Hydrogen diffusion in Zr-Pd amorphous alloys

N. Adnani, J. Titman

To cite this version:


HAL Id: jpa-00246822
https://hal.archives-ouvertes.fr/jpa-00246822
Submitted on 1 Jan 1993
Hydrogen diffusion in Zr-Pd amorphous alloys

N. Adnani (1) and J. M. Titman (2)

(1) University of Bejaia, B.P. 32, 06000 Bejaia, Algeria
(2) University of Sheffield, Department of Physics, UK

(Received 30 October 1992, revised 2 February 1993, accepted 4 March 1993)

Abstract. — Nuclear Magnetic Relaxation measurements of the dipolar relaxation rate due to hydrogen diffusion in Zr-Pd amorphous alloys have been conducted and the results interpreted in terms of the random alloy model. It is found that even though the measured activation energy using Torrey's theory changes as the range of composition and temperature are varied, it stays the same for all compositions at the low temperature range. This behaviour is shown to be related to the type and amount of spins participating in the diffusion process. It is also reported here, for the first time, that the interpretation of the NMR results is strongly related to the composition of the alloy under investigation.

1. Introduction.

The technique of nuclear magnetic relaxation is concerned with the measure of the dipolar relaxation rate as a function of temperature. This is then compared to its dependence on frequency calculated theoretically to yield an Arrhenius relation between the mean jump time and temperature, from which an activation energy can be extracted. This is certainly true for crystalline media. In disordered systems such comparison is not yet possible because of the absence of a model to calculate the relaxation rate.

Bowman et al. [1] measured the rate of the dipolar relaxation in a-Zr2PdH2.9 and analysed their results using the BPP theory [2]. They found that their data did not obey an Arrhenius temperature relation as it did in its crystalline counterpart. They associated this behaviour to the presence of a distribution of activation energies. The same attempt will be presented in this article with the difference that this departure from an Arrhenius relation is explained in terms of the random alloy model.

Crouch et al. [3] argued that due to the nature of the correlation of the dipolar fields, it is not possible for NMR data to reveal the presence of a distribution of activation energies. Chikdene et al. [4] using perturbed angular correlation (PAC) measurements arrived at the conclusion that their results did not indicate the existence of a broad distribution of activation energies for hydrogen jumps in a-Zr3NiH2.4. These two points are discussed in details later in this article.

NMR measurements performed on a-Zr4PdH0.8 and a-Zr3PdH0.6 are presented and the results explained in terms of the random alloy [5] coupled with Torrey's theory. This leads for
2. The relaxation rate.

The spin-spin or spin-lattice relaxation rate is expressed in terms of power spectra of randomly varying field $J^{(q)}(\omega)$ [6]. BPP [2] demonstrated that if the position coordinates $r_{ij}$, $\theta_{ij}$, $\varphi_{ij}$ between spin $i$ and spin $j$ are made to vary with time, an exchange of energy between the system of spins and the host lattice will occur inducing the spin-lattice relaxation. $J^{(q)}(\omega)$ is given by

$$J^{(q)}(\omega) = \int_{-\infty}^{\infty} G^{(q)}(t) e^{i\omega t} \, dt$$

where

$$G^{(q)}(t) = \sum_j \langle F_{ij}^{(q)}(t') F_{ij}^{(q)^{*}}(t' + t) \rangle$$

which is the correlation function of $F_{ij}^{(q)}(t) = Y_{2,q}(\theta_{ij}, \varphi_{ij}) d_q$ where $d_1 = \frac{8 \pi}{15}$; $d_2 = \frac{32 \pi}{15}$ and $Y_{2,q}$ is a normalised spherical harmonic. The reader is referred to [7] for more details.

In order to apply the formalism above it is important to evaluate the $G^{(q)}(t)$. This has been attempted by Torrey using the assumption of isotropic diffusion. His calculations are specific to a lattice type, although the published results [7] do not show big differences between fcc and bcc lattices. By comparing Torrey's results which give the variation of the relaxation rate with respect to $\omega \tau$ and the measured data as a function of temperature, it is possible to deduce the value of $\omega \tau$ for each temperature. Here $\tau$ is the time between jumps.


