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# $\mu$SR Investigations of Cerium Hydride*

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The Knight shift and transverse field spin relaxation rate of positive muons ($\mu^+$), implanted in $LaH_{2.75}$-, $CeH_{2.70}$- and $CeH_{2.95}$-powder samples, have been measured as a function of temperature and in the $CeH_x$-samples also as a function of field. These data are used to extract information on the $\mu^+$-site, $\mu^+$-diffusion and the magnetic properties of the $CeH_x$-samples.

## Introduction

Cerium hydrides $CeH_x$ are known to exhibit fascinating properties regarding their phase diagram /1/. Their electronic structure /2/ changes from metallic at $x = 2$ to insulating (or semiconducting) at $x = 3$ and their magnetic properties include both ferromagnetic order (for $2.3 \leq x \leq 2.7$) and antiferromagnetic order (for $x \leq 1.95$ and $x \geq 2.75$) /3/. In addition measurements of the electronic specific heat in a $CeH_{2.65}$ sample yielded evidence for heavy fermion behavior /4/. Hydrogen occupies up to $x = 2$ the available tetrahedral sites in the Ce fcc lattice. On increasing $x$ beyond $x = 2$ up to $x = 3$ the remaining octahedral sites are filled.

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The indication for heavy fermion behavior and the complex magnetic phase diagram in these systems motivated us to investigate them further by means of the $\mu$SR technique /5/ which has proven to be of considerable power in the study of heavy fermion systems (see e.g. /6/). In addition we were interested in the diffusional behavior of the $\mu^+$, in its site of residence (tetrahedral or octahedral) and its interaction with the neighboring protons.
In this contribution we report on first results from a systematic $\mu$SR study of cerium hydrides /7/. Two powder samples with nominal values of $x = 2.70$ and $x = 2.95$ which bracketed well the metal to semiconductor transition were investigated. The sample with $x = 2.95$ should show antiferromagnetism with $T_N \simeq 4$ $K$ while the other sample was expected to be either ferromagnetic with $T_c$ around $\sim 2$ $K$ or to fall within the narrow paramagnetic region above $x = 2.70$ /3/. For comparison also results from a nonmagnetic $LaH_{2.75}$ sample are included here. The experiments were performed at the Paul Scherrer Institute (formerly SIN).

## Results and discussion

Generally the $\mu$SR signal in the $CeH_x$ compounds consisted of two components, irrespective of the applied field. The amplitudes of the two components showed a weak temperature dependence and a stronger field dependence, however their sum remained independent of temperature or applied field. This implies that the muons do not probe two different phases in the samples but that the two components are probably originating from $\mu^+$ in different magnetic environments the extent of which is controlled by applied field and temperature. The two components are distinct by their relaxation rates and frequencies. At a field of 0.02 $T$ the minority component (called the fast component) displayed a rather temperature independent relaxation rate of $\sim 1.25$ $\mu s^{-1}$ for both $CeH_x$ samples. This component disappeared close to room temperature. At low temperatures the minority component ($\sim 25\%$) became the majority component ($\sim 75\%$) for applied fields above $\sim 0.08$ $T$. Above $\sim 0.1$ $T$ the relaxation rate increased linearly with the field. The other component (called the slow component) displayed always a much smaller relaxation rate with a pronounced temperature dependence but no field dependence. This signal resembles the single component found in the $LaH_{2.75}$ sample.

The magnitude of the relaxation rate of the fast component can only be explained if static electronic moments are invoked. Since we have no clear idea about the origin of this component, we will discuss here only the slow component which has many features in common with proton NMR signals in $LaH_x$ and $CeH_x$ /8,9,10/. Fig. 1a shows the temperature dependence of the $\mu^+$ relaxation rate or linewidth $\sigma$ in $LaH_{2.75}$, displaying the onset of motional narrowing around 50 $K$ and, more pronounced, above $\sim$ 150 $K$. Around the latter temperature hydrogen diffusion is known to set in /8/. Similar curves were obtained in $CeH_{2.70}$ (Fig. 1b) and $CeH_{2.95}$ (Fig. 1c). The low temperature plateau values of $\sigma$ can be used to learn about the $\mu^+$ position in the lattice. In Tab. 1 we compare the experimental values with calculated predictions for the two different possible sites, assuming for the lattice constant $a_o = 5.57$ Å. We see that in all cases the experimental values are significantly larger than the calculated ones. To obtain agreement we can scale down the lattice constants ($\sigma \propto a_o^{-3}$). For an octahedral site assignment this would imply a surprisingly large near neighbor lattice contraction of $-8.5\%$ in $CeH_{2.70}$, $-5.5\%$ in $CeH_{2.95}$ and $-3.2\%$ in $LaH_{2.75}$. These values would be even larger for a tetrahedral site assignment which seems to rule out the latter one. In $CeH_x$ the low temperature $\sigma$ may be enhanced by magnetic effects, nevertheless it appears as if there is a strong attractive interaction between the $\mu^+$ at an octahedral interstitial site and the nearest neighbor protons at tetrahedral interstitial sites.

