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Muon–proton correlated diffusion in TiH_x

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Abstract

The diffusion of positive muons embedded in the hydrogen sub-lattice of metal hydrides becomes highly correlated with the motion of the protons at temperatures high enough to cause rapid diffusion of the hydrogen. Hydrogen blocking and hopping diffusion dictate that the motion of the lighter particle should be more rapid than that of the heavier but the contrary has been reported in many experiments on metal hydrides. A convincing explanation of this ‘slow muon problem’, in which the muon diffusion rate is apparently less than the proton diffusion rate, has not been given so far. The present experiment confirms the existence of slow muons in TiH_x for $x \sim 2$ but show that as x is reduced the correlation times associated with the motion of the muons and hydrogen atoms become more comparable. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: μ^+ in metal hydrides; Diffusion

1. Introduction

Measurements of muon spin relaxation or rotation (MUSR) of positive muons implanted in metals and non-stoichiometric metal hydrides show that the diffusion rate of the muon is usually much greater in the metal at a given temperature than in the equivalent metal-hydride. In hydrides in which the sub-lattice of the hydrogen atoms (protons) is almost complete the presence of the hydrogen atoms appears to block the motion of the muon. At sufficiently high temperatures the protons become mobile with an interval between diffusion hops, τ_H, of the order of the correlation time, τ_μ, of the local magnetic field at the muon. Both τ_H and τ_μ then decrease with approximately the same apparent activation energy leading to the conclusion that the hydrogen atoms themselves diffuse and allow the muon to make a transition to a neighbouring site [1,2]. Since the muon is the lighter particle, it is reasonable to suppose that its intrinsic mobility is greater than that of the protons and on a simple interpretation of the blocking mechanism, that the observed hopping rate of the muon in the hydride will be somewhat greater than, or at least be equal to, that of the protons [1]. Paradoxically, in Ti hydrides [3] along with a number of others it is the muon that has been observed to have the lower hopping rate. A convincing explanation of this ‘slow muon’ effect has yet to be given [2].

In the present paper we report some new measurements of muon spin relaxation and nuclear magnetic resonance in the fcc γ-phase of TiH_x. Away from the stoichiometric composition TiH_2, our data show that τ_H and τ_μ converge in the temperature range where the protons are mobile and there is little evidence of a slow muon effect. On the other hand, we find that τ_μ is much greater than τ_H at compositions near TiH_2, thus confirming the earlier measurements which were also made at near-stoichiometric compositions. In the γ-phase the hydrogen atoms occupy a simple cubic lattice of tetrahedral interstitial sites and our new results show that the slow muon effect is related to the almost complete occupation of this sub-lattice.

2. Experimental details and results

The samples used in this experiment have the compositions $TiH_{1.5}$ and $TiH_{1.94}$ and were chosen to have hydrogen contents close to the extremities of the composition range of the non-stoichiometric fcc γ-phase of Ti hydride. The depolarisation of positive muons embedded in these samples was measured in zero magnetic field and longitudinal geometry on the ISIS muon instruments at the Rutherford-Appleton Laboratory. The profiles of the polarisation decays had the characteristic shape obtained in such measurements and could be fitted to the theoretical depolarisation curves derived from the dynamic Kubo-Toyabe model [4]. The diffusion of the protons was investigated by measuring their longitudinal nuclear mag-

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netic relaxation (NMR) time, T_1. This experiment was carried out solely on the $TiH_{1.5}$ sample, since our spectrometer is not capable of working at sufficiently high temperatures to obtain meaningful results from the other one.

The measured values of T_1 are shown in Fig. 1 where it can be seen that T_1 has the characteristic minimum associated with dipolar relaxation of diffusing spins. It is known from earlier NMR experiments [5] that in the γ-phase the protons occupy the simple cubic lattice of tetrahedral interstitial sites within the fcc metal matrix. The relaxation rate is given by $T_1^{-1} = T_{1d}^{-1} + T_{1e}^{-1}$, where T_{1d}^{-1} is the contribution from the nuclear spin dipolar coupling and T_{1e}^{-1} is a Korringa term due to electron–nuclear interactions. The second term only makes a significant contribution well away from the minimum in T_1 and for $x = 1.55$ has been found to be given by $T_{1e}T = 154$ sK [5]. Simple models for the relationship between T_{1d} and τ_H are inadequate at the proton concentrations found in the simple cubic sub-lattice of the γ-phase. Instead, it is necessary to employ a lattice-specific theory, which includes proton–proton interactions [6] in order to obtain the best possible values of τ_H from the NMR data. Unfortunately, the theoretical results are not presented in a sufficiently practical form and to interpret the NMR data we have had to resort to relaxation rates for simple cubic lattices obtained from Monte Carlo calculations [7,8]. These calculations agree in general terms with the theoretical model. Applying Bustard's [7] Monte Carlo calculations for nearest neighbour hops and assuming the Korringa relaxation rate given above, the values of τ_H shown by the open points in Fig. 2 were obtained. Very similar values were found using the alternative Monte Carlo model [8]. The linear fit to the data points indicates activated diffusion with an activation energy $E_a = 0.51$ eV which is ~4% lower than the value for $x = 1.55$ found in the earlier work [5]. The solid line Fig. 1, which has been fitted to the minimum, represents T_1 constructed on the basis of these models and data.

