

Hydrogen-induced local demixing revealed by ^{181}Ta spin relaxation measurements in amorphous Zr_2Ni hydrides

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1990 J. Phys.: Condens. Matter 2 8075

(<http://iopscience.iop.org/0953-8984/2/40/007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 10/05/2010 at 22:32

Please note that [terms and conditions apply](#).

Hydrogen-induced local demixing revealed by ^{181}Ta spin relaxation measurements in amorphous Zr_2Ni hydrides

A Baudry[†], P Boyer[‡] and M A Chikdene

Centre d'Etudes Nucléaires, Département de Recherche Fundamentale, Service de Physique, Laboratoire Magnétisme et Diffusion par Interactions Hyperfines, 85X, 38041 Grenoble Cédex, France

Received 30 October 1989; in final form 3 April 1990

Abstract. ^{181}Ta spin-relaxation measurements have been carried out in hydrides of the intermetallic glass Zr_2Ni ($[\text{H}]/[\text{M}] = 0.83$ and 1.5) using the perturbed angular correlation (PAC) technique. The absence of a broad distribution in the activation energy of the hydrogen hopping rate is confirmed. Moreover, the jump rate is found to be independent of H concentration. The results derived from PAC experiments suggest the existence of hydrogen-induced demixing in the amorphous hydrided alloy, with the H atoms located in tetrahedral Zr_4 sites.

1. Introduction

For both fundamental and technological reasons, a great deal of work has been dedicated in recent years to the study of hydrogen mobility in hydrides of amorphous intermetallic compounds (Suzuki 1983, Bernas *et al* 1986, Maeland 1986). In this respect, the binary alloys formed between early transition metals (Ti, Zr and Hf) and late transition metals (Co, Ni, Cu, Rh and Pd) are especially favourable systems; they are able to absorb large amounts of hydrogen in crystalline and amorphous phases, which then permits us to study the influence of chemical and topological disorder on the diffusion mechanisms.

In most of the amorphous hydrides already investigated, the activation energy which controls the hydrogen hopping rate is found to be significantly lower than in crystalline hydrides of similar compositions. This observation has been usually held as evidence for the existence of easier diffusion pathways in the amorphous phases. Moreover, broad distributions of activation energy with a typical relative width of about 30% are commonly observed, as anticipated in highly disordered systems (Richards 1983). However, it should be noted that two recently investigated amorphous hydrides seem to escape from this common behaviour. Thus, proton NMR studies on $a\text{-(Ti}_{65}\text{Ni}_{35})\text{H}_{1.5}$ have indicated an apparent sharpness of the activation energy distribution with a relative width $\Delta E_a/E_a$ of about 10% (Crouch *et al* 1986). A similar result has been found for $a\text{-Zr}_2\text{NiH}_{2.5}$ from ^{181}Ta spin-relaxation measurements (Chikdene *et al* 1988a). From consideration of such unexpected results, the ability of spin-relaxation phenomena to reflect the true distribution of H-site energies and saddle-point energies has been questioned. In their

[†] Affiliated to the CNRS.

[‡] Also from the Université Joseph Fourier, Grenoble, France.

attempt to interpret the data of Crouch *et al*, Richards and Shinar (1987) conclude that the distribution of activation energy observed by NMR almost exclusively results from the site energy distribution. However, the basic assumption of identical distributions for the site and saddle-point energy introduced by these workers in their model may be questioned (Chikdene *et al* 1988a). Nevertheless, the existence of a large number of possible pathways for a H atom to jump from a given site into a next-neighbour site, as well as the existence of collective effects due to strongly correlated motions, are expected to contribute in reducing significantly the 'apparent' width of the distribution of activation energies observed in spin-relaxation measurements.

A novel aspect of amorphous hydride phases has been revealed by recent investigations by Rodmacq *et al* (1988a, b) on CuTiH_x . The comparison of pair correlation functions measured by neutron diffraction experiments before and after the hydriding reaction indicates that a phase separation has occurred upon hydrogen absorption. Using numerical simulation techniques incorporating chemical order, the size difference between metallic atoms and Cu-Ti nearest-neighbour permutations in order to simulate microsegregation effects, these workers were able to reproduce satisfactorily the experimental radial distribution functions relative to a- CuTiH_x . From such observations it appears that the study of hydrogen mobility in hydrides, considered as a way for probing the structure of metallic glasses, should be carefully questioned.

