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PAC AND μSR INVESTIGATIONS OF LIGHT INTERSTITIAL DIFFUSION IN INTERMETALLIC HYDRIDES

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PAC and μSR Investigations of Light Interstitial Diffusion in Intermetallic Hydrides

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Abstract

Specific aspects of the Perturbed Angular Correlation (PAC) of γ-rays concerning its application to the study of atomic diffusion in solids are presented. PAC results recently obtained on the ^{181}Ta probe in several crystalline and amorphous phases of Zr_2Ni hydrides are briefly summarized. Preliminary μSR results relative to these intermetallic hydrides are presented and compared to the PAC data.

Introduction

The microscopic study of hydrogen diffusion in metallic hydrides has received a great deal of attention in the past ten years. Most investigations in this field have been conducted with quasi-elastic neutron scattering and ^{1}H NMR. However, less widespread techniques such as the perturbed angular correlation (PAC) of γ-rays emitted in cascade by a radioactive nucleus, and the spin rotation or relaxation of the positive muon (μSR) are also tools of choice for such investigations. Both techniques make use of the anisotropy properties of the desintegration of a spin-polarized probe. The quantity of interest for deducing informations about hydrogen motions is the depolarization rate of the spins. However, it should be underlined that the two techniques offer both different and complementary points of view on the dynamics of interstitial hydrogen atoms or vacancies.

The μ^+ is a diffusing interstitial probe which in highly-concentrated hydrides behaves as a tracer for hydrogen diffusion. With a spin 1/2 and a magnetic moment of 8.90 μ_N , the muon is able to sense very low magnetic fields. When implanted in non-magnetic hydrides it experiences the local field originating from the dipole moments of the nearby protons and metallic nuclei. The measurement of the depolarization rate of the implanted muon beam give access to the correlation time characteristic of random fluctuations in the local field experienced by the muon in the course of its diffusive motion. Several transverse-field μSR studies show that strong correlation effects exist between muon and hydrogen jumps (1-3). As a consequence the relation between the measured correlation time of dipolar fluctuations and the diffusion of μ^+ is far from being straightforward. Let us add that the muon site can be

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uniquely characterized from the depolarization rate measured at low temperature, i.e. when the muon is at rest.

In PAC experiments on non-magnetic hydrides a stationnary radioactive nucleus is used as a quadrupolar probe sensitive to the local electric field gradient (efg) produced by the charge environment. Magnetic dipole interactions can also be present, but they are smaller by 2 or 3 orders of magnitude and then quite negligible. If the efg fluctuations which cause the relaxation of the nuclear spins are due to the motions of nearby hydrogen atoms or vacancies, the correlation time of the quadrupolar fluctuations is just the mean residence time of the moving species in its equilibrium position. In order to detect properly quadrupole relaxation effects, hydrogen concentrations corresponding to the presence of at least one interstitial atom or vacancy in the vicinity of the probe are needed. Then the PAC technique is not appropriate for investigating diffusion in systems presenting very low concentrations of diffusing species. Pionneer PAC investigations of diffusion in solids were carried out by our group in zirconia-based ionic conductors with oxygenvacancy concentrations of $\simeq 5\%$ (4). Finally, it is worth to observe that the PAC probe is mostly a substitutional impurity in the metallic lattice. Nevertheless, no specific effects due to hydrogen trapping have been detected in PAC experiments conducted on metallic hydrides.

Quadrupole relaxation phenomena can also be observed by NMR on stationnary probes. However, in practice, the relaxation caused by diffusion effects is obscured by other contributions for almost all the candidates for studies in hydrides of interest. An exception is ^{45}Sc which has been used as an NMR probe for studies in scandium hydrides(5).

Among the numerous intermetallic lattices able to absorb large amounts of hydrogen, of special interest are those formed between early-transition (Ti,Zr,Hf) and late-transition (Co, Ni, Cu, Rh, Pd...) elements. Such intermetallic alloys are able to form hydrides in both amorphous and crystalline phases, and are then good candidates for investigating and comparing the mechanisms of hydrogen diffusion in the two phases. Furthermore, the question arises as whether the diffusion in highly disordered lattices is actually controlled by a broad distribution of potential barriers as it is reasonably anticipated (6). Recent studies on a-Ti_2NiH_x (7) and a-Zr_2NiH_x (8) by ^{1}H-NMR and ^{181}Ta-PAC respectively seems to indicate that such is not always the case.