The second moment, M_2, of the dipolar field at the protons calculated on the assumption that they lie on the tetrahedral sites is 1.43×10^{-10} s^{-2}. The minimum value of T_{1d} is $\sim \omega / M_2$, where $\omega / 2\pi$ is the Larmor frequency. The experimental value of ω is $2\pi \times 18$ MHz giving a minimum value of T_1, of 7.9 ms. The measured value is 9.4 ms. Given the approximation, these values are suffi-

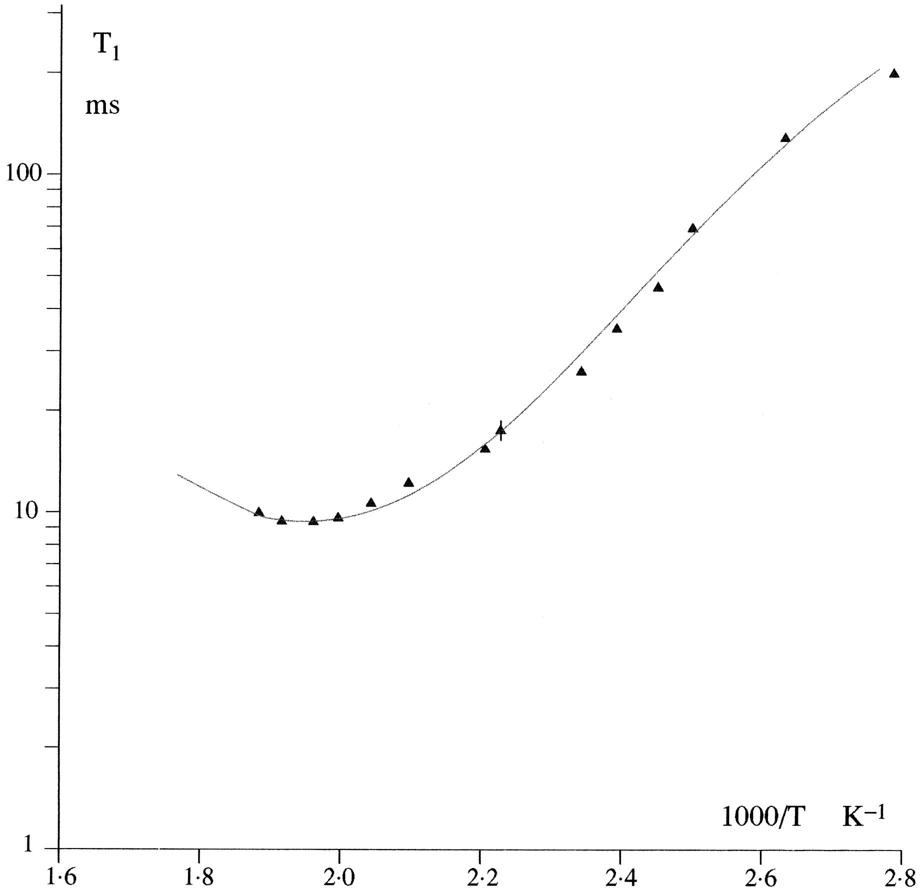

Fig. 1. The longitudinal nuclear magnetic relaxation time, T_1, measured at 18 MHz in $TiH_{1.5}$ as a function of reciprocal temperature, $1/T$. The solid line through the data is calculated from the sum of two components, T_{1d} calculated from Monte Carlo simulations of spin dipoles diffusing on a simple cubic lattice and an electronic contribution, T_{1e}, given by $T_{1e}T = 154$ sK. Details may be found in the text.

