μ^+ SR KNIGHT SHIFT IN SINGLE CRYSTAL PrNi_5 - EVIDENCE FOR MUON-INDUCED DISTORTION OF CRYSTAL-FIELD LEVELS

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New transverse field measurements on single crystal PrNi_5 have been carried out. The angular dependence of the Knight shift indicates μ^+ at f-sites of the hexagonal unit cell $[(1/2 \ 0 \ 0), (0 \ 1/2 \ 0), (1/2 \ 1/2 \ 0)]$ in apparent contrast to previous conclusions. It is confirmed that the temperature dependence of the Knight shift does not scale with the bulk susceptibility. While the latter shows a distinct maximum around 15 K and Van Vleck behaviour for $T \rightarrow 0$ K, the Knight shift does not exhibit any saturation down to 2 K. This peculiar behaviour is explained by a μ^+ -induced change of the crystal field level scheme of the nearest-neighbour Pr^{3+} -ions that significantly reduces the splitting between the lowest lying levels.

Introduction

The crystal electric field (CEF) splitting of the $^3\text{H}_4$ multiplet of the Pr^{3+} -ions in PrNi_5 leads to a well established level scheme with a Γ_4 singlet groundstate and the Γ_1 singlet as the lowest excited state [1-3]. On the basis of this level scheme the temperature dependence of the susceptibility is well understood. The contribution of Ni to the total susceptibility is regarded to be very small.

Previous μ^+ SR Knight shift measurements however have questioned this picture. The anisotropic Knight shift has been interpreted in terms of local moments on the Ni-sites with almost no contribution from Pr. It was also observed that the temperature dependence of the Knight shift does not follow the bulk susceptibility but no explanation was given [4, 5]. In view of the unequivocal inelastic neutron scattering results it has been noted that the observed behaviour of the μ^+ SR Knight shift could be muon-induced

Fig. 1. Temperature dependence of the Knight shifts of the doublet (○) and the singlet (□) observed for $H_{ext} \parallel \bar{a}$. Broken lines: behaviour expected for linear scaling of the shifts with the bulk susceptibility. Inset: Temperature dependence of the signal from the Cu-sample holder.

and originate from a change of the CEF level scheme of Pr^{3+} -ions due to the electric field gradient (EFG) produced by a neighbouring interstitial μ^+ [?]. This view is strongly supported by the present analysis of new Knight shift results on single crystal PrNi_5 .

Results

The μ^+ SR transverse field measurements have been carried out on the same sample as previously used for inelastic neutron scattering as well as new samples produced by the same procedure as described in ref. [?].

The temperature dependence of the Knight shift, corrected against demagnetisation effects, for $H_{ext} = 6.0$ kOe, $H_{ext} \parallel \bar{a}$, is shown in fig. 1. In contrast to the previous μ^+ SR results [4, 5] only *two* signals besides the signal from the sample holder were observed with an asymmetry ratio of 2:1. Only in the high-temperature region $T > 80$ K the shifts K scale linearly with the bulk susceptibility, that was taken from ref. [?], with $K_{doublet}/\chi_{ab} = 0.11$ mole/emu and $K_{singlet}/\chi_{ab} = -0.23$ mole/emu.

The extrapolation of this behaviour to lower temperatures is shown in fig. 1 as dashed lines. Two peculiarities of the temperature dependence are obvious:

- the shifts of both signals deviate strongly from the extrapolated behaviour for $T < 50$ K and do not exhibit any saturation down to 2 K; this is consistent with the earlier μ^+ SR results
- at $T \approx 20$ K the shift of the doublet changes its sign.

The extraordinary behaviour of the Knight shift is accompanied by a strong increase of the relaxation rates with decreasing temperature. This has to be related to a similar increase of the zero field relaxation that is the subject of another contribution to this conference [6].

A preliminary measurement of the angular dependence of the Knight shift at $T = 35$ K and $H_{ext} = 3.8$ kOe on a second sample, rotating the external field within an a-c-plane also exhibited only two signals with an asymmetry ratio of 2:1. For $\Theta = 90^\circ$ H_{ext} is parallel to a in this case.

Only the f-site $[(1/2 \ 0 \ 0), (0 \ 1/2 \ 0), (1/2 \ 1/2 \ 0)]$, situated in the basal plane right between two Pr-ions, can account for the observed singlet-doublet structure as illustrated in fig. 2. In the experimental geometries for $\Theta \neq 0$ always two of the three crystallographic equivalent sites are also magnetically equivalent, whereas the third site has a different magnetic environment.

