Original contributions

Crystal electric field next to a hydrogen-like interstitial – μ^+ in PrNi_5

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Received: 21 December 1994/Revised version: 30 January 1995

Abstract. Muon spin rotation measurements of the temperature dependence and the anisotropy of the μ^+ Knight shift in single crystals of the crystal electric field singlet ground state system PrNi_5 reveal pronounced deviations from a linear scaling of the Knight shift with the bulk magnetic susceptibility at $T \leq 50$ K. They are explained by a μ^+ induced modification of the atomic susceptibility of neighboring Pr^{3+} ions. From the Knight shift anisotropy at $T > 50$ K it is determined that the implanted μ^+ occupy a single interstitial site, namely the 6i site $(0.5, 0, 0.21 \pm 0.02)$. Using this site information, good model fits to the measured data are obtained assuming a μ^+ induced perturbation of the crystal electric field at the Pr^{3+} ions next to the μ^+ . Apparently, the presence of the μ^+ leads to a lowering of the local symmetry, causing a lifting of the degeneracy and a pronounced rearrangement of the low lying crystal electric field levels for these ions.

PACS: 76.75; 71.70.C; 75.20.E

1. Introduction

The changes of the magnetic and electronic properties of transition metals (TM), rare earths (RE) and TM/RE intermetallics on hydrogen absorption is a topic of continuing interest [1]. These changes are mainly ascribed to band structure effects, caused by charge transfer between the interstitial hydrogen and the conduction band. Extensive experimental and theoretical investigations of the RE hydrides have led to the picture of anionic hydrogen, carrying approximately one negative charge and forming a valence band far below the Fermi surface. Early arguments in favor of this model were derived from studies of the crystal electric field (CEF) experienced by the RE ions in REH_x [1–3]. Detailed studies of the systems $\text{CeH}_{2+\delta}$ and $\text{PrH}_{2+\delta}$ revealed that the changes of the magnetic properties on hydrogen uptake ($\delta > 0$) are produced by the reduced symmetry of the CEF, causing

a lifting of degeneracy of the CEF ground states [4–6]. Thus, besides effects of interstitial hydrogen on the band structure, also the influence on the CEF appears to be of great importance in RE-H systems. However, to our knowledge no attempt has been made to date to investigate CEF properties of RE-H compounds at low hydrogen concentrations, where band structure effects are negligible.

One experimental technique that has been applied successfully to the problem of CEF properties in RE hydrides is ^1H nuclear magnetic resonance (NMR) [7–10]. Below we present results by a similar technique, namely transverse field (TF) muon spin rotation (μSR) [11], where the Larmor precession of positive muons – implanted one by one into the sample – is measured in a magnetic field applied perpendicular to the μ^+ spin. Since the μ^+ may be regarded as a ‘light isotope’ of hydrogen, exhibiting equal electronic properties when residing at an interstitial site in a metal lattice, TF μSR experiments are an equivalent to ^1H -NMR Knight shift measurements in the limit of zero hydrogen concentration. In analogy with NMR, the hyperfine field derived from the μ^+ Knight shift is a manifestation of the local electronic susceptibility. The susceptibility of localized electrons can be analyzed in terms of CEF parameters.

In this report we present results on the μ^+ Knight shift in single crystals of the well known hexagonal CEF singlet ground state system PrNi_5 . These results indicate that already the presence of a single hydrogen like and interstitial μ^+ causes a pronounced modification of the CEF acting on neighboring Pr^{3+} ions. To our knowledge, the reported work is the first experimental evidence of such an effect. PrNi_5 is an ideal candidate for this type of investigation, because its CEF level scheme is well established (see [12] and references therein). A preliminary report of part of the new μSR results has been presented previously [13]. Here we describe new measurements of the temperature and angular dependence of the μ^+ Knight shift and give a more detailed account on our analysis of the Knight shift anisotropy and the observed deviations from a linear scaling of the Knight shift with the bulk susceptibility. The

previous μ^+ site assignment and the quantitative determination of the change of the CEF due to the presence of the μ^+ [13] are refined. It is shown that the perturbed CEF parameters cannot be explained in terms of a local lattice expansion or a point charge model for the interstitial muon and that the influence of the μ^+ is of a more subtle nature.

This article is organized as follows. After a description of the experimental procedure (Sect. 2) we review some theoretical μ^+ Knight shift aspects (Sect. 3). In Sect. 4 the experimental results on the temperature and angular dependence of the μ^+ Knight shift in PrNi₅ are presented. Section 5 describes the determination of the interstitial stopping site of the implanted μ^+ in PrNi₅ from the Knight shift anisotropy at $T > 50$ K. In Sect. 6 the observed deviation from a linear scaling of the Knight shift with the bulk susceptibility at $T < 50$ K is analysed in terms of a modified CEF acting on the Pr³⁺ ions next to the interstitial μ^+ . The modification of the CEF is discussed in Sect. 7.