In this paper we first present some specific aspects of the PAC spectroscopy concerning the study of atomic diffusion in condensed matter. Then, ^{181}Ta PAC data recently obtained in several crystalline and amorphous phases of Zr_2Ni hydrides are briefly summarized. Finally, these results are compared to the preliminary μSR data collected at the ISIS facility.

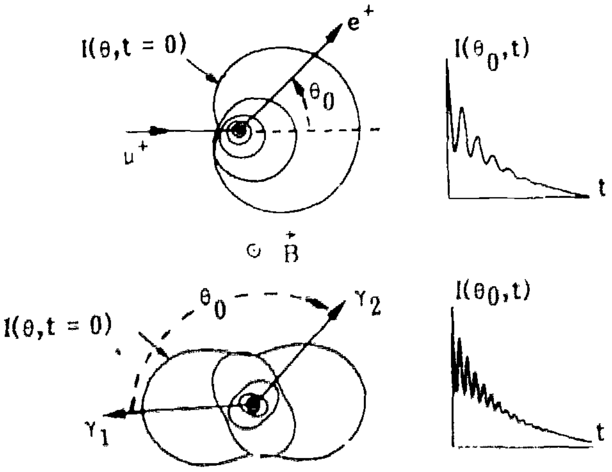

Fig. 1: Schematic description of transverse-field μSR (up) and PAC (down) experiments. The rotation of the asymmetric intensity patterns relative to the photon γ_2 and the positon emitted by the spin-polarized nucleus and the muon respectively takes place at the spin-precession frequency ω_L around the direction of the applied magnetic-field. The damping on the oscillating patterns reflects the depolarization effect produced by inhomogeneities and/or time-dependent fluctuations in the local field sensed by the muon or the nucleus.

Quadrupole relaxation in PAC

The basic principle of PAC and μSR experiments is illustrated in Figure 1. By looking at this figure the reader can observe the close similarity between the foundations of these two spin-precession techniques. The PAC technique is founded on the time-differential measurement of the intensity $I(\theta,t)$ of the gamma radiation emitted anisotropically by a spin-polarized nuclear level. In an appropriate γ_1-γ_2 nuclear cascade, the polarization of the intermediate level is achieved by selecting a fixed direction for the detection of the first radiation γ_1 at time $t = 0$. Two successive radiations are detected in directions separated by an angle θ and the coincidence rate $I(\theta,t)$ is then named "angular correlation function" of the nuclear cascade. When implanted in condensed matter the emitting nuclei experience electric and/or magnetic hyperfine fields during the lifetime τ of the intermediate state, and as a result a time-dependent perturbation of the angular correlation function takes place.

In our experiments on Zr_2Ni hydrides, ^{181}Ta in substitution on Zr sites was used as a PAC probe. The widely-used 133keV-482keV cascade of this nucleus is fed by β-decay from ^{181}Hf ($T_{1/2} = 45$ days) . With a spin $I = 5/2$, a quadrupole moment $Q = 2.5$ barn and a lifetime $\tau = 1.54\ 10^{-8}$ s, the intermediate level of this cascade is a highly sensitive quadrupole probe. In a polycrystalline sample, the time-dependent perturbation factor of the anisotropy of the ^{181}Ta cascade can be expressed as follows:

$$G_2(t) = e^{-\lambda t} S_{20}(\eta) + \sum_{n=1}^{3} e^{-\lambda t} P_n(t)\, S_{2n}(\eta) \cos 2\pi\nu_n t \quad (1)$$

If the exponential terms are ignored, the above expression describes a situation in which the quadrupolar probe interacts with a single randomly-oriented static efg. The interaction can be characterized by the coupling frequency ν_Q and the asymmetry parameter η of the efg tensor. The modulation frequencies are related to ν_Q through $\nu_n = f_n(\eta)\ \nu_Q$ .In addition to the oscillating terms we note the existence of a "hard-core" term $S_{20}(\eta)$ which results from the fact that part of the initial polarization is preserved in the presence of interactions with static efgs oriented at random. With a time resolution of $5\ 10^{-10}$ s now currently available, quadrupole interactions corresponding to modulation frequencies between 20 MHz and 300 MHz can be detected by PAC on the ^{181}Ta probe.

