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Muon spin relaxation in hydrogen-loaded ZrV_2

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Abstract. Using the zero-field μSR technique, the diffusional behaviour of muons in a hydride system was investigated. The sample was made from ZrV_2 that was loaded with hydrogen up to a composition of $ZrV_2H_{4.14}$. The results differ slightly but significantly from earlier transverse-field μSR data.

1. Introduction

It is well known that a few intermetallic compounds eagerly take up hydrogen on interstitial sites thereby forming interstitial hydrides. One such compound is ZrV_2, and the ZrV_2H_x system is of particular interest for several reasons. The structure of the mother compound is of the simple C15 Laves phase type and it therefore represents a good prototype material for a wide range of structurally related materials. Also of great importance is the wide range of hydrogen concentrations, $0 \leqslant x \leqslant 6$, that is accessible to investigations. Furthermore, Zr and V have different nuclear magnetic moments which give information on the sites because of their contributions to the dipolar width of the μSR signal. Thereby, one can in principle determine in which interstitial sites the muons may be localized [1]. However, the aim of the present investigation is to determine the diffusional behaviour of the muons in the material.

In an earlier experiment, Hempelmann *et al* [1] investigated muon diffusion by means of transverse-field (TF) μSR for a series of compositions of ZrV_2H_x. They came to the surprising conclusion that the muon correlation time is significantly larger than the hydrogen residence time, from which they assumed that the muon motion is slower than that of hydrogen. Also, the activation energy of the μ^+-diffusion was found to be lower than that for hydrogen diffusion.

In the present investigation we carried out a zero-field (ZF) μSR experiment on a ZrV_2 hydride in order to get more insight into the diffusion process of the muon in this material. Also, one should in principle be able to derive from muons in ZrV_2H_x a more general explanation for the behaviour of muons in the whole class of similar materials (e.g. NbH_x, $LaNiH_x$ or $NiTiH_x$).

2. The system ZrV_2/H

ZrV_2 is an intermetallic compound of the cubic Laves phase type. It is a brittle material that ignites upon pulverization. ZrV_2 absorbs hydrogen very easily, without any activation

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procedure, forming a broad solid-solution regime extending from ZrV_2 to approximately ZrV_2H_6. This reaction does not change the host lattice structure, but it leads to a considerable increase of the lattice constants (α-phase). There are also a number of ordered phases that can be observed at lower temperatures (i.e. lower than approximately 320 K) such as ZrV_2H_2 (fct), ZrV_2H_3 (bco), ZrV_2H_4 (fct) and ZrV_2H_6 (bco) (β-, γ-, δ- and ε-phases) [2].

In a series of neutron diffraction experiments, Didisheim *et al* [3] determined the hydrogen sites. For concentrations lower than $ZrV_2H_{2.8}$ the hydrogen first enters ZrV_2 sites and then at higher concentrations also ZrV_3 sites.

In a series of neutron vibrational spectroscopy experiments, Hempelmann *et al* [1] were able to demonstrate that the hydrogen occupies another third site at concentrations higher than $ZrV_2H_{3.6}$, and from a complementary μSR experiment in a transverse field [1] this was suggested to be the V_4 site.

3. Sample preparation

The ZrV_2 compound was prepared by induction melting of Zr and V in a cold Cu crucible under an argon inert-gas atmosphere. Temperatures up to 2000 °C were used and by repeatedly melting and remelting an apparently homogeneous compound was obtained.

However, according to the phase diagram, ZrV_2 is formed in a peritectic solid-state reaction at a temperature of 1300 °C. To obtain a single-phase compound the sample material was sealed into a silica tube, together with a getter material, and annealed for two weeks at 1100 °C in an argon atmosphere. From a metallographic study, the resulting material proved to have less than 1% of phases other than ZrV_2, a value that was also confirmed by x-ray diffraction analysis [4].

In the next step the sample was hydrogenated at room temperature. The metal disintegrates into a fine powder and within a few hours the stoichiometric amount of hydrogen gas is absorbed (the equilibrium pressure at room temperature is below 1 mbar). From the initial pressure of hydrogen, a composition of $ZrV_2H_{4.04\pm0.10}$ was calculated.

From the position of the peaks in an x-ray pattern of the α-phase ($T = 336$ K), the lattice parameters could be determined. The resulting value, $a_0 = 7.875 \pm 0.005$ Å, corresponds to a composition of $ZrV_2H_{4.14\pm0.05}$ [5], which agrees with the gas-volumetric value within the limits of error.