For $\Theta = 0^\circ$ ($H_{ext} \parallel c$) the Knight shift on the f-sites is given by

$$K_{\parallel} = (A_{hf} + A_{dip})\chi_c \quad ,$$

where A_{hf} is the hyperfine coupling constant and A_{dip} denotes the dipolar contribution. A theoretical value for A_{dip} and the full angular dependence of the dipolar shift can be calculated from a lattice sum over the dipolar

Fig. 2. Experimental geometries for a) $H_{ext} \parallel a$, b) $H_{ext} \parallel \bar{a}$. The muon sites are marked $\circ$ (doublet) and $\square$ (singlet).

fields from the Pr-ions. One obtains

$$A_{dip,theor.} = -0.198 \text{ mole/emu.}$$

From the high temperature values for $K_{singlet}$ and $K_{doublet}$ both, A_{hf} and A_{dip} , can be calculated separately. One derives $A_{hf,exp} = -0.087 \text{ mole/emu}$ and $A_{dip,exp} = -0.164 \text{ mole/emu}$. The reduction of $A_{dip,exp}$ against the theoretical value can be accounted for by the reasonable assumption that the two Pr ions closed to the μ^+ are displaced outwards by $\approx 6\%$ ($0.15 \text{ \AA}$).

The peculiar temperature dependence of the Knight shifts at $T < 50 \text{ K}$ is explained as follows. There is no doubt, that the bulk susceptibility of our samples behaves as usual. A small temperature dependence of the signal from the sample holder that is produced by the macroscopic magnetisation of the sample very nicely mirrors the bulk susceptibility (see inset in fig. 1). A gradual change of A_{hf} with decreasing temperature to a large negative value is not a possible explanation since the splitting between doublet and singlet should stay proportional to χ_{ab} in contrast to the experimental finding. A large change of A_{dip} is impossible since it is determined by the lattice geometry. One has to conclude that *the local susceptibility monitored by the muon is different from the bulk susceptibility*. Hence the magnetic response of at least the two next neighbour (nn) Pr-ions of the muon is altered due to the presence of the muon itself.

We have calculated the susceptibility of the two nn-Pr-ions from the experimental Knight shifts under the following assumptions:

- temperature independent A_{hf} and A_{dip} as given above,
- A_{hf} determined only by the two nn-Pr-ions,
- change of CEF properties only of the two nn-Pr-ions.

The calculated anisotropic susceptibility is shown in fig. 3. Note that the anisotropy is defined with respect to the axis connecting the muon and the Pr-ion. The singlet shift is determined by χ_y . Due to the anisotropy the dipolar contribution to the doublet shift is produced by moments *not* parallel to the external field. The angle between moments and field increases with decreasing temperature. Actually, *this* is the reason for the change of sign of the doublet shift at 20 K .

The change of the susceptibility implies a change of the CEF level scheme of the nn-Pr-ions. We attempted to understand the observed χ_x, χ_y on the basis of a point charge model by simply placing an effective charge Z_{eff} on the muon site and calculating the associated changes of the crystal field parameters. For the quadrupolar terms one finds $\Delta B_2^0 = -0.15 \text{ meV} \cdot Z_{eff}$ and

Fig. 3. Anisotropic susceptibility ($\circ$) of the nn-Pr-ions of the muon calculated under the assumptions discussed in the text. The anisotropy is defined with respect to the axis connecting muon and Pr-ion as illustrated in the inset. The dashed line is the bulk susceptibility. The full lines is a three parameter CEF field fit explained in the text.

$\Delta B_2^0 = 0.45 \text{ meV} \cdot Z_{eff}$. No choice of Z_{eff} provided a satisfactory description of the data, but qualitatively it could be concluded that the muon introduces a $B_2^0 \neq 0$, that causes the observed anisotropy. (It was also found that a displacement of the Pr ions about $0.15 \text{ \AA}$ causes only negligible changes of the CEF parameters. A displacement of the two nn-Ni however has a more pronounced influence with $B_2^0/B_2^0 \approx -1/3$, like for a Z_{eff} at the μ^+ site, e.g. $\Delta B_2^0 = -0.018 \text{ meV}$ for a displacement about $0.25 \text{ \AA}$.)