The damping factor $P_n(t)$ affects the oscillating part of $G_2(t)$ only. It accounts for the existence of static efg inhomogeneities which can be reproduced in most cases by a Lorentzian $[P_n(t) = \exp(-\delta\nu_n t)]$ or Gaussian $[P_n(t) = \exp(-1/2\ \delta^2\nu_n^2 t^2)]$ distribution of quadrupole coupling frequencies, with a relative width δ. The linewidths $\delta\nu_n$ can be understood as the result of a loss of coherence due to dephasing effects in the precession of the spins in the inhomogeneous local efg.

The exponential factor $\exp(-\lambda t)$ which equally affects the hardcore term and the amplitudes of the oscillating terms, conveys the relaxation of the spins in the presence of time fluctuations in the field gradient. The correlation time τ_c of the quadrupolar fluctuations sensed by the PAC stationnary probe is also the mean residence time τ_R of the moving atom or vacancy on its equilibrium position. The characterization of spin- relaxation effects by a single relaxation rate λ is strictly valid for asymptotic conditions of very slow ($\tau_c\nu_n \gg 1$) and very fast ($\tau_c\nu_n \ll 1$) fluctuations only. If an exponential correlation function is postulated for the fluctuations, the relaxation rate λ can be then related in a simple way to the correlation time τ_c within the asymptotic limits: $\lambda = \tau_c^{-1}$ and $\lambda = A\langle(\nu_Q^f)^2\rangle\tau_c$ respectively.The average should be taken over the different orientations and amplitudes of the field-gradient tensor, and$A \simeq 3.96\ 10^3$ for ^{181}Ta. This non lattice-specific description of relaxation effects has been shown to be a valuable approximation of more realistic models within quite large ranges of fluctuation rates (9). However, when static and time-fluctuating efg components are simultaneously present at the probe site as it is expected in hydrides of non-cubic metallic lattices, λ is actually found to be proportionnal to τ_c^{-1}, i.e. $\lambda = \alpha\tau_c^{-1}$, in the range of slow fluctuations. $\alpha = 1$ in the absence of any static efg component, and then decreases together with the relative contribution of the fluctuating component. In ^{181}Ta PAC spectroscopy, the above relationships between λ and τ_c constitute a quite good approximation everywhere but for τ_c values $\sim 10^{-8}$ s. If the jump rate $\nu = \tau_c^{-1}$ of the diffusing species obeys an Arrhenius law $\nu = \nu_0 \exp(-\frac{E_a}{kT})$ as it is expected for a classical hopping process, we obtain the $\mathrm{Ln}\lambda$ vs.T^{-1} pattern displayed in Figure 2.

The similarity of this symmetrical pattern with the $\mathrm{Ln}(T_1^{-1})$ vs.T^{-1} plot used in NMR should be noted. For the essential it is made of two straightlines with opposite slopes corresponding to slow- and fast-relaxation regimes respectively, separated by a flat maximum corresponding to jump frequencies $\simeq 10^8 s^{-1}$. Around this maximum, the PAC spectra cannot be properly reproduced with a single relaxation rate, but it is yet possible to define a relaxation rate which accounts roughly for the damped behaviour of the perturbation factor. The value λ_{max} observed at the maximum can be used to estimate the ratio α between λ and ν in the slow-fluctuation regime.

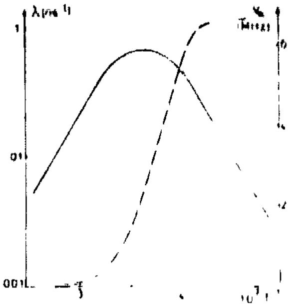

Fig. 2 : Temperature behaviour of the quadrupolar relaxation rate λ and coupling frequency ν_Q in PAC spectroscopy. The values indicated are typical of ^{181}Ta PAC experiments in Hydrides.