4. Experimental details

The experiment was carried out in a longitudinal geometry at the ISIS pulsed muon beam line at the Rutherford Appleton Laboratory, UK, and the magnetic field at the sample position was compensated to zero. The sample temperature for the zero-field measurements was varied from 20 to 297 K (i.e. within the δ-phase) using a closed-cycle refrigerator. Transverse-field data were taken at selected temperatures with an applied field of 20 G in order to determine the asymmetry parameter needed in the fitting of the ZF data using the expression

$$a_0 P(t) = (N_F - \alpha N_B)/(N_F + \alpha N_B) \tag{1}$$

(where a_0 = instrumental asymmetry and N_F and N_B are the forward and backward count rates). The target holder was made from silver. It consisted of a thick plate with a recessed area of 38 mm diameter and a depth of 3 mm which led to a sample volume of 3400 mm^3. Even with the rather large cross-section of the muon beam, the large size of the sample means that the observed signal stems primarily from the sample, and consequently the

background signal should be low. Nevertheless, we cannot totally exclude slight systematic errors that may originate from the uncertainty in the determination of the background.

5. Data analysis

Our approach for deriving the correlation time τ_c from the ZF data follows the strong-collision version of the Kubo–Toyabe model, given by Hayano *et al* [6]. This model implies that there are two parameters influencing the shape of the relaxation curve: the correlation time τ_c, i.e., the average time between two μ^+-jumps, and Δ, the second moment of the distribution of fields at the muon site. The advantage of using ZF data is their higher accuracy for τ_c^{-1} and the possibility of independently fitting both Δ and τ_c^{-1}.

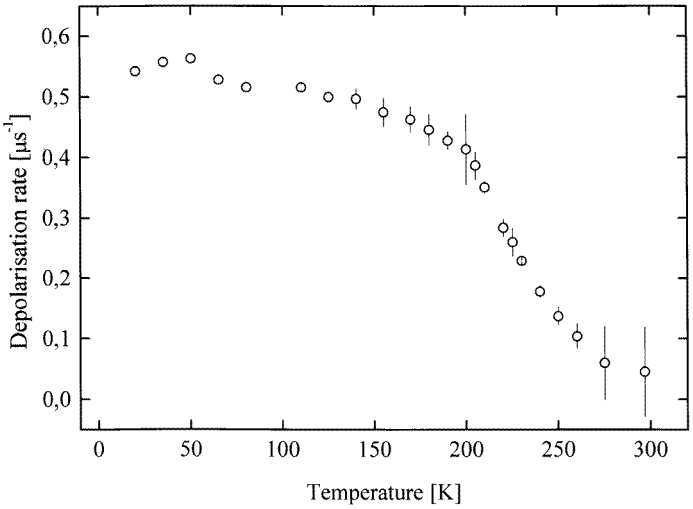

Figure 1. Zero-field Gaussian depolarization rates. The values were obtained from fits for the first few microseconds of the data.

6. Results

In order to describe the overall temperature dependence of the muon relaxation, we initially display the results of a model-independent fit to the data, in which we fit a Gaussian function

$$G(t) = \exp(-\Delta_f^2 t^2) \tag{2}$$

for the first few microseconds of the spectra. The fit parameter Δ_f describes the initial part of the relaxation and is plotted versus temperature in figure 1. The muon behaviour is as follows. Up to $\sim$50 K the muon is static showing an average depolarization rate of 0.55 μs^{-1}. When diffusion sets in, Δ_f decreases down to a value of about 0.4 μs^{-1} at $\sim$200 K. This situation stems from muons that are initially distributed over all of the given sites in the lattice, but, once they gain enough energy (at 50 K), diffuse to the energetically more favourable sites where they remain trapped. At temperatures above $\sim$200 K the muons get released from those traps and long-range diffusion sets in.

In order to quantitatively describe the diffusional behaviour in the temperature range above 200 K, the strong-collision form of the Kubo–Toyabe function was applied and solved