| | $\sigma_{exp}(\mu s^{-1})$ | $\sigma_{cal}(a_o = 5.57$ Å) | | $a_{o,eff}$ (Å) | $a_{o,exp}$ Å | $\Delta a/a$ (%) |
|---|---|---|---|---|---|---|
| | | octh. | tetr. | octh. | | octh. |
| $LaH_{2.75}$ | 0.26 | 0.244 | 0.220 | 5.450 | 5.63 /8/ | −3.2 |
| $CeH_{2.70}$ | 0.31 | 0.233 | 0.196 | 5.064 | 5.54 /11/ | −8.5 |
| $CeH_{2.95}$ | 0.28 | 0.235 | 0.212 | 5.254 | 5.54 /11/ | −5.5 |

Tab. 1. Compilation of results on $\sigma$ and comparison with calculations.

The temperature dependence of $\sigma$ at higher temperatures was used to extract the $\mu^+$ diffusion rate $\nu_\mu$ or more precise, a correlation rate $\nu = \nu_\mu + \nu_p$ which contains also the proton jump rate $\nu_p$. It is found that $\nu(T)$ followed an Arrhenius law for temperatures above about 180 $K$. Tab. 2 contains the fitted activation energies and preexponential factors together with corresponding data from a proton NMR

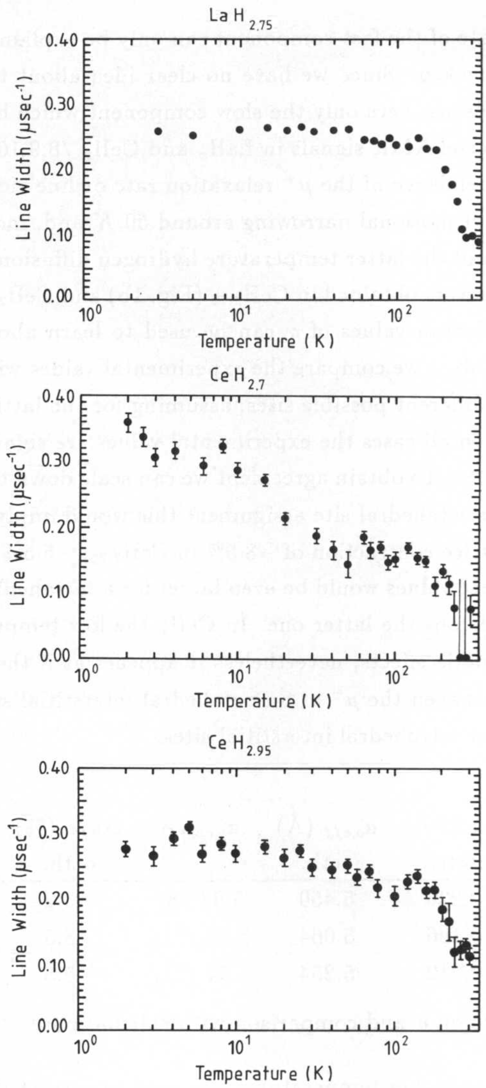


Fig. 1.
Temperature dependence of $\sigma_{slow}$ in (a) $LaH_{2.70}$, (b) $CeH_{2.70}$ and (c) $CeH_{2.95}$. The data were obtained in an applied field of 0.02 $T$.

study. It is seen that the present activation energies and preexponential factors are significantly smaller than in the proton case. A similar observation was also made in $PdH_x$ /12/. This is hard to understand, because one expects always $\nu \geq \nu_p$. A way out would be a highly correlated $\mu^+$-proton diffusion or a kind of immobilization of the tightly bound $\mu^+ - nn$ proton complex. Another possibility is a stoichiometric $CeH_3$ environment in the $\mu^+$ vicinity which should also inhibit strongly uncorrelated jump events.