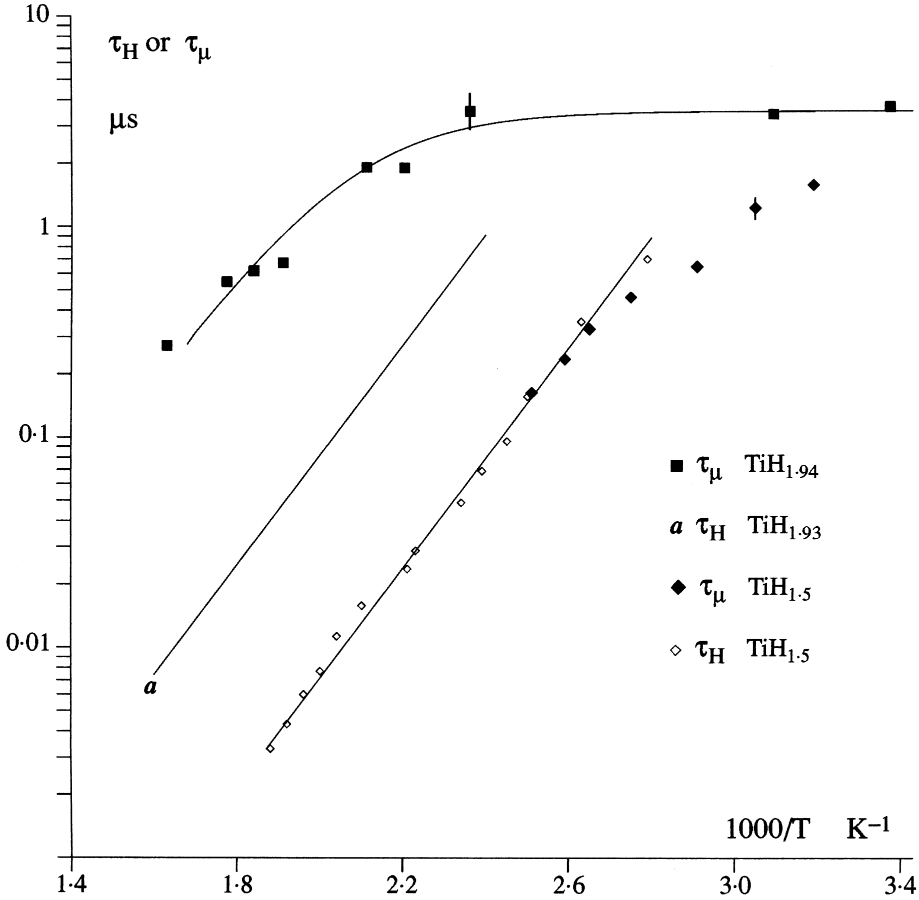

Fig. 2. Measured values of the correlation time, τ_μ, of the local magnetic field at positive muons embedded in TiH_x are shown by the solid data points. The open points are calculated values of the interval between diffusion hops, τ_H, of the protons in $TiH_{1.5}$ derived from the relaxation data of Fig. 1. The line 'a' is an estimate of τ_H in $TiH_{1.93}$. The data demonstrate the slow muon effect in $TiH_{1.94}$ in which $\tau_\mu > \tau_H$, whereas in $TiH_{1.5}$, τ_μ and τ_H are comparable. In the latter case the origin of τ_μ is principally the fluctuation of the local field due to the correlated diffusion of the protons and muon.

ciently close to allow us to draw the conclusion that the protons do indeed lie on the tetrahedral sites in the $TiH_{1.5}$ sample, especially as the measured value is also comparable with the earlier data [5].

The correlation time of the local field at the muon, τ_μ, was obtained from the depolarisation measurements by fitting relaxation profiles given by the strong-collision theory of Hayano et al. [4]. The initial relaxation is sufficiently Gaussian-like at the lower temperatures of the data range to allow us to separate the two parameters, Δ and τ_μ, which characterise the theoretical depolarisation. Good fits were obtained with Δ, the square root of the second moment of the local field distribution, equal to 0.41 μs^{-1} for $x=1.5$ and 0.475 μs^{-1} for $x=1.94$ and independent of temperature. The contribution to the second moment from the nuclear dipoles of the Ti atoms is negligible and, assuming the muons occupy the same tetrahedral sites as the protons, the calculated value of Δ is 0.40 μs^{-1} for $x=1.5$ and 0.46 μs^{-1} for $x=1.94$. These values are slightly smaller than the observed values and it seems reasonable to conclude that, in the temperature range of the experiment, muons can occupy the tetrahedral sites without the need for spatial relaxation of the neighbouring hydrogen atoms.