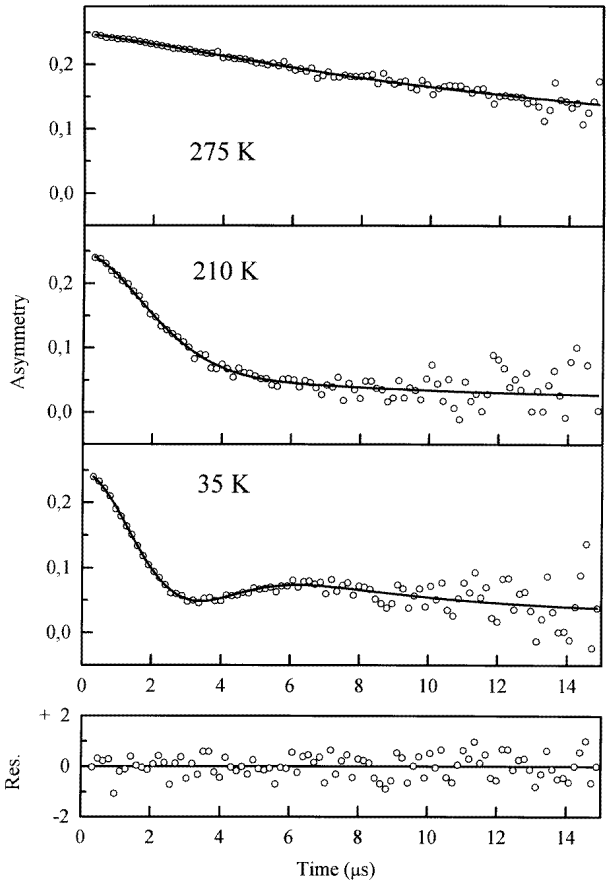

Figure 2. Observed ZF relaxation functions of μ^+s for $ZrV_2H_{4.14}$. The solid lines represent fits with the strong-collision version of the dynamical Kubo–Toyabe function which was solved numerically. The residuals are those of the 210 K function.

numerically in Laplace space with the help of mathematical subroutines. The basic idea is that the observed relaxation function depends on the static linewidth Δ (corresponding to the second moment of the field distribution) and—in the case of diffusion—on the correlation time or muon jump time τ_c. These two parameters cannot be fitted independently when the motion is rapid; therefore a common approach is that of determining the static linewidth where relatively slow diffusion is observed and then keeping this value fixed over an extensive temperature range, where muons move.

In the present investigation, fits to individual spectra with both Δ and τ_c as free parameters gave as the result a continuous decrease of Δ from 0.55 μs^{-1} to 0.40 μs^{-1} at about 200 K. Above this temperature the faster diffusion sets in. Since we associate the slow changes below 200 K with possible changes of muon sites (see also [1]) we determine Δ from the initial part of the fast-diffusion regime. A simultaneous fit of the spectra between 200 K and 230 K gives $\Delta = 0.39 \pm 0.01$ μs^{-1}. A value of $\Delta = 0.39$ μs^{-1} was then used as a fixed value for the determination of correlation times at higher temperatures, where the simultaneous fitting of both parameters is less reliable.

Figure 2 shows a set of fits of the dynamical Kubo–Toyabe function to the data. Also shown are the residuals for the intermediate temperature. Initially, the static Kubo–Toyabe function decreases similarly to a Gaussian, but then shows a typical recovery to one third of its initial value. This is significantly suppressed as soon as diffusion sets in (at $\sim$50 K) and is very well described by the strong-collision model, as one can see from the fits.

In general, the diffusion of muons exhibits the same behaviour as was described in [1]: muons appear to be essentially static up to 50 K, where some motional narrowing sets in. The slow diffusion that can be observed allows the muons to occupy new sites where they remain trapped (thus leading to the formation of a plateau region). Although this plateau is not very distinct, the transition to the long-range diffusion at temperatures above 200 K is clearly visible.

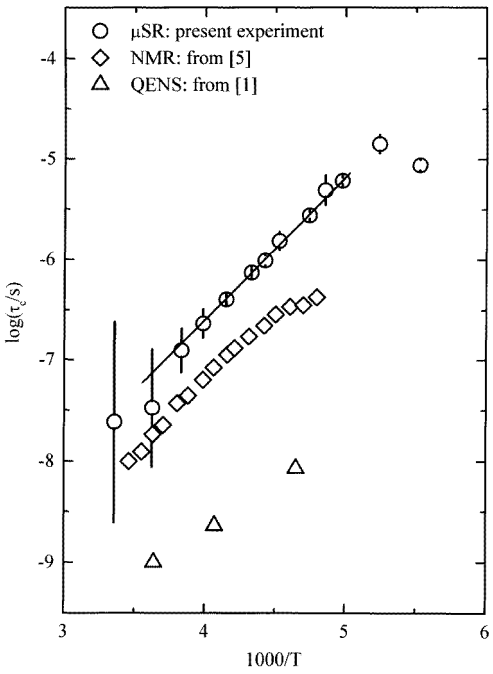

Figure 3. A comparison of correlation times τ_c of μ^+-diffusion (○) and H diffusion as determined by NMR (◇) and QENS (△) investigations.

Figure 3 shows an Arrhenius diagram of the muon jump times for $ZrV_2H_{4.14}$ together with information from NMR and QENS investigations. The solid line is a fit to the resulting correlation times within the temperature region 200–297 K from which we deduce a value of $E_a = 281 \pm 10$ meV for the activation energy of muon diffusion. It should be mentioned that the fits are very sensitive to variations in Δ, which, unfortunately, cannot be determined exactly. Therefore the error in E_a also reflects this uncertainty.

