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Muon spin relaxation in niobium-hydrogen

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Abstract

Nuclear magnetic relaxation and muon spin relaxation in $NbH_{0.8}$ are reported. The correlation time of the muon local field in the bcc β-phase above 240 K is found to be equal to the interval between hops of the hydrogen atoms, providing care is taken to chose relaxation models specifically related to Nb-H.

Keywords: Nuclear magnetic relaxation; Disordered metal hydrides; Rotating frame relaxation diffusion

It has been reported in a number of papers on muon spin relaxation (musr) in metal-hydrogen systems that, at temperatures typically above 200 K, the correlation time of the local field at the muon, τ_{μ}, depends on the diffusion of the hydrogen atoms [1]. For example, measurements in longitudinal geometry and zero external field on particular amorphous alloys containing hydrogen [1] show that the local fields arise principally from the dipole coupling with the hydrogen nuclear spins and the correlation time is approximately constant and somewhat greater than 1 μs from 15 K to ~200 K. At higher temperatures, where the interval, τ_{h}, between the diffusion hops of the hydrogen atoms becomes less than 1 μs, the muon correlation time decreases in an Arrhenius manner with an activation energy equal to that of the hydrogen diffusion. However, it has been reported that a detailed examination of these results and others show that τ_{μ} and τ_{h} are not the same, in some cases the motion of the muon is apparently slower than that of the hydrogen atoms [1,2]. There are some differences between the effect in alloys and elemental metals, namely that in the latter the two activation energies are often not equal, in spite of very strong evidence that hydrogen motion is the salient factor. Typical examples are to be found in musr measurements on Nb hydrides [2]. These measurements clearly demonstrate the motional narrowing effect due to the diffusion and have established that the muons, like the hydrogen atoms, occupy tetrahedral sites. In most cases the correlation time of the muon local field has an Arrhenius dependence on temperature but the activation energy is less than that found by nuclear magnetic relaxation (nmr) for the hydrogen diffusion.

Diffusion in alloys is often complicated by the differing jump probabilities that can exist at the various hydrogen sites and there may be several reasons connected with this for a difference in the average motions of the muon and hydrogen atoms. On the other hand diffusion in elemental metals is relatively simple. The experimental evidence points to the fact that the hydrogen atoms and muons occupy similar sites and the former block the motion of the latter. If this is the case, it requires very special arguments to explain why the diffusion of the muon, which presumably has the greater intrinsic mobility, is different from that of the hydrogen [2]. With these features in mind we decided to make some new measurements of musr and nmr in the Nb-H system. The musr measurements were made in longitudinal geometry, which is generally superior in diffusion measurements to the transverse method adopted in the earlier work. The results are reported in this paper.

A sample of Nb-H was made by heating 99.9% pure Nb to about 400 °C in hydrogen gas and subsequently cooling to room temperature. The final composition was found to be $NbH_{0.8}$ from measurements of the pressure and volume. At 300 K NbH_{x}, with $x>0.72$, forms the β-hydride [3] based on bcc Nb in which the hydrogen atoms are situated along chains in the (110) directions. The vacancies due to non-stoichiometry are randomly distributed along the chain but at lower temperatures the vacancies order to form several different phases. Samples with the composition $NbH_{0.8}$ change from the β-phase to the ordered λ-phase at 240 K on cooling [3].

Measurements of the hydrogen nuclear magnetic relaxa-

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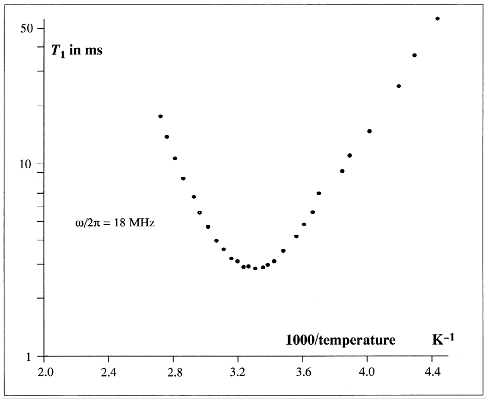