Also in Figure 2 is shown the decrease of the quadrupole coupling frequency which takes place together with the spin-relaxation phenomenon. This "motional decreasing" effect is comparable to the motional narrowing effect observed on the dipolar linewidth in NMR and μSR spectroscopies. In practice, this effect is expected to set in as soon as the jump rate becomes comparable with the quadrupolar linewidth $\delta\nu_1$ corresponding to the lower modulation frequency ν_1. In ^{181}Ta PAC experiments the motional decreasing of the quadrupole coupling frequency appears typically for jump rates $\nu \simeq 10^7 s^{-1}$. Assuming the diffusion takes place on a cubic lattice, such a value corresponds to a self-diffusion coefficient $D \simeq 10^{-9}$ cm^2 .s. The temperature dependence of the quadrupole frequency yields an absolute, non model-dependent estimation of the hopping rate. It also allows to determine the static component of the quadrupole coupling , which corresponds to the residual frequency observed on the high-temperature side. In conclusion, the PAC technique yields accurate values of activation energy, but only approximate values for the residence time of the moving atom.

The observation of low relaxation rates is limited by the "time window" of the PAC probe, and also by the signal to noise ratio which depends on the number of fortuitous coincidence events. In practice, the time scale extend roughly over 5τ, τ being the lifetime of the nuclear spin level. For ^{181}Ta $5\tau \simeq 8\ 10^{-6}$ s, which allows to detect relaxation times as long as $5\ 10^{-7}$ s under the best experimental conditions. Consequently, quadrupolar fluctuations with correlation times standing roughly between 10^{-12} s and 10^{-6} s can be observed by ^{181}Ta PAC spectroscopy.

Summary of ^{181}Ta PAC results in Zr_2Ni hydrides.

The main results deduced from the PAC relaxation data obtained by our group in crystalline and amorphous phases of several Zr_2Ni will be now briefly summarized. Several papers have been published on the subject (8,10).

In crystalline hydride compositions, the activation energy of hydrogen jumps increases with the hydrogen concentration from 0.15 eV for $Zr_2NiH_{2.1}$ to 0.38 eV for $Zr_2NiH_{4.8}$. For the last concentration which corresponds to hydrogen saturation, a second Arrhenius process corresponding to a very low activation energy (0.11 eV) is observed and is attributed to the motion of H atoms weakly bound in 2Zr2Ni tetrahedral holes. For the hydride compositions $Zr_2NiH_{2.1}$ and Zr_2NiH_3, the PAC data well agree with the ^{1}H NMR data of Aubertin et al.(11). The values of the pre-exponential factors display a broad dispersion on about 3 orders of magnitude. This could be partially explained by blocking effects related to site occupancies and short range interactions between H atoms in the different sublattices of interstitial holes. Plausible jump pathways for the protons can be proposed by combining PAC relaxation results with interstitial site occupancies determined by neutron diffraction(12).

In the amorphous hydride $Zr_2NiH_{2.6}$ the PAC experiments indicate a lower activation energy (0.135 eV) in comparison to those observed in crystalline hydrides of nearby compositions. Such a result agrees with the observations made in other amorphous hydride phases and is usually considered as an evidence for the existence of easier diffusion pathways for interstitial hydrogen in highly disordered lattices. More surprising is the absence of any broad distribution for the activation energy. A similar situation has already been found in $Ti_{65}Ni_{35}H_{1.5}$ by T_1-NMR measurements (7) These two systems appear as exceptions among a lot of disordered hydride phases till now investigated, and speculative explanations only can be put forward about this point which remains open. Finally, the hydrogen hopping rate does not change by varying the composition from $H_{2.6}$ to $H_{4.5}$, and this does not seems to be related to an anomalous volume expansion.

Results of μSR Experiments in Zr_2Ni Hydrides

Studies on Zr_2Ni hydrides using μSR spectroscopy have been undertaken on the muon beam of the ISIS facility at R.A.L. This pulsed source of low-energy muons is well adapted to measurements of rather low depolarization rates ($\leq 0.1\ \mu s^{-1}$) such as those usually observed in non- magnetic metallic hydrides. Presently, the structure of the muon pulse in two successive bunches separated by 330 ns does not permit to work with precession frequencies higher than $\simeq$ 3MHz ($B \simeq 200G$). In such conditions, depolarization rates in the range .01-1MHz can be measured in transverse-field experiments. This corresponds to correlation times for the dipolar magnetic fluctuations standing roughly between 10^{-8} s and 10^{-6} s. This range can be extended towards longer correlation times in experiments without applied magnetic field. We report here some preliminary results obtained in transverse-field ($B = 200$ G) μSR experiments.