The corresponding values of τ_μ are shown as filled data points in Fig. 2. The solid line through the data points for $x=1.94$ has been constructed on the basis that $\tau_\mu^{-1} = \tau_d^{-1} + \tau^{-1}$, where τ is a temperature-independent term equal to 4.1 μs and τ_d is a correlation time having an Arrhenius temperature dependence with an activation energy of 0.51 eV. The absolute values of τ_d have been chosen to fit the data points for τ_μ at the upper end of the temperature range and are more than an order of magnitude greater than τ_H estimated from earlier NMR data for $x=1.93$ and the knowledge that the activation energy is essentially independent of temperature [9]. The temperature dependence of τ_H ($x=1.93$) is shown by line 'a' in the figure. A similar curve can be constructed to fit the data points for $x=1.5$ but, as the data clearly show, τ_d can be made equal to τ_H in this case.

3. Discussion

The results of the present experiment for the $TiH_{1.94}$ sample confirm those of the earlier measurements on $TiH_{1.97}$ [3], particularly as the values of τ_{μ} are essentially the same in both cases. One difference is that in the present case the value found for the second moment can be taken to imply that the muon occupies the same interstitial tetrahedral site as the protons without any significant shift in the positions its neighbours. The second moment found earlier was too small to allow this conclusion to be reached and it was proposed that, although the experiment pointed to the occupation of the tetrahedral sites, there must be a 3% relaxation of the proton nearest neighbour positions. The explanation for the difference is that in the earlier transverse geometry experiments it is not possible to measure long correlation times and the assumption was made that the second moment, as measured at ~350 K, was a consequence of the muon being stationary. This is clearly not the the case according to the present experiments in which the longitudinal geometry offers the possibility of separating Δ and τ_{μ}, especially under the conditions where $\Delta\tau_{\mu}$ is ~1. At 350 K τ_{μ} is ~3.5 μs and, based on the extrapolation of the NMR data, τ_{H} is about an order of magnitude greater. At this temperature the diffusion rate in the proton sub-lattice is small and the measured correlation time must indicate motion of the muon. The earlier value is therefore an underestimate and this has led incorrectly to the proposed spatial relaxation.

Other measurements we have made on similar Ti hydride samples indicate that this value of τ_{μ} persists to temperatures of ~10 K, a feature which we have observed in a number of alloy hydrides as well [1,10]. In view of the weak temperature dependence, the most likely explanation is that the muon can tunnel through the stationary proton sub-lattice. A higher temperatures, where the interval between diffusion hops of the protons becomes considerably less than 3 μs, it is reasonable to suppose that τ_{μ} would then decrease in line with τ_{H} given that the local field at the muon is a consequence of the muon–proton dipolar coupling. Even if the muon was static, it is difficult to envisage that it would be more than ~2 or 3 times τ_{H} [1]. The observed difference of more than an order of magnitude, the slow muon effect, appears to indicate that the motions of the protons and the muon are unconnected in spite of the dipolar coupling and the similarity of the apparent activation energies.

On the other hand, the results for the $TiH_{1.5}$ sample are clearly amenable to the above explanation. Given that $\tau_{\mu}^{-1} = \tau_{d}^{-1} + \tau^{-1}$ as indicated above, τ is then the correlation time associated with the tunnelling and τ_{d} ($\sim\tau_{H}$) is a consequence of the fluctuations of the local field at the muon caused by the diffusion of the protons. The fact that it has not been possible to observe more overlap between the MUSR and NMR data is due to limitations of the MUSR method which is not conducive to the measurements of long depolarisation times. A preliminary examination of some MUSR measurements on a $TiH_{1.68}$ sample, which will be reported in detail in a future paper, indicate that it behaves in a similar manner to the $TiH_{1.5}$ sample. Taken together with the earlier data, which show a diminution of the slow muon effect in a $TiH_{1.8}$ sample compared with $TiH_{1.97}$ [3], the measurements indicate that the slow muon effect is related to the increasing population of the sublattice of tetrahedral sites by the protons.

The proton–muon dipolar coupling, which is a constant feature of all these measurements, is short range, approximately to nearest neighbours. An obvious explanation of the slow muon effect is that at $x \sim 2$ the protons neighbouring the muon do not diffuse in the same manner as the remainder. Whether this is a consequence of some muon–proton interaction or is due to the muon being forced to special sites such as grain boundaries or dislocations by the high proton concentration is a question which cannot be answered by the present experiment.

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