In this paper we report on the results obtained in hydrides of the Zr_2Ni intermetallic glass by spin-relaxation measurements using substitutional ^{181}Ta as a stationary quadrupolar probe. The ^{181}Ta spin-relaxation data relative to a- $\text{Zr}_2\text{NiH}_{4.5}$ confirm the absence of a broad distribution of the activation energy for the hydrogen hopping rate in these glassy hydrides, as already indicated by the same experiments in a- $\text{Zr}_2\text{NiH}_{2.5}$ (Chikdene *et al* 1988a). Moreover, the comparison between the results obtained for a- and c- Zr_2NiH_x support the idea that local demixing takes place in the amorphous alloy during the hydriding reaction.

2. Experimental details

Glassy Zr_2Ni doped with 2 at. % Hf in substitution for Zr was prepared by the rapid quenching technique under an argon atmosphere. Small pieces of the amorphous ribbon so obtained were then exposed for several days to a low hydrogen pressure (about 2×10^3 Pa) after degassing at 200 °C under high vacuum. Prior to the introduction into the hydriding reaction chamber, either abrasion with silicon carbide powder or coating with palladium was carried out on the surface of the ribbon. The composition of the hydrides was determined directly from the pressure difference observed during the loading process and confirmed by weight-loss determination under vacuum. The amorphous character of the hydride phases was checked by x-ray diffraction. From the shifts observed on the position of the first maximum of the diffraction intensity patterns, volume expansions $\Delta V \approx 0.8 \text{ \AA}^3/\text{H atom}$ and $\Delta V \approx 2.4 \text{ \AA}^3/\text{H atom}$ can be roughly estimated for the hydrides a- $\text{Zr}_2\text{NiH}_{2.5}$ and a- $(\text{Zr}_2\text{Ni})\text{H}_{4.5}$, respectively. Such values can be compared with the value $\Delta V \approx 2.3 \text{ \AA}^3/\text{H atom}$ observed for various compositions of crystalline Zr_2Ni hydrides (Chikdene 1989). We note the non-linear behaviour of the volume expansion against the H concentration in the amorphous hydrided alloy.

About 200 mg of the hydrided material were exposed to a thermal neutron flux in order to produce radioactive ^{181}Hf isotopes which disintegrate by β^- decay toward ^{181}Ta . After irradiation, the sample was placed in a quartz tube sealed under air for perturbed angular correlation (PAC) measurements varying the temperature.

Spin-quadrupole-relaxation measurements on the ^{181}Ta probe were performed using the PAC technique. The relevant quantity measured in a PAC experiment is the perturbation factor $G_2(t)$ of the anisotropy of a convenient $\gamma\text{-}\gamma$ cascade emitted by the nuclear probe. For the 133–482 keV cascade emitted by the ^{181}Ta nucleus implanted in non-magnetic, polycrystalline or amorphous materials, $G_2(t)$ can be written in the following way:

$$G_2(t) = \exp(-\lambda t) \left(S_{20}(\eta) + \sum_{n=1}^3 S_{2n}(\eta) P_n(t) \cos(2\pi\nu_n t) \right).$$

This expression contains modulation terms and depolarisation factors. The modulation corresponds to the interaction of the $I = \frac{5}{2}$ intermediate level of the cascade with the randomly oriented electric field gradient (EFG) present at the probe site. This interaction is characterised by the quadrupole frequencies $\nu_n = f_n(\eta)|V_{zz}|$, and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ of the EFG tensor. Depolarisation effects can result either from inhomogeneities of static EFG or from dynamical EFG fluctuations. As large EFG distributions exist in amorphous materials, Gaussian distributions of quadrupole frequencies $P_n(t) = \exp(-\frac{1}{2}\delta_n \nu_n t^2)$ have been assumed for fitting the PAC spectra following the procedure proposed by Forker (1973), as indicated in a previous paper (Chikdene *et al* (1988a)). Time fluctuations of the EFG caused by hydrogen jumps in the vicinity of the probe are taken into account by an exponential damping characterised by the spin-relaxation constant—or depolarisation rate— λ . The validity of this quite simple expression of relaxation effects in PAC spectroscopy has been extensively discussed in various papers (Baudry and Boyer 1987, Boyer and Baudry 1989). Let us just mention that the assumption of isotropic fluctuations of the EFG tensor appears reasonable in view of the existence of jump pathways along several directions of space in intermetallic hydrides. It is worth remembering that $\lambda = \alpha\nu$ for EFG fluctuation frequencies, i.e. H jump frequencies $\nu \leq 10^8 \text{ s}^{-1}$, and $\lambda = A\langle V_{zz}^2 \rangle \nu^{-1}$ for $\nu \geq 10^9 \text{ s}^{-1}$. In the last relation, V_{zz} is the major principal component of the fluctuating EFG assumed to be axial. The value of the coefficient α in the slow-hopping regime depends on the ratio of the static to fluctuating components of the full EFG ($\alpha = 1$ if no permanent static EFG is present).

