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Muon diffusion in metallic hydride systems

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Abstract

We report measurements of the depolarisation rate of the muon in $ZrTi_2H_{3.6}$ and in $HfV_2H_{0.1}$ in zero field in the temperature range from 15 K to room temperature. The data have been analysed using the Kubo–Toyabe model which yields values of the muon residence times. These are compared to values obtained from QNS and NMR measurements on the same systems. In both cases, we find that, in contrast to the behaviour of most other systems, the diffusion rate of the muon is the same as that of the proton measured by these techniques.

Keywords: Diffusion; Muon; Hydrogen

1. Introduction

The behaviour of hydrogen in metals has been subject of quite intensive investigation for some years and many models have been developed to provide good descriptions of its behaviour in many circumstances [1]. However, the behaviour of muons in metals, being a fairly new subject, is not so fully understood. Although the behaviour of the two isotopes are very similar, there are important differences which are comparable, but, of course, more pronounced than the differences between any other pair of hydrogen isotopes. The positive muon is a charged particle of spin 1/2 and 9 times lighter than hydrogen. When implanted in a metal, after a few picoseconds the muon becomes thermalised. If it now remains fixed on one site, its spin will become depolarised at a rate that depends on the dipolar interaction with the neighbouring nuclei. However, if the muon is diffusing, this depolarisation effect will be reduced because the muon is sampling the field in different sites (motional narrowing). Measurements of the depolarisation rate can, therefore, be analysed to determine the jump rate and, therefore, the diffusion coefficient.

The C15 Laves phase compounds have been extensively investigated due their ability to absorb large quantities of hydrogen which make them a potential compound for battery materials. As part of a programme designed to extend the knowledge of hydrogen diffusion in C15 Laves phase compounds, muon spectroscopy has been used to investigate the diffusion mechanism of the muon in comparison with the hydrogen diffusion in the same material using different techniques.

In the present work we report results obtained on two different C15 Laves phase compounds, namely $ZrTi_2H_{3.6}$ and $HfV_2H_{0.1}$. A comparison between the muon spin relaxation, the nuclear magnetic resonance and the quasi-elastic neutron scattering is given.

2. Experimental details

The muon experiments were carried out at ISIS on the EMU and MUSR spectrometers, Rutherford Appleton Laboratory, UK, using the zero field technique. Most of the measurements were carried out in the temperature range 10–350 K. The alloys used were made by melting the correct proportions of the constituent metals, of purity better than 99.95%, in an argon arc furnace. Before performing the hydrogenation procedure, the samples were well annealed. The ingots obtained were then crushed under argon in a glove box to produce powdered samples with a particle size less than 75 mm. The samples were then hydrogenated (hydrogen purity >99.999%) using Sievert's apparatus and the hydrogen content was calculated by observing the pressure drop in a calibrated

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volume. The structures required, namely cubic C15 Laves phase, were verified by X-ray diffraction at 295 K.

3. Results

3.1. $ZrTi_2$

Unlike other C15 Laves phase compounds, the $ZrTi_2$ C15 Laves phase is formed only when hydrogenated. Furthermore, although the g-sites have the bigger hole, it is only the e-sites which are occupied. This is probably due to the fact that the hydrogen atoms have to order in this geometry to facilitate the formation of this phase. $ZrTi_2$ is also an interesting system to study using muons because both metals forming the alloy have a very weak nuclear moment, and hence any depolarisation observed by the muon will be solely due to the dipolar interaction between the muon and the hydrogen. Fig. 1 shows the normalised asymmetry from which the high frequency fluctuations have been removed by Fourier transformation as a function of time at three temperatures. The time scale has been chosen to accentuate the early part of the relaxation profile which is more sensitive to the value of the second moment. The smooth curves are obtained using the Kubo–Toyabe model [2] with the second moment, $\Delta=0.293\ \mathrm{ms}^{-1}$. Using the second moment for the rigid lattice, we calculated the first-order separation distance between the muon and the hydrogen atoms, which gave a value of $r_{\mathrm{exp}}=2.758$ Å. This value compares well with the calculated value, $r_{\mathrm{cal}}=2.93$ Å, between e-sites using the lattice parameter of 8.16 Å. Fig. 2 shows the correlation time τ_μ of the diffusing muon compared with quasielastic neutron scattering (QNS) data measured on the same sample [3], and the nuclear magnetic resonance (NMR) data obtained by Skripov for the same composition [4]. Unlike most previous results published on metal hydride systems, the correlation time between jumps of the muon τ_μ, at high temperature, fit very well with the correlation times of the proton obtained from the QNS and the NMR.