As a second step we allowed the parameters B_2^0 , B_2^2 and λ to vary independently. A reasonably good agreement of the CEF-fit with the observed susceptibility was found with $B_2^0 = 0.54 \text{ meV}$, $B_2^2 = 0.08 \text{ meV}$ and $\lambda = 2.7 \text{ mole/emu}$ and the other parameters as for the unperturbed case. For comparison, $B_2^0 = 0.51 \text{ meV}$, $B_2^2 = 0$ and $\lambda = 4.73 \text{ mole/emu}$ for the unperturbed case. The fit is shown in fig. 3 as full lines. The associated CEF level schemes are reproduced in fig. 4.

Discussion

It is possible to explain the peculiar temperature dependence of the Knight shift by assuming the muon to induce rather small changes in the CEF parameters. The main source of these changes is the EFG produced by the muon charge and its screening cloud.

Fig. 4. Left: CEF level scheme for PrNi_5 (see [1,2,3]); right: CEF level scheme that gives the fit to the observed nn-Pr susceptibility (compare fig. 3)

The influence of this EFG on nuclear quadrupoles is well known since O. Hartmann's theory of muon depolarisation due to nuclear moments in the presence of competing quadrupolar interactions [7]. The influence on the magnetic moments of ferromagnetic rare-earth (RE) hosts has been discussed by Campbell [8]. It is argued that due to the CEF effect the EFG produced by the muon in the case of Gd will force the moments into a direction perpendicular to the axis connecting the Gd-ion and the muon. The influence on RE impurities in noble metals has been discussed by Schillaci et al. [9]. They conclude that a crystal field term introduced by the muon dominates the Hamiltonian of the muon-impurity interaction.

To our knowledge in no other context the influence of the muon on the magnetic properties of its local environment has been discussed. In view of the cited as well as the present results this influence has to be regarded as essential.

In the context of RE-hydrides the influence of interstitial hydrogen on the *macroscopic* magnetic properties is well known (see latest review [10]). Since the μ^+ is electronically equivalent to the proton it seems reasonable to expect that it perturbs the magnetic properties of its local environment in the same way as hydrogen. Our results show that the main perturbation is the change of the CEF properties.

The present results on PrNi_5 demonstrate that the magnetic properties monitored by the muon may be completely different from the bulk behaviour. The large increase of the susceptibility of the perturbed Pr-ions,

together with the ferromagnetic coupling between the Pr-ions ($\lambda > 0$) may give rise to a tendency to magnetic ordering of the Pr-moments. This could be the reason for the observed steep increase of both, the transverse field and the zero field relaxation rates at low temperatures [6].

References

- [1] K. Andres, S. Darack and H. R. Ott, Phys. Rev. **B19** (1979) 5475
- [2] V.M.T.S. Barthem, D. Gignoux, A. Nait-Saada, D. Schmitt and G. Grenzet, Phys. Rev. **B37** (1988) 1733
- [3] A. Amato, W. Bührer, A. Grayevsky, F.N. Gygax, A. Furrer, N. Kaplan and A. Schenck, Solid State Commun. **82** (1992) 767
- [4] N. Kaplan, A. Grayevsky, P. Birrer, F.N. Gygax, B. Hitti, E. Lippelt and A. Schenck, Phys. Rev. Lett. **62** (1989) 2732
- [5] B. Hitti, P. Birrer, A. Grayevsky, F.N. Gygax, N. Kaplan, E. Lippelt, A. Schenck and M. Weber, Hyperf. Int. **59** (1990) 377.
- [6] N. Kaplan, A. Grayevsky, D. Shaltiel, S. Barth, P. Birrer, F.N. Gygax, B. Hitti, E. Lippelt, A. Schenck and M. Weber, μ SR-93-Maui (1993)
- [7] O. Hartmann, Phys. Rev. Lett. **39** (1977) 832
- [8] I.A. Campbell, J. Physique Lett. **45** (1984) L24
- [9] M.E. Schillaci, R. H. Heffner, R.L. Hutson, M. Leon, D.W Cooke, A. Yaouanc, S.A. Dodds, P.M. Richards, D.E. MacLaughlin and C. Bookema, Hyperf. Int. **17-19** (1984) 351
- [10] G. Wiesinger and G. Hilscher, in Handbook of Magnetic Materials, vol. 6, K.H.J. Buschow ed., Elsevier Science Publ. 1991. p.511ff.