If the jump frequency obeys an Arrhenius law $\nu = \nu_0 \exp(E_a/kT)$, the plot of $\ln \lambda$ against $1/T$ is symmetric and appears as two straight lines with opposite slopes on either sides of a flat maximum (Boyer and Baudry 1989). In ^{181}Ta PAC experiments this maximum corresponds to jump frequencies nearby 10^8 s^{-1} . The existence of either several distinct Arrhenius processes or a distribution in the activation energy results in asymmetry in the slopes of the $\ln \lambda$ versus $1/T$ plot. The same effect is currently observed in the temperature dependence of the spin–lattice relaxation rate measured in NMR experiments. Pronounced asymmetries, interpreted with Gaussian distributions of relative widths $\Delta E_a/E_a \approx 20\%$, were observed for the ^{181}Ta quadrupole relaxation generated by the diffusion of oxygen ions in highly defective oxides such as stabilised zirconia and ceria (Baudry *et al* 1982). The existence of broad distributions of the activation energy in these disordered solid solutions has been confirmed by later measurements of the ^{17}O NMR relaxation time T_1 (Fuda *et al* 1985). This interpretation was also found to be consistent with conductivity measurements (Abelard and Baumard 1982).

3. Results and discussion

Examples of $G_2(t)$ patterns obtained in amorphous hydrides Zr_2NiH_x between 200 and 470 K are shown in figure 1. In the same figure is presented the PAC spectrum relative to

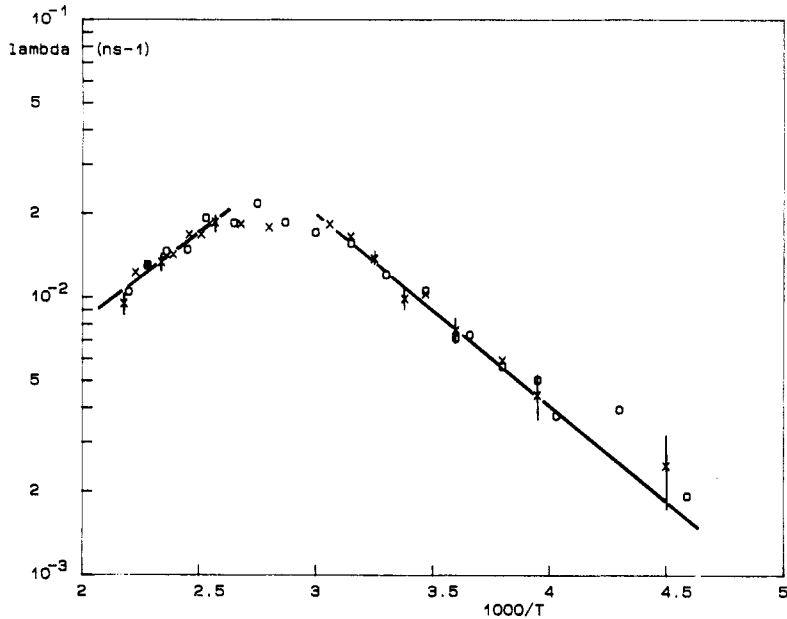


Figure 1. Examples of time-dependent perturbation factors of the ^{181}Ta PAC measured (a) for glassy Zr_2Ni at room temperature and (b)–(d) for a- $\text{Zr}_2\text{NiH}_{2.5}$ at temperatures of (b) 200 K, (c) 360 K and (d) 460 K: results of a fitting procedure as implemented in the text.

Table 1. ^{181}Ta quadrupole coupling parameters measured in c- and a- Zr_2Ni , and in amorphous hydrides of Zr_2Ni . δ is the relative width of the distribution of quadrupole coupling frequencies.

