INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 36 (2011) 1601–1605

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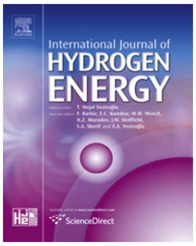

Exchange model for proton relaxation in disordered metallic hydrides

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ARTICLE INFO

Article history:
Received 2 September 2010
Received in revised form
22 October 2010
Accepted 24 October 2010
Available online 30 November 2010

Keywords:
NMR
Spin-lattice relaxation
Ti–V–Cr hydrides

ABSTRACT

The experimental frequency and temperature dependences of proton spin-lattice relaxation in metallic hydrides are often treated within the Bloembergen-Purcell-Pound model. However, even the consideration of activation energy (or correlation time) distribution does not provide a satisfactory agreement with experimental data. It was experimentally detected that in metallic hydrides hydrogen atoms can be in two states: mobile and bounded to the lattice. Here, we suggest treating the proton spin-lattice relaxation in such systems within the model, which implies an exchange between these two states. The correlation times and activation energies values for the hydrogen motion in a hydride of the disordered $TiV_{0.8}Cr_{1.2}$ alloy have been estimated applying this exchange model.

1. Introduction

During the last decades metal-hydrogen systems were subject of intensive experimental and theoretical studies especially as hydrogen storage materials. For better understanding of intrinsic mechanisms that govern the hydrogen kinetics in these hydrides the deeper knowledge on local structure and hydrogen mobility are required. Appreciable enlightening of main characteristics (static and dynamics) of microstructure can be provided using nuclear magnetic resonance (NMR) method which is a powerful tool to investigate metal-hydrogen systems.

The temperature dependences of spin-lattice (T_1) and spin-spin (T_2) relaxation of the ^1H nuclei can provide information on hydrogen mobility in metallic lattice [1–6]. However, for the adequate interpretation of experimental data one needs an appropriate model, which can provide insight on hydrogen state. Commonly the proton relaxation in metallic hydrides is analysed using the isotropic model firstly proposed by Bloembergen, Purcell and Pound (BPP) [7]. Metal-hydrogen systems are usually inhomogeneous, that leads to larger minima in T_1 temperature dependence [4–6]. This smoothing is often treated by incorporating the distribution of hydrogen motional parameters [8–10]. Moreover, some features of temperature dependencies of the proton relaxation in metallic hydrides can not be explained within the framework of the BPP model even taking into account the distribution of activation energies and correlation times: (i) – at high temperature T_1 values measured at different frequencies do not coincide [4,11]; (ii) – the second moment of a spectral line obtained from the relaxation data is much smaller than the calculated one or measured by the cw method [5,12,13]; (iii) – T_1 and T_2 do not coincide at high temperatures [3,14,15].

Among a number of publications concerning the study of the hydrogen mobility via the NMR relaxation there are only a few ones in which the problems mentioned above were discussed. For example, the authors of the works [4] proposed the two-jump model of movement for the

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doi:10.1016/j.ijhydene.2010.10.082

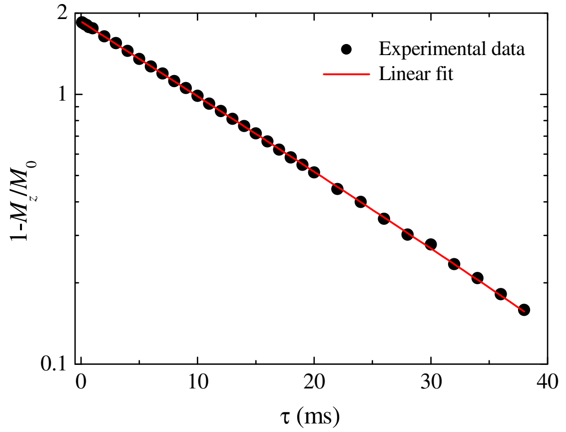

Fig. 1 – ^{1}H magnetization recovery curve in $TiV_{0.8}Cr_{1.2}H_{5.29}$ at 14 MHz (T = 298 K).

description of the proton relaxation in binary Ti–V hydrides but this model could not describe correctly the experimental T_1 behaviour at high temperatures. Moreover, the authors supposed that the second moment, which determines the spin-lattice relaxation rate, is due only to the interaction with protons located in the third coordination sphere, whereas the first and the second spheres are vacant. This assumption is correct only for small hydrogen concentrations, and fails to explain the temperature dependence of T_1 in hydrogen-rich systems. A better model with introducing the distribution of correlation times was reported in Ref. [5]. It allowed the authors to describe better the frequency dependence in a high temperature range but failed to explain the significant disagreement between the second moment values calculated using the Van Vleck expression and obtained from the fitting of $T_1(T)$ curves.