Thin ribbons of c-Zr₄Pd and c-Zr₃Pd were prepared by the standard melt-spinning method. The crystalline state was analysed by X-rays and found to be a bcc structure. The amorphous state was achieved by solid state reaction with hydrogen. The reactions were conducted at room temperature and a-Zr₄PdH₀₈ and a-Zr₃PdH₀₆ were obtained.

To make the measurements, an 18 MHz NMR spectrometer was used. Usually, the experimental procedure when using NMR requires either a 90° or a 180° pulse to disrupt the static magnetization from its equilibrium direction along the applied field, then observe its recovery to this direction. Since the induction coil only detects the magnetisation in the x-y plane, a further 90° pulse is necessary to turn the recovered magnetisation into the detection plane. A PID temperature controller kept sample temperature correct to ± 5 K. The pulse spacing, data acquisition and averaging are done by the on-line micro-computer.

4. Experimental results and analysis.

Figure 1 shows the proton spin-lattice relaxation time measurements against temperature in both a-Zr₃PdH₀₆ and a-Zr₄PdH₀₈. To explain the data, it is important to rely on a model which calculates the NMR correlation functions taking into account the disordered structure of the host lattice. Such a model has been developed on a computer and direct calculation have been made as the diffusion proceeds [8]. The results were compared to experimental data where the fit was only possible at a certain range of composition of the alloy forming the hydride. This is the case of a-Zr₂Ni and a-Ti₂Ni hydrides. However, as the amount of Zr in the
sample is increased, the fit becomes more and more difficult to make. The reader is referred to reference [9] for further details.

To overcome this difficulty and explain the failure of the simulation model to interpret the data of figure 1, a new method of analysis is attempted. Torrey's theory for a cubic lattice is applied. This step is necessary to show the departure from the Arrhenius relation of the jump time with respect to temperature. Such behaviour is later associated with another activation energy.

Fig. 2. — Results of Torrey's analysis showing the jump time against the reciprocal of temperature. (+) is the data taken on a-Zr$_3$PdH$_{0.8}$ and (*) that taken on a-Zr$_3$PdH$_{0.6}$. Notice the presence of two distinct slopes corresponding to two activation energies at low and high temperatures.
Figure 2 shows the results of Torrey's analysis on both samples. It is clear from the figure that it is possible to separate at least two distinct slopes corresponding to two different activation energies.

What is remarkable about this analysis is that the slope at the low temperature range stays the same for both samples. If we note \( E(\text{al}) \) and \( E(\text{ah}) \) the activation energy at the low and high temperatures respectively, then \( E(\text{ah}) = 1.02 \text{ eV} \pm 0.01 \text{ eV} \); \( E(\text{al}) = 0.18 \text{ eV} \pm 0.01 \text{ eV} \) for \( \text{a-Zr}_4\text{PdH}_{0.8} \) and \( E(\text{ah}) = 0.60 \text{ eV} \pm 0.01 \text{ eV} \); \( E(\text{al}) = 0.18 \text{ eV} \pm 0.01 \text{ eV} \) for \( \text{a-Zr}_3\text{PdH}_{0.6} \). The ratio \( K = E(\text{ah})/E(\text{al}) \) varies from one type of composition to another.

The same thing happens with the work of Bowman et al. [1] on \( \text{a-Zr}_2\text{Pd} \) hydride. Almost in the same temperature range, Bowman arrived at a value for the activation energy of 0.19 eV which is close to our value of 0.18 eV \( \pm 0.01 \text{ eV} \) for both samples. This result is very important for it means that the spins participating in the diffusion process at this range of temperature are the same in nature and proportion for the three samples. So far the only topological model that can offer such a situation is the random alloy model presented by Harris and coworkers [5].