Sample	T (K)	$\nu_Q = eQV_{zz}/40h$ (MHz)	$\eta = (\langle V_{xx} \rangle - \langle V_{yy} \rangle) / \langle V_{zz} \rangle$	δ
c- Zr_2Ni	293	15.8 (2)	0.84 (2)	0.02
a- Zr_2Ni	293	15.8 (2)	0.30 (3)	0.37
a- $\text{Zr}_2\text{NiH}_{2.5}$	200	15.2 (2)	≈ 0	0.47
a- $\text{Zr}_2\text{NiH}_{2.5}$	450	13.3 (2)	≈ 0	0.54
a- $\text{Zr}_2\text{NiH}_{4.5}$	210	17.2 (1)	0.55 (5)	0.49
a- $\text{Zr}_2\text{NiH}_{4.5}$	450	15.3 (1)	0.59 (5)	0.57

glassy Zr_2Ni at room temperature. The attenuation observed along the time on the amplitude of the non-oscillating contribution to the perturbation factor (the ‘hard-core’ component) is a clear signature of relaxation effects. As expected, the quadrupole oscillations are completely wiped out because of the existence of broad distributions of static EFG at the Ta sites. It should be noted, however, that the spectra relative to the amorphous hydrides display small oscillations corresponding to a fairly high quadrupole frequency. We are tempted to attribute the existence of such oscillations, which are not observed in the glassy alloy, to a small fraction—not exceeding a few per cent—of ^{181}Ta probes located in crystallised zones. The values of the quadrupole coupling parameters given by the fitting procedure for a- Zr_2Ni and the two hydrides investigated are reported in table 1. Looking at this table we note that, except for the width of the EFG distribution,

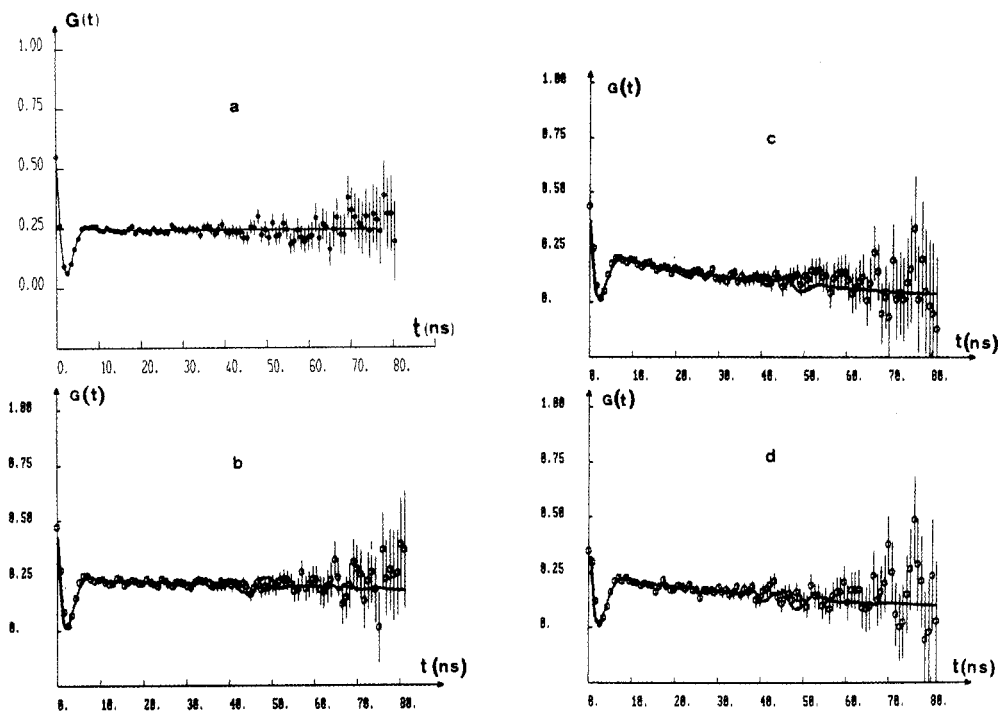


Figure 2. ^{181}Ta spin-relaxation constant λ plotted against the inverse of temperature for α -Zr₂NiH_{2.5} (\times) and α -Zr₂NiH_{4.5} (\square): —, result of a least-squares fitting procedure assuming a Gaussian distribution of the activation energy.

Table 2. Values of the hopping rate parameters for hydrogen in hydrides of glassy Zr₂Ni. The values measured in several hydrides of crystalline Zr₂Ni are given for comparison.