It should also be mentioned that, if one assumes no site changes and a constant Δ of 0.54 μs^{-1}, the corresponding correlation times in figure 3 would be close to those presented in the upper temperature range but would have a curvature similar to that of the NMR correlation times shown in figure 3. In that case, the deduced activation energy would depend on the temperature interval chosen and, as mentioned, the fits to the data would describe the data less accurately in the interval $T = 200$–300 K.

7. Discussion

Several experiments have been carried out to measure muon diffusion properties in different binary metal hydrides: ZrV_2H_x was studied by Hempelmann *et al* [1], Harris *et al* [7] performed experiments on CuTi, Boyer and Baudry [8] studied Zr_2Ni hydrides and Asif *et al* [9] investigated hydrogen-loaded amorphous Ni–Ti alloys. The basic idea is that the muon motion must be strongly correlated to the hydrogen motion since the majority of the available sites for muon diffusive jumps are blocked by the hydrogen. In a regular metal lattice the intrinsic muon diffusion is otherwise faster than that of hydrogen, since the muon is lighter and can diffuse by means of phonon-assisted tunnelling. The muon diffusion parameters in a saturated metal hydride should then be practically the same as for hydrogen in the same system. If, on the other hand, the intrinsic muon rate were slower than that of hydrogen, the muon data on the hydride would also indicate somewhat slower diffusion. This situation could occur for amorphous systems as discussed by Asif *et al* [9].

When we compare the information that we gained for μ^+-diffusion in ZrV_2H_x with data from experiments on H diffusion, we observe the following: the muon correlation times obtained in the present experiment are more than one order of magnitude longer than those obtained for hydrogen in a QENS experiment on ZrV_2H_x [1]. This would imply that muons move considerably more slowly than hydrogen in this system.

On the other hand, the difference is much smaller between correlation times for μ^+s and values that we extracted from the NMR measurements of Skripov *et al* [5], where the diffusion parameters of hydrogen for several C15 hydrides were determined. These correlation times, which we have deduced from figure 3 of reference [5], are also one order of magnitude larger than those from the QENS experiment. However, it must be pointed out that Skripov *et al* [5] do not interpret their data for ZrV_2H_4 as a simple Arrhenius behaviour, but as a combination of one process with a single activation energy and a second process with a distribution of E_as.

Further attention has to be paid to the activation energies: while the QENS measurements presented in [1] indicated 180 ± 30 meV for hydrogen diffusion, the present data correspond to a value of 281 ± 10 meV for μ^+-diffusion. The NMR data [5] included in figure 3 lead to a similar result for hydrogen diffusion in the upper temperature range. It is important to restrict the comparisons to the same temperature range and phase (another QENS experiment which was carried out on the phase $ZrV_2H_{4.0}$ [4] determined a value of 88 ± 31 meV).

When comparing our experiment to former TF-μSR experiments on $ZrV_2H_{4.0}$ [1] we observe some deviations. The conclusion reached in [1] that the muons appear to diffuse significantly more slowly than hydrogen, as measured via QENS, is still valid, but there is a discrepancy as far as the muon activation energies are concerned: while our ZF experiment yields a value of $E_a = 281 \pm 10$ meV, the analysis of the TF data in [1] gave the result $E_a = 145 \pm 20$ meV. Those transverse-field experiments were carried out at field strengths of about 150 G. An analysis of the few TF ($B = 20$ G) points (recorded for calibration purposes) for the present sample would lead to a value of E_a of 125 ± 30 meV, significantly lower than our ZF value. Although we recognize that $B = 20$ G is too low for a reliable TF diffusion experiment, it indicates possible weaknesses of transverse-field experiments on this system. In principle the ZF method should be more reliable for obtaining activation energies, since it is more sensitive than the TF method, especially at both ends of the active temperature interval.

Finally it has to be taken into account that—due to progress in μSR instrumentation—the quality of the present ZF data is far superior to that of the old TF data as far as statistics and determination of the background contribution is concerned. Furthermore, the

theoretical model of strong collisions works very well with our zero-field data, and this model is especially sensitive to changes that originate from diffusion. The prefactor for diffusive jumps of muons in $ZrV_2H_{4.14}$ is now found to be approximately $\tau_0 = 5 \times 10^{-12}$ s, such a correlation time indicating a classical jump motion of the hydrogen in the system.

In summary, the present zero-field μSR experiment has given more reliable results for τ_c than those obtained earlier, but the discrepancies as compared to hydrogen diffusion in the same system (determined using QENS) are still an open question.

Acknowledgments

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