The activation energy obtained from the three techniques within the experimental error, also agree well, as shown in Table 1.

It is reasonable to assume, from the agreement between the activation energies and the jump rate, that the muon indeed occupies the same site as the proton, i.e. the e-sites in this system.

3.2. $HfV_2H_{0.1}$

In the C15 Laves phase compounds, the sites occupancy of hydrogen follows the model proposed by Westlake [5]. In the present sample, due to the low concentration of hydrogen, only the g-sites are believed to be occupied. Fig. 3 shows the relaxation function obtained at 50 K for $HfV_2H_{0.1}$ during, both cooling and heating. There is a clear difference in the jump rate between the two data sets, although measured at the same temperature. This is probably due to the fact that HfV_2H_x, on cooling, undergoes a phase transition at 120 K, from C15 to tetragonal. Due to this phase transition, the second moments of the muon depolarisation in the two phases are expected to be different and hence it is necessary to correct the second moment of the relaxation function fitted to the data above the transition temperature. However, in the two phases, the hydrogen occupies a tetrahedral site with the same atoms at the vertices and hence the sites are very similar. Furthermore, the vanadium (^{51}V) forming the sample and hence the g-site (2Hf–2V) has a fairly high nuclear

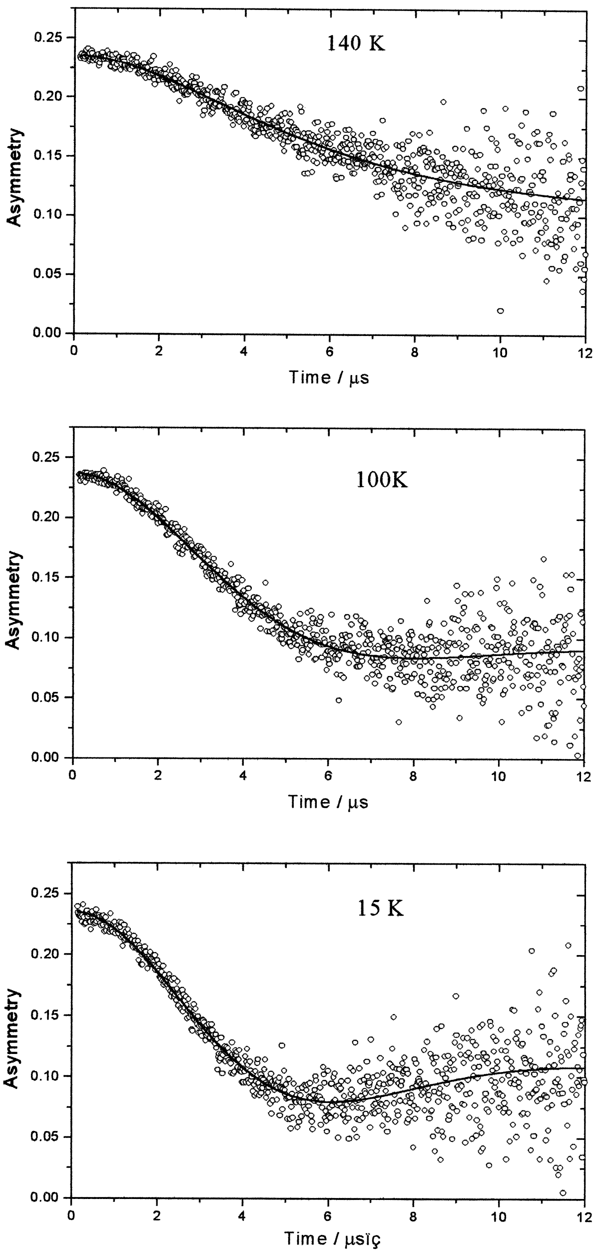

Fig. 1. Fits to the C15 $ZrTi_2H_{3.6}$ data using the dynamic Kubo–Toyabe function at three different temperatures.