Harris proposed a model for early-late transition metal alloys where the amorphous state is just a cluster of tetrahedrons formed by the metal atoms which are distributed randomly but in the right proportions on their vertices. The result of this is that sites surrounded by a different number of Zr atoms (a maximum of 4) are present in the lattice in different proportions. This is shown in table I where depending on the composition of the alloy, the proportion of each type of sites is given by the statistical weight.

A simple examination of table I shows that effectively the number of 3 Zr 1 Pd sites in the three compositions discussed above is the same. In all three cases it is around 40 % of the total number of sites. Since only sites of more than 2 Zr atoms are believed to be occupied [5], it is natural to suggest that at low temperatures only H-atoms coming from these sites will diffuse (because of their low binding energy). The result is a measure of an activation energy corresponding to this particular site. As the temperature is increased, the measured activation energy increases as more and more atoms from 4 Zr 0 Pd sites diffuse. This increase should in principle be proportional to the amount of such atoms in the samples which is related to the number of 4 Zr 0 Pd sites. This condition is to be verified for the random alloy model to be realistic. This is exactly what is happening as shown in figure 3 which reveals a strong dependence of the ratio \( K \) on the alloy composition.

Table I. — The table shows the proportion of the sites that can be occupied by hydrogen in the alloy as a function of its composition. A stands for early and B for late transition metal element.

<table>
<thead>
<tr>
<th>Type of site</th>
<th>A4B</th>
<th>A3B</th>
<th>A2B</th>
<th>AB</th>
<th>AB2</th>
</tr>
</thead>
<tbody>
<tr>
<td>4A 0B</td>
<td>40 %</td>
<td>31 %</td>
<td>21 %</td>
<td>6  %</td>
<td>1   %</td>
</tr>
<tr>
<td>3A 1B</td>
<td>42 %</td>
<td>41 %</td>
<td>40 %</td>
<td>26 %</td>
<td>10 %</td>
</tr>
<tr>
<td>2A 2B</td>
<td>15 %</td>
<td>22 %</td>
<td>27 %</td>
<td>38 %</td>
<td>29 %</td>
</tr>
</tbody>
</table>

5. Conclusion.

This study is presented as an attempt to relate the NMR experimental results to the sample composition forming the hydride under investigation. This has never been done so far and a
number of authors [4] noticed an absence of a broad distribution in some cases. Others found that a large distribution of activation energies is necessary to fit their data [10]. In all cases the fundamental difference lied in the composition of the hydride.

Chikdene arrived at a similar conclusion reached by Crouch [3] where it was difficult to confirm the presence of an activation energy. On the other hand Bowman and co-workers did find different slopes indicating different activation energies. However the ratio between the measured energies is about 1.89 as reported in figure 3. This small difference in the measured energies has mislead some authors [3] into concluding that only a single activation energy is measured in such samples. These three studies conducted by Chikdene, Crouch and Bowman were all based on a composition of the type A2B where A is the early transition element and B the late transition element. In this case according to the random alloy model, H-atoms from 3A 1B sites dominate the diffusion leading to a difficulty to observe the contribution from other occupied site.

Markert et al. [10] however, working on a sample of a A3B type found that a distribution of activation energies is necessary to fit their data. This is in total agreement with the random alloy model which predicts an increase in the 4A 0B sites and consequently a measure of their contribution to the diffusion.

We can then conclude from the study presented above that there is a possibility for NMR to detect a distribution of activation energies. However, computer simulation calculations similar to these presented on reference [9] are necessary to make direct comparison between the calculated relaxation rate based on the random alloy model, which has been proved here to be successful in explaining the NMR data, and the experimental results. This has already been started and will be the subject of another paper.

Fig. 3. — Variation of the ratio \( K = E_{(ab)}/E_{(al)} \) with respect to the amount of 4A 0B sites in the amorphous hydride investigated according to the random alloy model. The lowest point is taken from Bowman et al.'s results.
References