Sample	E_a (eV)	$\Delta E_a/E_a$	ν_0 (s ⁻¹)
α -Zr ₂ NiH _{2.5}	0.135 (5)	0.12	1.5×10^{10}
α -Zr ₂ NiH _{4.5}	0.138 (5)	0.13	1.7×10^{10}
c -Zr ₂ NiH _{2.1}	0.15 (1)	≈ 0	2.4×10^{10}
c -Zr ₂ NiH ₃	0.27 (1)	≈ 0.10	6.5×10^{12}
c -Zr ₂ NiH _{4.8}	0.38 (2)	—	1.8×10^{13}

the parameters for c -Zr₂Ni and glassy Zr₂Ni are very close. This suggests that the Ta probes are placed in rather similar environments in both materials. On the other hand, contrary to what is observed in hydrides of c -Zr₂Ni, the presence of hydrogen in α -Zr₂Ni does not modify drastically the quadrupole coupling.

The values of the quadrupole relaxation constant λ are plotted against T^{-1} in figure 2. In table 2 are reported the values of the parameters which control the hydrogen hopping rate ν , as deduced from fitting the $\lambda(1/T)$ data assuming an Arrhenius behaviour for the hydrogen jump frequency and a Gaussian distribution of the activation energy. The values of the pre-exponential factors ν_0 take into account the existence of a proportionality coefficient $\alpha \approx 5$ between λ and ν in the low-jump-rate regime. This coefficient was estimated from the value of λ at the maximum of the $\lambda(1/T)$ curve, which

depends on the ratio of the quadrupole frequencies associated with the static component of the EFG tensor to the quadrupole frequencies associated with the fluctuating component (Baudry and Boyer 1987). In table 2 are included the jump rate parameters obtained for different hydrides of c-Zr₂Ni (Chikdene *et al* 1988b).

Three interesting features emerge from the PAC data. First, the values of the parameters E_a and ν_0 which determine the hopping rate in the amorphous hydrides do not depend on the hydrogen concentration. Secondly, these values are very close to those measured in c-Zr₂NiH_{2.1}. Finally, the data relative to a-Zr₂NiH_{4.5} confirm that no broad distribution in the activation energy is revealed by spin-relaxation measurements in the hydrides of glassy Zr₂Ni, as previously indicated by PAC experiments on a-Zr₂NiH_{2.5} (Chikdene *et al* 1988a).

As can be seen from the data in table 2, the activation energy and pre-exponential factor of the hopping rate measured by PAC in different hydrides of c-Zr₂Ni are both highly dependent on the hydrogen concentration. These PAC data are in excellent agreement with the ¹H NMR results recently reported on hydrides of similar compositions (Aubertin *et al* 1987, 1989). The variation in the jump parameters with the hydride composition can be satisfactorily rationalised from the interstitial site geometries and occupancies determined from the neutron diffraction data (Chikdene *et al* 1988c, Chikdene 1989).

In c-Zr₂NiH_{2.1}, the occupancy of Zr₄ sites is close to the saturation if one takes into account H–H repulsion, whereas Zr₃Ni and Zr₂Ni₂ sites are empty. The low activation energy and pre-exponential factor measured for this hydride are consistent with a diffusion pathway generated from hydrogen jumps between Zr₄ sites exclusively. Significantly higher values of the same parameters were measured for c-Zr₂NiH₃ where the diffusion is reasonably believed to be primarily controlled by hydrogen jumps within the partially filled sublattice of Zr₃Ni sites. The observation of a narrow distribution in the activation energy (see table 2) is in agreement with recent measurements of ¹H NMR relaxation rates (Aubertin *et al* 1989). Further significant increase, possibly related to H–H interactions, is observed on the activation energy in c-Zr₂NiH_{4.8}. At this composition the neutron diffraction data indicate the existence of a small population (H_{0.2}) in Zr₂Ni₂ sites. It has been suggested that this fraction of weakly bonded—and then highly mobile—H atoms is associated with the additional Arrhenius process which dominates the ¹⁸¹Ta relaxation rate at low temperatures (Baudry *et al* 1988).

