purity hydrogen systems. Thus, the samples could be exposed to controlled hydrogen atmosphere and temperature in a similar way as reported in [24]. As in addition to the known NMR methods, the in situ measurement of hydrogen concentration in the samples was used [25] as well as what is operative in minute time range and makes the NMR method applicable for the simultaneous measurements of NMR parameters and characteristic hydrogen content in equilibrium state.

2.3. Methods of NMR measurements

The NMR experiments and data acquisition were accomplished by a Bruker SXP 4–100 spectrometer at ^{1}H resonance frequencies of 27.7 and 82.5 MHz. The recovery time of the NMR spectrometer at frequency 27.7 MHz after the $\pi/2$ pulse was 7 μs.

FID, solid echo, and Hahn echo signals were detected. The $(\pi/2)_X$ (pulse with shorthand X, the $(\pi/2)_X$–τ–$(\pi/2)_X$ pulse sequence with shorthand X–τ–X and $(\pi/2)_X$–τ–$(\pi/2)_Y$ pulse sequence with shorthand X–τ–Y were used in the investigation. The appropriate responses to pulse sequences are: FID to a single X pulse, Hahn echo or inhomogeneous echo (HE) to the X–τ–X pulse sequence and solid echo (SE) to an X–τ–Y pulse sequence.

When it was possible to fit the initial part of FID by an empirical function or to describe the X–τ–Y echo around its maximum by an analytical function with sufficient precision, then the M_2 was determined by taking the second time derivative of the signal envelope

$$-\frac{[\mathrm{d}^2 M_x(t, \tau)/\mathrm{d}t^2]_{t=\tau}}{M_x(\tau, \tau)},$$

where the $M_x(t, \tau)$ is echo amplitude as a function of time t and inter-pulse delay τ.