2. Experimental

Three single crystals of PrNi₅ have been prepared and characterized at the Hebrew University using materials and methods described in [12]. Their magnetic susceptibility was measured with a commercial squid susceptometer (Quantum Design) at temperatures between 5 K and room temperature. It was found in excellent agreement with previous data of Barthem et al. [14]. One of the samples was also used for the previous inelastic neutron scattering measurements [12]. It was grown with its cylinder axis parallel to the $\bar{a} = [1\ 2\ 0]$ direction of the hexagonal crystal structure. A second cylindrical sample was cut into several slices with faces $\perp \bar{a}$ and $\perp c$, respectively. The third sample is another cylinder of about the same size as the first one (7 mm diam. $\times$ 24 mm long) with its axis $\parallel c$. As the present results on all three samples, prepared independently, are perfectly consistent, we will not refer to them separately. All samples were glued to high purity copper or silver sample holders.

The μ SR TF measurements have been carried out on the μ E1 beam line using our own high precision spectrometer and on the general purpose μ SR spectrometer on the π M3 beam line at the Paul Scherrer Institute in externally applied magnetic fields of $H = 3.3$ kOe and 6.0 kOe, covering the temperature range $4\text{ K} \leq T \leq 300\text{ K}$. The applied magnetic field was determined either by a commercial NMR probe to an accuracy of better than 10 ppm, or alternatively from a reference signal (sample holder) to an accuracy of better than 50 ppm. For the measurements of the angular dependence of the Knight shift the cylindrical samples were turned around their symmetry axes, the external magnetic field applied perpendicularly. Thus the demagnetization factors were independent of the rotation angle. In the investigation of the sliced samples the field was applied perpendicularly to their flat faces.

3. Theory

The magnetic field B_μ at the μ^+ interstitial site inside a crystal lattice is derived from the μ^+ Larmor precession

frequency $\omega = \gamma_\mu B_\mu$, where γ_μ is the gyromagnetic ratio of the μ^+ , $\gamma_\mu = 2\pi \times 13553.879\text{ s}^{-1}\text{ G}^{-1}$ (± 0.2 ppm). In a compound exhibiting no spontaneous magnetic order B_μ is nonzero only in an external (applied) magnetic field H . The relative field or frequency shift

$$K_\mu = \frac{|B_\mu| - |H|}{|H|} = \frac{B_\mu}{H} - 1 = \frac{\omega}{\omega_0} - 1, \quad (1)$$

where $\omega_0 = \gamma_\mu H$, contains important information about the internal magnetic hyperfine fields B_{hf} induced by the external field H in the investigated compound. Neglecting the Lorentz and the demagnetization fields (that originate from the macroscopic magnetization of the investigated sample induced by the external field and can be easily corrected for, as will be demonstrated in sec. 4) as well as small diamagnetic contributions, we may write $B_\mu = B_{\text{hf}} + H$, resulting in

$$K_\mu = K_0 + K_f, \quad (2)$$

where K_0 and K_f originate from hyperfine fields produced by the polarization of conduction electrons and localized f electronic moments, respectively, induced by the external field. The source of K_0 is the Pauli paramagnetism of the conduction electrons and the Fermi contact interaction of these electrons with the μ^+ . In PrNi₅ the Pauli paramagnetic susceptibility χ_0 is dominated by the contribution from the $3d$ electrons of Ni [14]. The localized electrons, in the present work the $4f$ electrons of the Pr³⁺ ions, contribute via two channels to the Knight shift K_μ . The first is the indirect RKKY interaction, producing an additional spin polarization of the conduction electrons and thus an additional hyperfine contact field at the interstitial μ^+ . The second contribution to K_f arises from the dipole-dipole interaction between the local moments and the μ^+ that may be described as an effective dipolar field at the μ^+ interstitial site. Both contributions are proportional to the $4f$ paramagnetic susceptibility χ_f . In contrast to K_0 and χ_0 the contribution from the localized f electronic moments will exhibit a strong temperature dependence. In the simplest case χ_f follows a Curie law $\chi_f \propto 1/T$ at least at higher temperatures. Noting that the total susceptibility (again neglecting small diamagnetic contributions) is given by

$$\chi = \chi_0 + \chi_f, \quad (3)$$

it follows that K_0 and χ_0 can be determined from the experimental $K_\mu(\chi)$ data via an extrapolation to $1/T \rightarrow 0$, where $\chi_f \rightarrow 0$ and $K_f \rightarrow 0$.