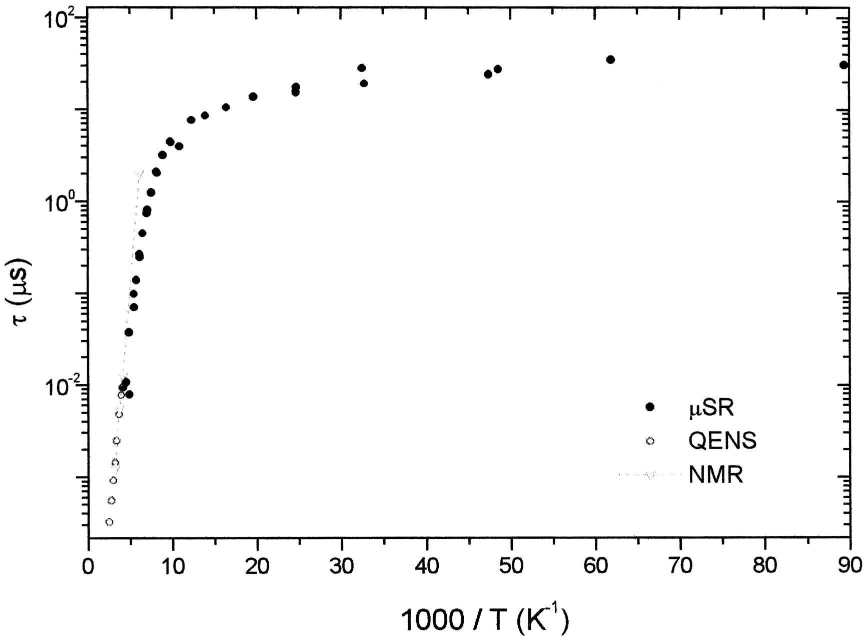

Fig. 2. A comparison of correlation times, τ_c, of μ^+ diffusion (●) and H diffusion as determined by QENS (○) and NMR (▼) for C15 $ZrTi_2H_{3.6}$.

Table 1
Comparison between the activation energies obtained from MUSR, QNS and NMR

Technique used	Activation energies (eV)	Temperature (K)
MUSR	0.16±0.02	150–250
QNS	0.18±0.02	280–450
NMR	0.20±0.02	150–400

moment. Therefore the contribution of vanadium to the depolarisation is not negligible due to the high power of the distance, r, ($\sim r^{-6}$) in the second moment expression, which makes the contribution of the nearest neighbour metal atoms predominant. Zirconium has a weak nuclear moment and hence its contribution can be neglected. We have, therefore, calculated the frequencies of the second moment for the first nearest neighbour of the g-site and

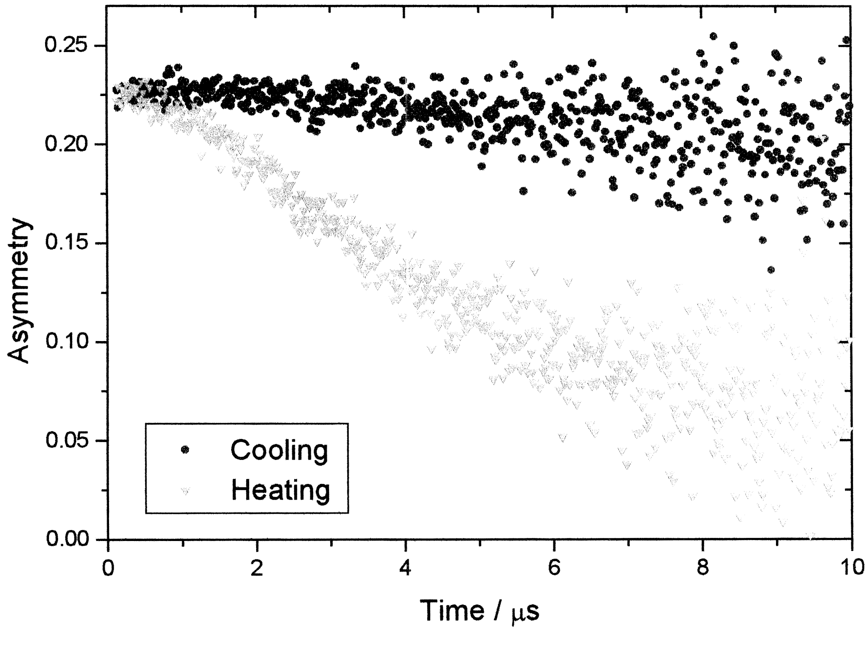

Fig. 3. Data measured at a temperature of 50 K for $HfV_2H_{0.15}$ during both cooling (●) and heating (▼).