Fig. 1. The hydrogen nuclear magnetic relaxation time T_1 in $NbH_{0.8}$. The dip in T_1 is characteristic of dipolar relaxation and diffusing spins and has slopes above and below the minimum value which are proportional to the activation energy. The asymmetry is due to the onset of a phase change near 370 K. The activation energy derived from the low temperature slope is 0–25 eV.

tion time, T_1, were made at the frequency $\omega/2\tau=18$ MHz over the temperature range 225 K to 370 K, so that the characteristic dip in the hydrogen dipolar rate could be observed. The results are shown in Fig. 1 and are generally consistent with earlier data for other compositions and frequency [2]. The relaxation clearly has an Arrhenius dependence on the low temperature side of the dip. The activation energy is 0.25 eV and a value for τ_h, can be calculated from the condition that $\omega\tau_h=1$ at the minimum of T_1. The relaxation rate on the high temperature side of the dip deviates from this activation energy. The deviation is almost certainly related to yet another phase change which occurs near 370 K.

The musr measurements, carried out in longitudinal geometry and zero external field on the same sample, were made on the ISIS muon beam at the Rutherford–Appleton Laboratory, Chilton, UK. The initial asymmetries and relaxation profiles were typical of results obtained from this instrument. Procedures for calculating muon correlation times often involve the dynamic Kubo–Toyabe depolarisation curves [4]. However, in Nb-hydrides the principal source of the muon local field is the coupling to the nuclear spins of the metal atoms and the Kubo–Toyabe model requires modification to account for electric quadrupolar effects. Unfortunately the relaxation cannot easily be calculated under these conditions and the available results are not sufficiently well documented for practical use. Consequently, we also have analysed our data by means of the K–T model to give the τ_μ shown in Fig. 2. The second moment of the local field distribution is found to vary only slightly with temperature. A break in the decreasing trend in τ_μ can be seen near 240 K and we are of the opinion that it is due to the transition from the λ- to the β-phase in spite of the fact that there is apparently no corresponding break in the nmr data, which just overlaps this temperature.

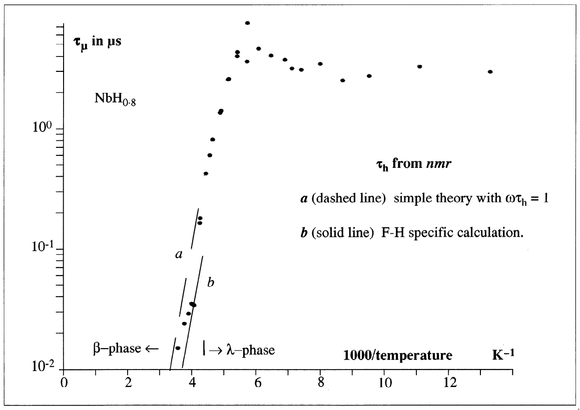

Fig. 2. The muon correlation time, τ_μ, derived from the muon spin relaxation by means of the Kubo–Toyabe model. The square root of the second moment of the local field distribution, Δ, is also shown. The dashed and solid lines show the hydrogen jump interval, τ_h, derived from the nuclear magnetic relaxation time as given in the text.

The dashed line in Fig. 2 shows τ_h derived in the manner described above. We believe that the apparent agreement between τ_h and the τ_μ of the λ-phase is fortuitous. It is well known that the value of τ_h derived from nmr is very model dependent and in fact several models specifically directed at the Nb-H system have been discussed by Faux and Hall [5]. Applying any of these models to the nmr data gives values of τ_μ which are consistently less than those represented by the dotted line, although the activation energies remain roughly the same. An example (the simple hopping model of [5]) is shown by the solid line in Fig. 2. Notwithstanding the fact that more data in the β-phase is required for a definitive conclusion, we are of the opinion that agreement between τ_μ and τ_h can be obtained by careful choice of models for the nmr and musr.

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