Figure 3 displays the temperature dependence of the depolarization rate λ in crystalline $Zr_2NiH_{4.8}$ and amorphous Zr_2NiH_4. The raw data were analyzed assuming an exponential depolarization function and inserting in the expression of the time-dependent counting rate a background component. The precessing background was determined by replacing the actual sample by a hematite dummy. The same figure allows also to compare the depolarization rates measured in Zr_2Ni hydrides and non-charged Zr_2Ni. It clearly appears that the contribution of the metallic lattice to the depolarization is quite small and can be reasonnably neglected. The dipolar and quadrupolar fluctuation rates measured by μSR and PAC respectively in a-$Zr_2Nih_{4.5}$ and crystalline $Zr_2NiH_{4.8}$ can be compared from the plots given in Figure 4. The values of τ_c^{-1} relative to the muon diffusion were calculated from the relation $\lambda = \sigma^2 \tau_c$ where σ is the Gaussian linewidth measured at low temperature. For the two samples $\sigma \simeq 0.2$MHz.

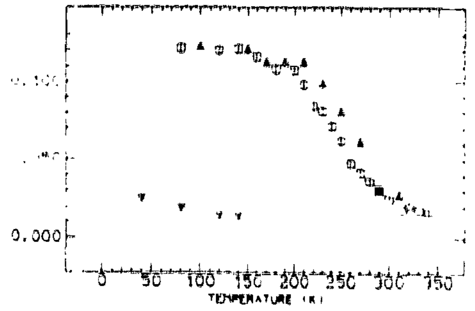

Fig. 3 : Experimental depolarization rates (Lorentzian lineshapes) of μ^+ in Zr_2Ni (∇), $Zr_2NiH_{4.8}$ (Δ), and amorphous Zr_2NiH_4 (□).

Some interesting conclusions can be drawn from these very preliminary data. First, in both hydrides the rate τ_c^{-1} of the dipolar fluctuations appears to be much lower than the quadrupolar fluctuation rate deduced from PAC experiments. For uncorrelated jumps one expects the following relation to hold:

$$\tau_c^{-1} = \tau_\mu^{-1} + \tau_H^{-1} \quad (2)$$

where τ_μ^{-1} and τ_H^{-1} are the muon and proton hopping rates respectively. In such conditions one should always have $\tau_c^{-1} \gtrsim \tau_H^{-1}$, which is just opposite to what is actually observed. The comparison between μSR and PAC relaxation data gives then evidence for the existence of a strong correlation between muon and proton jumps. However, a difference as large as an order of magnitude between the correlation times observed by the two techniques in crystalline $Zr_2NiH_{4.8}$ is hard to explain. Let us note that a very similar difference is found between the correlation times measured by μSR and quasi-elastic neutron scattering in ZrV_2H_x (13).

The second result concerns the activation energy of the hopping rate, which is found to be ~ 20% lower for the muon in the amorphous hydride phase, and roughly the same for both particles in crystalline$Zr_2NiH_{4.8}$. Thus the situation appears as differing from

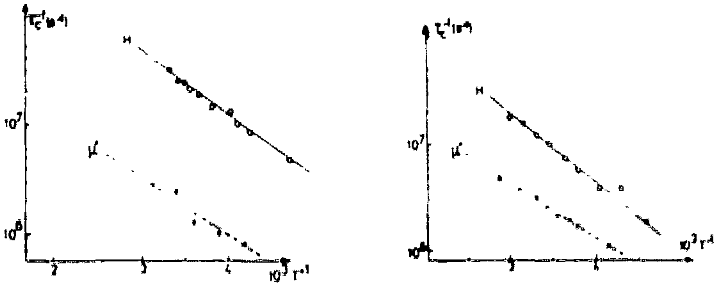

Fig. 4 : Temperature dependence of the inverse of the correlation time derived from μSR (μ^+) and PAC (H) in crystalline $Zr_2NiH_{4.8}$ (left) and amorphous Zr_2NiH_4 (right).

the one observed in other crystallized hydrides such as NbH_x (1), PdH_x (2) and TiH_x (3), in which quite different activation energies but correlation times of the same order of magnitude are found for μ^+ and H motions. We believe that new experiments, including zero-field measurements, on different hydride compositions in both crystallized and amorphous phases could bring more insight into the problem of μ^+-H correlations. We also hope that such measurements can add in understanding why no broad distribution of activation energies is detected in some amorphous hydrides.

The μSR experiments benefited the collaboration of A.CHIKDENE, S.COX, P.DALMAS and S.SCOTT.

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