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A muon spin-relaxation study of LaH_x ($x = 2.75$)

M R Chowdhury†‡, G A Styles†, E F W Seymour†, S F J Cox§, C A Scott§ and G H Eaton§

† Department of Physics, University of Warwick, Coventry CV4 7AL, UK

§ Rutherford Appleton Labortatory, Chilton, Didcot, Oxon OX11 0QX, UK

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Abstract. Transverse-field muon spin-rotation measurements have been carried out on $LaH_{2.75}$ over the temperature range 15–300 K. The muon depolarisation rate σ remains constant in the temperature range 15–160 K, indicating that in this region muons are immobile. The measured value of σ is in good agreement with a rigid-lattice second-moment calculation based on the assumption that the muons occupy vacant octahedral interstitial sites. Motional averaging sets in at about the same temperature ($T > 165$ K) at which the NMR line narrowing due to proton diffusion occurs. The muon correlation time τ follows an Arrhenius-like behaviour up to $T \simeq 240$ K with an activation energy of 185 meV, which is very similar to that of the NMR value for the proton. The measured τ-value shows a sharp, discontinuous drop by an order of magnitude at $T \simeq 241$ K, a clear indication of a phase transition. The nature of this transition is discussed in relation to the heat capacity anomalies and lattice distortions observed at about the same temperature.

1. Introduction

Lanthanum, like a number of other light rare-earth elements (Ce, Pr and Nd), combines with hydrogen to form LaH_x up to $x = 3$ and in the composition range $x \simeq 1.9$ to 3.0, LaH_x is known to form a homogeneous phase. The dihydride, LaH_2, has the cubic fluorite structure with the hydrogen occupying predominantly the tetrahedral (T) interstitial sites. As the hydrogen concentration increases, the octahedral (O) interstitial sites accommodate the additional hydrogen and at the composition limit LaH_3, all the T and O sites are occupied, forming a BiF_3-type structure.

The hydride system exhibits a series of interesting physical properties as a function of composition and temperature. LaH_2 exhibits metallic conductivity, but as x approaches 3 semiconducting behaviour is observed [1]. Electronic structure calculations [2, 3] for stoichiometric hydrides predict metallic behaviour for $x = 2$ and semiconducting behaviour for $x = 3$. Early electrical resistivity measurements [4] indicated semiconducting behaviour in the composition range $2.86 \leqslant x \leqslant 2.92$, while more recent measurements [5] indicated both composition- and temperature-dependent transitions. The λ-type heat capacity anomaly observed in $LaH_{2.69}$ at 239 K [6] and in LaH_3 [7] at 241 K have been atrributed to a metal–semiconductor transition. NMR Knight shift measurements [8] of the ^{139}La resonance for $2.89 \leqslant x \leqslant 3.0$ indicated metallic behaviour for $T > 210$ K and semiconducting behaviour for $T < 210$ K. In marked contrast, the proton T_1-data

‡ Attached to: Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK.

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taken on the same samples were found to be consistent with metallic behaviour down to at least 77 K. Photoemission measurements [9] indicate that near $x = 2.98$ the material is a small-band-gap semiconductor at 300 K. Structurally, neutron diffraction [10, 11] for LaD_3 and samples with lower deuterium concentrations has shown that the octahedral deuterium atoms are randomly displaced along the ⟨111⟩ directions at 295 K, and below 230 K there appears to be an ordering of the O-site deuterium atoms on the off-centre positions. X-ray diffraction studies [12] have shown that the cubic lattice parameter decreases with increasing hydrogen concentration, and that in a narrow range of composition, $2.65 \leqslant x \leqslant 2.85$, and over the temperature range 197–256 K, a small tetragonal distortion ($\leqslant 1\%$) of the lanthanum sublattice takes place. NMR measurements [13] show that the hydrogen diffusion in the trihydride phase ($x > 2$) remains rapid and indeed increases as x aproaches 3 with an apparent lowering of the activation energy. This is somewhat surprising since all T and O sites are occupied at this latter composition and diffusion would be expected to be slower since it can only take place via thermally generated vacancies. To add to the puzzlement, low-temperature heat capacity data [7] show four λ-type anomalies for LaD_3, but only two for LaH_3.

Accordingly, in an attempt to clarify the situation we have undertaken a study of this system for a number of compositions in the range $2 \leqslant x \leqslant 3$ by positive muon (μ^+) spin-relaxation measurements. Here we report the first results of our muon spin-rotation (μSR) measurements on a powder sample of $LaH_{2.75}$. This is a particularly interesting composition. The metal–semiconductor transition is known to occur for $x \geqslant 1.80$; a structural phase transition characterised by a cubic–tetragonal distortion of the metal lattice [12] occurs at about this composition, with the maximum distortion occurring in the range $2.75 \leqslant x \leqslant 2.80$; the λ-type specific heat anomaly [6] at $\simeq$240 K also occurs very close to this composition.