From neutron diffraction experiments (Kaneko *et al* 1983) it has been concluded that hydrogen atoms occupy Zr₄ and Zr₃Ni holes in a-Zr₂NiH_{4.3}. More recently, Harris *et al* (1987) claimed that chemical potential measurements give evidence that Zr₂Ni₂ sites store quite significant amounts of hydrogen in glassy Zr–Ni alloys. If the filling scheme proposed from neutron diffraction and electrochemical investigations is truly achieved in our samples, a broad distribution in the activation energy together with a significant variation in this energy with hydrogen concentration are anticipated in view of the results obtained for the hydrides of c-Zr₂Ni. As mentioned before, such effects are actually not observed in the PAC experiments which rather indicate that the hydrogen atoms are placed in fairly similar environments. Moreover, the close similarity of the jump rates measured in a-Zr₂NiH_x and in c-Zr₂NiH_{2.1} suggests that the hydrogen atoms occupy Zr₄ sites and migrate within a network of adjacent Zr₄ tetrahedra in the two hydride phases under study.

Using a statistical model based on a random packing of icosahedral atomic clusters and incorporating H–H repulsion effects, the number of Zr₄ tetrahedra available to hydrogen in a-Zr₂Ni is easily estimated. With a minimum distance of nearly 2 Å between

hydrogen neighbours, the maximum occupancy of Zr₄ holes is found to correspond to the composition Zr₂NiH_{1.5}. Then, in order to accommodate hydrogen amounts corresponding to [H]/[M] ratios greater than 0.5 in Zr₄ sites, it is necessary to assume that permutations between Zr and Ni atoms occur in the amorphous lattice under hydrogenation. If short-range ordering is introduced in the model, the number of Zr₄ tetrahedra available to hydrogen can be estimated as a function of the Cowley–Warren ordering parameter (Mangin 1983). The value of the Cowley–Warren coefficient calculated assuming that all the H atoms are localised in Zr₄ sites is 0.37 and 0.89 for the compositions Zr₂NiH_{2.5} and Zr₂NiH_{4.5}, respectively. Such values correspond to a strong demixing effect which is compatible with recent observations made by electron microscopy on a-(Zr_xNi_{1-x})H_y compounds (Cziraki *et al* 1988). The microstructure of these hydrides was found to display Zr-rich zones corresponding to a high H concentration.

It is worth noting that the value of the pre-exponential factor ν_0 of the jump frequency is three orders of magnitude lower than the frequency of the local vibration modes of hydrogen measured by inelastic neutron scattering (Kaneko *et al* 1983). Such a strong reduction in the jump frequency can be understood if blocking effects take place because the H concentration closely approach the maximum concentration permitted by repulsive H–H interactions within a particular interstitial sublattice. This type of situation is achieved in c-Zr₂NiH_{2.1}. So, it can be reasonably admitted that the demixing effect takes place progressively during hydrogenation, in such a way that the occupancy of Zr₄ sites is close to the maximum value permitted by H–H repulsions.

Clearly, the absence of a broad distribution in the activation energy of hydrogen jumps can result from short-range ordering, because the hydrogen diffusion takes place in zirconium-enriched regions which are expected to display a greater homogeneity than the structure of the alloy before hydrogenation. However, we believe that collective phenomena can also play a significant role in this respect. Preliminary μ SR experiments conducted on c-Zr₂NiH_{4.8} and glassy Zr₂NiH₄ suggest that muon and hydrogen motions are strongly correlated (Boyer and Baudry 1989). A narrowing effect due to correlations between hydrogen jumps may be anticipated on the distribution of activation energies measured in PAC or NMR experiments. The reducing factor on the width of this distribution can be roughly estimated as the square root of the number of H atoms in a ‘diffusing cluster’.

One last point deserves some comment: as previously noted, the difference between the quadrupole couplings measured in a-Zr₂Ni and its hydrides is surprisingly small (less than 10%). In the hydrides of c-Zr₂Ni this difference is between 30% and 50% according to the H concentration, the quadrupole frequency being lower in the presence of hydrogen (Chikdene *et al* 1988b). No clear explanation can be given at present for such a different behaviour. It has been suggested that this rather surprising result could originate from d-orbital mixing effects in the s–d interaction between Zr and H atoms (Chikdene *et al* 1988a). However, as a result of possible demixing effects, the local environment of Ta probes in the amorphous hydrides probably differs significantly from the environment of Ta (Zr) atoms in the crystalline hydrides. So, the meaning of any comparison between the effects of hydrogen on the EFG measured at Ta (Zr) sites in crystalline and amorphous hydrides of Zr₂Ni is doubtful.