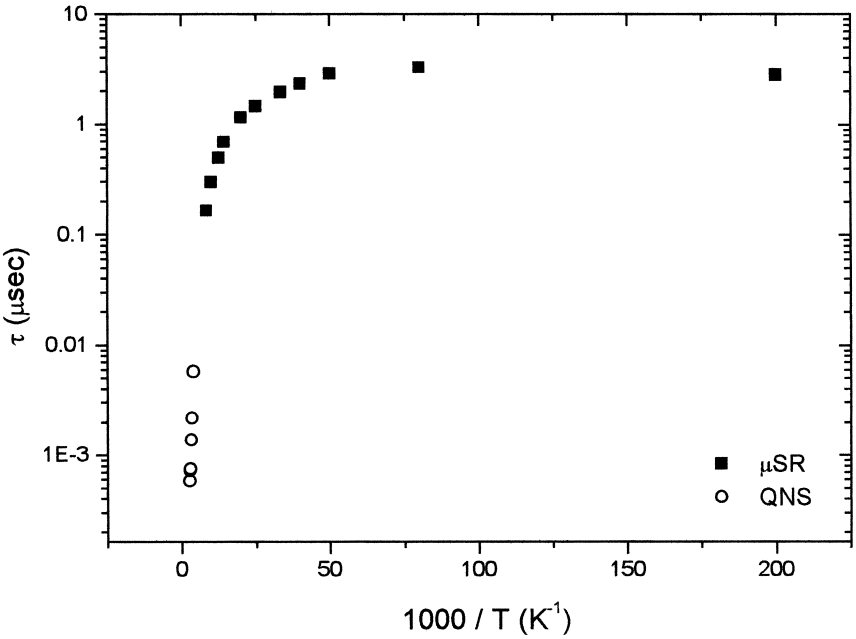

Fig. 4. A comparison of correlation times, τ_c, of μ^+ diffusion (■) and H diffusion as determined by QENS (○) for HfV_2H_x.

also the frequency of the second moment arising only from the vanadium forming the site. It was found that the difference between the two values was negligible and, therefore, we can keep the second moment value constant over the whole temperature range.

Fig. 4 shows the temperature dependence of the jump rate obtained by MUSR on $HfV_2H_{0.1}$. As for the previous sample, at high temperature, the muons jump rate is in good agreement with the QNS data that have been measured on the same sample. The experimental evidence, particularly on metallic-glasses, and for samples at high concentration, seems to suggest that the muon diffusion is, in fact, normally slower than that of the proton. Although one would expect that the muon would diffuse faster than the proton due to its highest zero point energy as this would tend to give it a rather lower barrier to diffusion. This would be particularly so in the second sample, where the concentration is very low and hence the site blocking effect will be negligible. We think the fact that the muon is not faster than the proton is because its larger wave function may effectively raise the barrier to diffusion even more because of the higher zero point energy at the top of the barrier where the channel between the sites is at its narrowest. It should also be noted that it is probable that the potential well will be deeper in the muon case because the lattice will relax so as to minimise the sum of the lattice distortion energy and the zero point energy. This will also tend to increase the barrier height in the muon case.

4. Conclusion

We have measured the jump rate and associated activation energy of the muon in two Laves phase hydrides, $TiZr_2H_{3.6}$ and $HfV_2H_{0.1}$. In the former case, the high concentration of the hydrogen would suggest that the muon should diffuse at the same rate or slower than the proton and we found that it does indeed diffuse at the same rate, suggesting that its diffusion is controlled by the proton. In the latter case, the hydrogen concentration is so low that we should observe the intrinsic jump rate of the muon. Because the attempt frequency of the muon is three times that of the proton, this suggests that the barrier height must be greater for the muon. This is perfectly feasible because, although the muon will have a higher zero point energy in the bottom of the well, it will also have a higher zero point energy at the saddle point.

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