The μSR technique primarily depends on the measurement of the muon spin depolarisation rate as a function of temperature. In a system like LaH_x the depolarisation is caused by the spread in the nuclear dipolar fields originating predominantly from the protons. At low temperatures where both the muon and the hydrogen nuclei are stationary, the depolarisation rate is determined by the rigid-lattice second moment of the dipolar-field distribution, which in turn is determined mainly by the structural arrangement of the protons and to a lesser extent of the lanthanum nuclei around the muon. At higher temperatures both muons and protons can become mobile through diffusion. The depolarisation rate is then determined by the correlation time of the fluctuating dipolar fields seen by the muon, together with the spread of the field distribution. The muon depolarisation rate as a function of temperature may therefore be used to study phase transitions involving rearrangement of the hydrogen positions, as well as the diffusive motions of both protons and muons. In addition, the μSR data may also reveal information on the metal–non-metal (semiconductor) transition through the formation of muonium ($\mu^+ + e^-$) in the semiconducting state. In a transverse-field experiment, the effect will be observed as a reduction in the amplitude of the precession signal (the so-called asymmetry).

2. Experiment and methods

The μSR measurements were made on the recently commissioned spectrometer on ISIS at the Rutherford Appleton Laboratory [14], using the transverse-field geometry. The external magnetic field used was 22 mT, providing a muon precession frequency of about

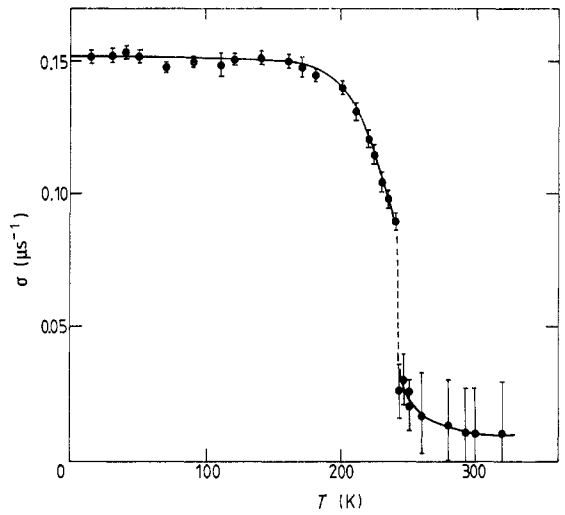

Figure 1. The measured muon depolarisation rate (Gaussian line shape) in $LaH_{2.75}$. The curve through the data points is meant to guide the eye.

3 MHz. A helium closed-circuit refrigerator was used to attain the temperature range 15–300 K. The $LaH_{2.75}$ sample used was prepared from the highest-purity Ames Laboratory lanthanum metal containing less than 0.0002 at.% of impurities like Fe, Cu, Ta, Ni and rare earths. The sample, in the form of a powder, was contained in a helium atmosphere within a sealed aluminium cell, which was provided with a Mylar window to admit the incident muons with little attenuation. Data analysis consisted of fitting the observed time distribution of the μ^+ precession signal $N(t)$ to the standard expression

$$N(t) = N_0 \exp(-t/\tau_\mu)(1 + a_0 P(t) \cos(\omega_\mu t + \phi)) + B \tag{1}$$

where N_0 is a normalisation constant, τ_μ the muon lifetime, a_0 the asymmetry, ω_μ the muon precession frequency, ϕ the phase angle and B a time-independent background. The additional background due to the muon stopping in the cryostat wall etc. was separately determined using a dummy sample and the data analysis took proper account of this background. The depolarisation function $P(t)$ was taken initially to be a Gaussian of the form $P(t) = \exp(-\sigma^2 t^2)$ at all temperatures and the values of σ shown in figure 1 were obtained on this basis. At low temperatures where both muons and protons are static the polarisation decay is expected to follow this Gaussian time dependence with $2\sigma^2 = 2\sigma_0^2 = \Delta^2$, Δ^2 being the rigid-lattice second moment of the dipolar-field distribution (in frequency units). At high temperatures where motional averaging sets in due to the mobility of the muons and/or protons, the Gaussian form of $P(t)$ is not expected to hold and in this region the data were analysed using the more general Abragam formula:

$$P(t) = \exp\big(-2\sigma_0^2 \tau^2 (\exp(-t/\tau) - 1 + t/\tau)\big). \tag{2}$$

where τ is the muon correlation time characterising the fluctuations of the dipolar fields seen by the muon. In the circumstance where the muon is diffusing through a static lattice, $1/\tau$ may be interpreted as the muon jump rate.