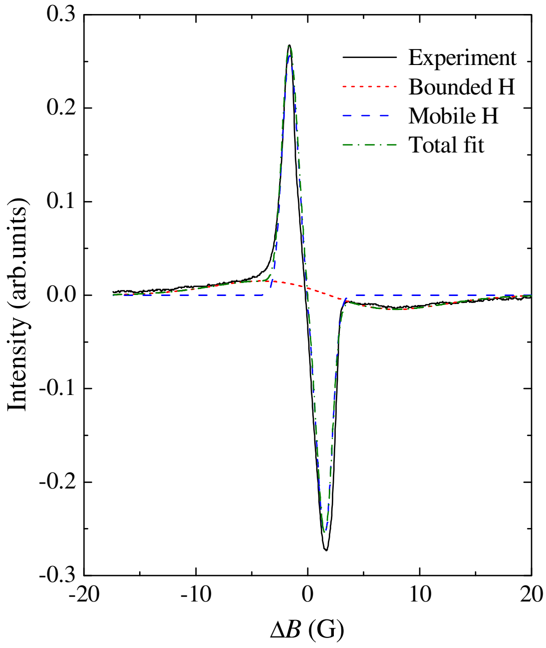

Fig. 2 – Proton NMR cw spectrum in $TiV_{0.8}Cr_{1.2}H_{5.29}$ at 42 MHz at room temperature.

The difference between relaxation times T_1 and T_2 in Zr–Ni–Cu–H amorphous alloys at high temperatures [15] was explained within the Redfield–Slichter model [16]. It was supposed that the main contribution to the spin-spin relaxation was caused by magnetic field fluctuations due to the proton diffusion in local magnetic fields created by nearest magnetic nuclei. This model succeeded in the explanation of the small values of T_2 at high temperatures but failed to describe correctly the frequency dependence of T_1.

As it is evident from the ^{1}H NMR spectra, in metallic hydrides the hydrogen can exist in two states: mobile (m) and bounded to the lattice (b), see for example Refs. [17,18], and that there is an exchange between these two states. In this paper, we suggest to apply the exchange model, originally developed for multiphase heterogeneous systems [19], for the treatment of proton spin-lattice relaxation in metallic hydrides. The consideration is equally valid for the both physical exchange and spin-diffusion process.

The model has been tested on the example of the $TiV_{0.8}Cr_{1.2}H_{5.29}$ hydride. Ti–V–Cr alloys belong to a class of potentially high characteristic materials in terms of hydrogen storage properties [20–22]. In the $TiV_{0.8}Cr_{1.2}$ alloy the metals Ti, V, Cr are randomly distributed in the two body-centred-cubic (bcc) atomic positions [23]. The formation of a binary MH_x hydride operates via a first order martensitic type transition, the final hydride structure is of face-centred-cubic (fcc) type [23–25], where hydrogen occupies tetrahedral interstitial positions [23,24].

2. An exchange model

Originally the exchange model was developed by Zimmerman and Brittin to study multiple phase systems: water molecules in an adsorbing phase on silica gel [19]. Further it was successfully applied to various heterogeneous systems, such as water in porous media [26], surface active agents [27], electrolyte solutions [28] etc.

If there is an exchange between two states (m and b) the experimentally observed relaxation functions $F_{1,2}(t)$ depend on the ratio between relaxation time ($T_{1,2}$) and life time (τ) of the nuclei in this state. In the case of slow exchange, when $\tau_m \gg T_{1,2,m}$ and $\tau_b \gg T_{1,2,b}$, the relaxation functions can be written as:

$$F_{1,2}(t) = p_m \exp\left(-\frac{t}{T_{1,2,m}}\right) + p_b \exp\left(-\frac{t}{T_{1,2,b}}\right), \tag{1}$$

where p_m and p_b are relative concentrations of hydrogen in each state ($p_m + p_b = 1$). In the case of fast exchange, i.e., $\tau_m \ll T_{1,2,m}$ and $\tau_b \ll T_{1,2,b}$, the single exponential relaxation function is realized:

$$F_{1,2}(t) = \exp\left(-t\left(\frac{p_m}{T_{1,2,m}} + \frac{p_b}{T_{1,2,b}}\right)\right). \tag{2}$$

In the case of intermediate exchange the function $F_{1,2}(t)$ can be written in form (1), but with parameters p'_m, p'_b, $T'_{1,2,m}$ and $T'_{1,2,b}$, which could be different from real.