The Knight shift of the $\mu^+$ Larmor frequency in $LaH_{2.75}$ was too small to be detected in the present study. In contrast the Knight shift in the $CeH_x$-samples was quite sizeable and showed remarkable temperature dependencies (see Fig. 2a,b). In $CeH_{2.70}$ the Knight shift changes from about $-0.2\%$ at room temperature to about $+0.25\%$ at $\sim 5$ $K$, displaying a shallow maximum there. In contrast in $CeH_{2.95}$ the Knight shift is

| $\mu^+$ | E(kcal/Mol) | $\nu_o(s^{-1})$ |
|---|---|---|
| $LaH_{2.75}$ | $\sim 2.28$ | $1.2 \cdot 10^8$ |
| $CeH_{2.70}$ | $\sim 0.50$ | $4.6 \cdot 10^6$ |
| $CeH_{2.95}$ | $\sim 1.63$ | $3.2 \cdot 10^7$ |
| p | | |
| $LaH_{2.85}$ | $\sim 3.50$ | $\sim 10^{11}$ /8/ |

Tab. 2. Diffusion parameter for $T > 180$ $K$.

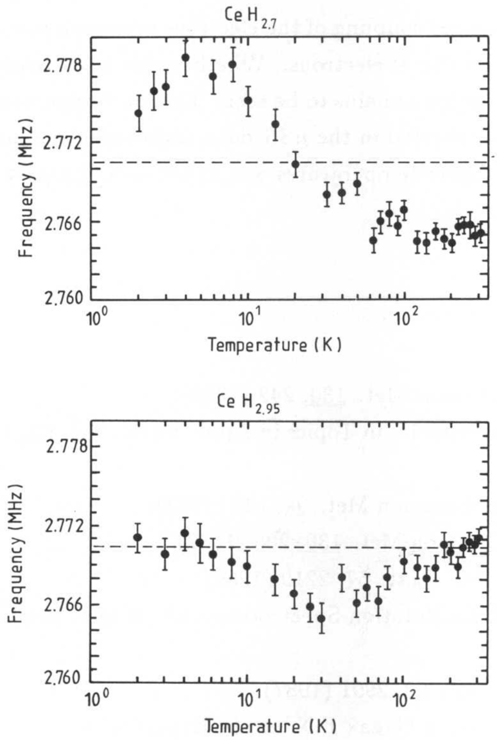


Fig. 2.
Temperature dependence of $\mu^+$-Larmor frequency of the slow component in (a) $CeH_{2.70}$ and (b) $CeH_{2.95}$. The dashed line corresponds to the external field ($\sim$ 0.02 $T$).

close to zero both at room temperature and below 5 $K$ and has a shallow minimum of $\sim$ $-0.2\%$ at 30 $K$. A few proton Knight shift data for $CeH_x$ with $x = 2.85$ can be found in /13,9/ for temperatures between 6 $K$ and 180 $K$. They agree relatively well with the present results in $CeH_{2.70}$. The magnitude of the Knight shift in Fig. 2 clearly points to a strong influence of the Ce 4f-moments. The negative shift in $CeH_{2.70}$ at room temperature seems to suggest an antiferromagnetic coupling of the conduction electrons (or what ever screens the $\mu^+$-charge) to the 4f-electrons. The change of sign at $\sim$ 20 $K$ is for now a mystery as is the difference between the results in Figs. 2a and 2b.

## Conclusions

Positive muons implanted in $CeH_x$ ($x = 2.70,\ 2.95$) and $LaH_{2.75}$ seem to occupy the octahedral interstitial sites. The nearest neighbor protons at tetrahedral interstitial sites are contracted towards the $\mu^+$ by a few %. Uncorrelated diffusional motion of the $\mu^+$ and its proton neighbors is slowed down considerably compared to proton diffusion in the bulk of the material. The $\mu^+$ Knight shift shows quite a different and unusual temperature dependence for the two $CeH_x$ samples. It is suggested that the hydrogen concentration via the density of free carriers has a pronounced influence on the (exchange) coupling of the electrons screening the $\mu^+$ (mostly conduction electrons?) and the 4f-electrons. Whether this is correlated with the metal-semiconductor transition remains to be seen. The low temperature magnetic phase transition was not reflected in the $\mu$SR data, although some kind of weak static magnetism also at higher temperatures was experienced by part of the implanted $\mu^+$.

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