3. Results and discussion

The measured depolarisation rate σ as a function of temperature is shown in figure 1. σ is independent of temperature up to about 165 K, indicating that both μ^+ and proton remain static up to this temperature. At higher temperatures σ decreases due to the motional averaging effects. The general features of the present μSR results, as shown in figure 1, are similar to the corresponding proton NMR linewidth data [13]. The onset of motional narrowing of the NMR linewidth occurs at progressively lower temperatures with increasing hydrogen concentration in the composition range $1.9 \leqslant x \leqslant 3$, and for the present composition the NMR line narrowing sets in at about the same temperature at which the present μSR depolarisation rate decrease occurs. This, as expected, shows that the proton motion determines muon mobility, for in the high-hydrogen-concentration sample $LaH_{2.75}$, muons residing on the same sublattice as hydrogen can only hop into vacant sites created by hydrogen jumps.

Above 165 K, σ shows a steady decrease up to about 240 K, at which point it drops discontinuously to a value which is about a quarter of its 240 K value. At this point, it should be mentioned that although the actual σ-values shown in figure 1 are not physically significant in this temperature range because the muon relaxation in this region is non-Gaussian, the significance of the observed 240 K discontinuity remains unaffected and will be discussed later. (The relaxation rate λ obtained from fitting the exponential form of the depolarisation function $P(t) = \exp(-\lambda t)$, which is more appropriate for this region, exhibits a similar behaviour to σ. The 240 K drop of λ is even larger than that of σ.)

We first examine the low-temperature region where the depolarisation rate is independent of temperature. The rigid-lattice second moment of the frequency distribution Δ^2 for a polycrystalline material containing nuclei of spin T, at a separation r_i from the muon site, may be computed using the Van Vleck expression [15]:

$$\Delta^2 = (\tfrac{4}{15})\, I(I+1)\, \hbar^2 \gamma_I^2 \gamma_\mu^2 \sum_i r_i^{-6} \tag{3}$$

where γ_I and γ_μ are the gyromagnetic ratios of the nucleus and the muon respectively. For LaH_x, Δ^2 may be written as the sum of three terms: $\Delta^2 = \Delta_T^2 + \Delta_O^2 + \Delta_L^2$, the subscripts T, O and L referring to the contributions due respectively to the T-site protons, O-site protons and the lanthanum nuclei (^{139}La, $I = \frac{7}{2}$).

In almost all the cases of the metal hydrides so far studied using μSR—which include hydrides of Nb, V, Pd, Zr, Ti and Y—the magnetic moment of the metal nucleus when compared with that of the proton is negligibly small, and so the metal contribution to the second moment has generally been ignored. In the present case, however, although the ^{139}La (~100% abundance) dipolar field is still small compared with that of the proton, it is not negligible and accordingly we have included the lanthanum term in our calculation.

In $LaH_{2.75}$ as all the available T sites are already occupied by hydrogen atoms, implanted muons would be expected to occupy vacant O sites. Assuming that the muons occupy O sites and that the protons are in the regular interstitial sites in an undistorted lattice (nearest-neighbour distances $r_T = (\sqrt{3}/4)a$, $r_O = (1/\sqrt{2})a$ and $r_L = 0.5a$, where a is the lattice parameter) the Δ_T-term accounts for ≈84%, the Δ_L-term 11% and the Δ_O-term the remaining 5% of the total Δ^2, indicating thereby that the measured depolarisation rate will be most sensitive to the structural arrangement of the tetrahedral

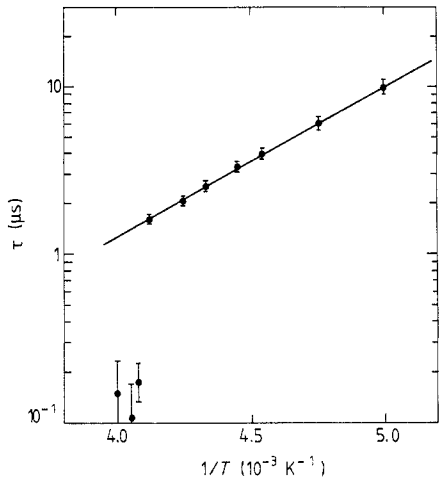

Figure 2. The muon correlation time τ as a function of $1/T$ for $LaH_{2.75}$.

protons and least to the octahedral ones. This is a consequence of the lattice sum $\Sigma_i r_i^{-6}$ being dominated by the nearest neighbours.