In short, it can be said that spin-relaxation measurements on the ¹⁸¹Ta stationary probe in substitution on Zr sites suggest that demixing effects take place in glassy Zr₂Ni during the exothermic hydriding reaction in such a way that H atoms have a Zr₄ coordination. The absence of a broad distribution in the activation energy which controls the hydrogen hopping rate is confirmed. However, this result does not permit any

conclusion to be drawn concerning the site and saddle-point energy distributions in the uncharged glassy alloy. Following the observations reported for hydrides of a-CuTi and Zr_2Ni , it is believed that similar microsegregation phenomena can occur in the hydrides of other intermetallic glasses. In particular, it is believed that a-($Ti_{65}Ni_{35}$) H_x could be an interesting candidate for further investigations in this field.

Acknowledgments

Thanks are due to R Longobardi and J P Pezetti for their valuable collaboration in sample preparation.

References

- Abelard P and Baumard J E 1982 *Phys. Rev. B* **26** 1005
- Aubertin F, Campbell S J, Pope J M and Gonser U 1987 *J. Less-Common Met.* **129** 297–303
- 1989 *Proc. 8th Int. Conf. on Hyperfine Interactions (Prague, 14–19 August 1989)* at press
- Baudry A, Boyer P and de Oliveira A L 1982 *J. Phys. Chem. Solids* **43** 871–80
- Baudry A and Boyer P 1987 *Hyperfine Interact.* **35** 803–7
- Baudry A, Boyer P and Chikdene A 1988 *J. Less-Common Met.* **143** 143–50
- Bernas H, Traverso A and Janot C 1986 *Proc. Workshop on Amorphous Metals and Semiconductors (Coronado, CA, 12–18 May 1985) (Acta Scr. Metall. Proc. Ser. 3)* ed P Haasen and R Jaffee (Oxford: Pergamon).
- Boyer P and Baudry A 1989 *Inst. Phys. Short Meet. Ser. 22* (Bristol: Institute of Physics) pp 65–72
- Chikdene A 1989 *Thesis* Université Joseph Fourier, Grenoble
- Chikdene A, Baudry A and Boyer P 1988a *J. Phys. F: Met. Phys.* **18** L187–93
- 1988b *Proc. Int. Symp. on Metal-Hydrogen Systems (Stuttgart, 4–9 September 1988)* vol I, pp 443–8
- Chikdene A, Baudry A, Boyer P, Miraglia S, Fruchart D and Soubeyroux J L 1988c *Proc. Int. Symp. on Metal-Hydrogen Systems (Stuttgart, 4–9 September 1988)* pp 219–24
- Crouch M A, Havill R L and Titman J M 1986 *J. Phys. F: Met. Phys.* **16** 99–108
- Cziraki A, Fogarassy B, Tompa K, Bakonyi I, Lovas A and Schone H E 1988 *Proc. Int. Symp. on Metal-Hydrogen Systems (Stuttgart, 4–9 September 1988)* vol I, pp 355–60
- Forker M 1973 *Nucl. Instrum. Methods* **106** 121–6
- Fuda K, Kishio K, Yamauchi S and Fueki K 1985 *J. Phys. Chem. Solids* **46** 1141–6
- Harris J H, Curtin W A and Tenhover M A 1987 *Phys. Rev. B* **36** 5784–97
- Kaneko H, Kajitani T, Kirabayashi M, Ueno M and Suzuki K 1983 *J. Less-Common Met.* **89** 237–41
- Maeland A J 1986 *Hydrogen in Disordered and Amorphous Solids* ed G Bambakidis and R C Bowman Jr (New York: Plenum) pp 127–38
- Mangin Ph 1983 *Les Amorphes Métalliques (Aussois, 1983)* (Paris: Les Editions de Physique) pp 175–317
- Richards P M 1983 *Phys. Rev. B* **27** 2059–72
- Richards P M and Shinar J 1987 *J. Phys. F: Met. Phys.* **17** 1659–69
- Rodmacq B, Billard L, Maret M and Chamberod A 1988a *Proc. Int. Symp. on Metal-Hydrogen Systems, (Stuttgart, 4–9 September 1988)* vol I, pp 349–54
- Rodmacq B, Maret M, Laugier J, Billard L and Chamberod A 1988b *Phys. Rev. B* **38** 1105–15
- Suzuki K 1983 *J. Less-Common Met.* **89** 183–95