Taking into account the expected reduction of ≈5% due to the proton–proton interaction (mutual spin flips) [16, 17], the calculated value for the depolarisation rate turns out to be 0.158 μs^{-1}. This may be compared with the measured value of σ, which is 0.152(2) μs^{-1}. This small difference, if real, could be accounted for by a small lattice expansion (≈1%) around the muon. The temperature independence of σ from the lowest temperature measured (15 K) to ≈160 K is indicative of both the immobility of the muon and an unaltered muon local environment over the temperature range. This is in agreement with known data on LaH_x phase transitions, with perhaps one exception, namely that of Schlapbach and co-workers [18], who have reported a surface metal–semiconductor transition in $LaH_{2.7}$ (and a number of other rare-earth hydrides) at 25 K. For the reasons stated above, on the basis of the muon depolarisation rate alone it is not possible to draw conclusions as to which of the possible ordering, rearrangement or superlattice formation of the octahedral protons, although such have been proposed by a number of authors to explain the various low-temperature phase transitions in LaH_x [7, 12], occurs.

We now examine the high-temperature region. The data in this region have been analysed in terms of the muon correlation time τ using equation (2). The τ-values thus obtained are shown in figure 2 on a logarithmic scale, as a function of $1/T$. The principal features of the data are: (i) for $T < 240$ K, τ-values follow an Arrhenius-like behaviour of the form $\tau = \tau_0 \exp(E_a/kT)$, with the activation energy $E_a = 185(5)$ meV and $\tau_0 = 3.0 \times 10^{-10}$ s; (ii) near $T = 241$ K, τ abruptly drops by an order of magnitude from 1.6 μs to about 0.2 μs. By 250 K the μSR line narrowing is nearly complete and therefore the τ-values beyond this temperature cannot be determined with any acceptable degree of certainty.

The activation energy for proton diffusion, deduced from NMR relaxation measurements [13], shows a sharp fall from the dihydride phase value of about 1.1 eV at $x = 1.92$ to 0.43 eV at $x = 1.95$ and, in the trihydride phase itself, E_a further decreases with increasing hydrogen concentration to a value of about 0.15 eV at $x = 2.85$. In the composition range relevant to the present experiment, the proton activation energy is

$\simeq$0.19 eV. The closeness of the two activation energies again suggests that the motional narrowing process for the muons is governed by the motion of the proton and that the diffusion process is activated by the ocathedral protons which share the same sublattice as the muons. This is in line with our own recent measurements of the hydrogen vibrational frequency [19] and earlier measurements by Kamitakahara and Crawford [20] showing that the binding of the hydrogen in the octahedral site is much weaker than that of the hydrogen in the tetrahedral site. The pre-exponential factors, τ_O, for the two, however, differ by more than an order of magnitude, $\tau_O(\mu)$ being the larger. Similar disagreements between the diffusion parameters for the muon and those for the proton have been reported in a number of μSR studies involving metal hydrides, including TiH_x [21], NbH_x [22], PdH_x and $LaNi_5H_6$ [23], and the apparent discrepancy has usually been explained in terms of muon–proton correlation. In the present case, however, it is difficult to ascertain the reality of the disagreement, since the quoted accuracy of the NMR parameter ($\tau_O(p)$) is not better than an order of magnitude.

The 241 K anomaly in τ (and the corresponding depolarisation rate) is indicative of a phase transition. Heat capacity measurements on $LaH_{2.69}$ [6] and LaH_3 [7] show λ-type anomalies at 239 and 241 K respectively. The structural transition characterised by the cubic–tetragonal distortion of the lanthanum sublattice occurs at composition-dependent temperatures and for $x = 2.76$ the transition takes place at 242 K [12]. Considering that no distortion of the La sublattice has been detected for $x > 2.86$, it is difficult to see how one can attribute the heat capacity anomalies, especially the LaH_3 anomaly, to the same underlying cause as that responsible for the tetragonal distortion. The heat capacity anomaly in both cases has been attributed to a metal–semiconductor transition, while the driving mechanism responsible for the lattice distortion has been thought to be an ordering or rearrangement of the hydrogen atoms, but the true position is yet to be determined. Neutron diffraction measurements on LaD_x [11], while showing deviation of the deuterium atoms from their regular sites and possible superlattice formations at low temperatures, have not provided any definite structure for the deuterium positions. We believe the phase transition observed in the present measurements owes its origin to the same cause as the lattice distortion, but in order to be certain, and also to be able to draw conclusions as to the nature of this transition, further measurements on samples with different compositions will have to be made. Preparations for such measurements are in progress.

Muonium formation which may result as a consequence of a metal–semiconductor transition has not been detected. The amplitude of the precession signal was found to remain constant throughout the temperature range studied.

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