The goal of the present work is the determination of the Pr $4f$ electron contribution K_f to the Knight shift that is expected to be much larger than K_0 which, in μ SR, is usually of the order of 100 ppm [11]. The f electron contribution to the hyperfine fields, $B_{\text{hf},f}$, can be expressed [15] in terms of an effective hyperfine coupling tensor $\mathbf{A}_f = (A^{ij})$, with $i, j = x, y, z$:

$$B_{\text{hf},f} = \mathbf{A}_f \mu_f = \mathbf{A}_f \chi_f H, \quad (4)$$

where $\chi_f = (\chi^{ij})$ is the atomic susceptibility tensor and $\mu_f = \chi_f H$ represents the localized moment induced by the external field. To first order the Knight shift is given by the

projection of $\mathbf{B}_{\text{hf},f}$ onto $\mathbf{H}$:

$$K_f = \mathbf{h} \mathbf{A}_f \chi_f \mathbf{h} \quad (5)$$

where $\mathbf{h} = \mathbf{H}/|\mathbf{H}|$ is the unit vector parallel to the external field. The elements of $\mathbf{A}_f \chi_f$ can be determined experimentally from the Knight shift anisotropy. If the principal axes of χ_f are chosen as the coordinate frame (x, y, z) , the Knight shift K_i for $\mathbf{H} \parallel i$ ($i = x, y, z$) is simply given by

$$K_i = A^{ii} \chi_i. \quad (6)$$

Thus, with the knowledge of χ_i (or A^{ii}), the tensor elements A^{ii} (or χ_i) can be determined from the observed shifts K_i .

As described above the effective hyperfine coupling $\mathbf{A}_f$ is the sum of a dipolar and a contact contribution $\mathbf{A}_f = \mathbf{A}_{\text{dip}} + \mathbf{A}_{\text{con}}$. By making the reasonable assumption that the hyperfine contact coupling is independent of the orientation of the external field, one can write $\mathbf{A}_{\text{con}} = A_{\text{con}} \mathbf{E}$, where $\mathbf{E} = (E^{ij}) = (\delta_{ij})$ is the unit tensor. Thus, an experimentally observed effective hyperfine coupling $\mathbf{A}_f$ can be decomposed into a sum of a traceless (dipolar) and a scalar (contact) part, using the relation $\mathbf{A}_{\text{con}} = 1/3 \text{Tr}(\mathbf{A}_f) \mathbf{E}$.

The dipolar coupling tensor at a given site r_μ is given by $\mathbf{A}_{\text{dip}} = (A_{\text{dip}}^{ij})$, with

$$A_{\text{dip}}^{ij} = \sum_{4f \in L} (1/r^3) (3x_i x_j / r^2 - \delta_{ij}), \quad (7)$$

where $r = |\mathbf{r}|$, $\mathbf{r} = \mathbf{r}_{4f} - \mathbf{r}_\mu = (x_1, x_2, x_3) \equiv (x, y, z)$. It is derived from the sum over the dipolar fields produced at the site r_μ by all $4f$ moments at positions r_{4f} inside a Lorentz sphere L . Note that $\mathbf{A}_{\text{dip}}$ is defined in a coordinate frame centered at the μ^+ site r_μ . $\mathbf{A}_{\text{dip}}$ is traceless but in general $\mathbf{A}_{\text{dip}} \chi_f$ (compare Eq. 5) is not. By comparison of an experimentally observed dipolar coupling $\mathbf{A}_{\text{dip}}$ with theoretical values calculated with the use of (7) for possible interstitial sites a precise determination of the actual μ^+ site may be possible as will be demonstrated in Sect. 6.

Sometimes it is convenient to express (5) in form of an explicit angular dependence of K_f . It may be expressed in terms of the spherical angles θ and φ by introducing $\mathbf{h} = (\sin \theta \sin \varphi, \sin \theta \cos \varphi, \cos \theta)$ into (5). Then (5) transforms to

$$\begin{aligned} K_f(\theta, \varphi) = & \frac{1}{3} (A^{xx} \chi_x + A^{yy} \chi_y + A^{zz} \chi_z) \\ & + \frac{2}{3} (A^{zz} \chi_z - \frac{1}{2} (A^{xx} \chi_x + A^{yy} \chi_y)) P_2^0(\cos \theta) \\ & + \frac{1}{3} A^{xz} (\chi_x + \chi_z) P_2^1(\cos \theta) \cos \varphi \\ & + \frac{1}{3} A^{yz} (\chi_y + \chi_z) P_2^1(\cos \theta) \sin \varphi \\ & + \frac{1}{6} (A^{xx} \chi_x - A^{yy} \chi_y) P_2^2(\cos \theta) \cos 2\varphi \\ & + \frac{1}{6} A^{xy} (\chi_x + \chi_y) P_2^2(\cos \theta) \sin 2\varphi. \end{aligned} \quad (8)$$

Equation (8) can be converted into the general form

$$\begin{aligned} K_f(\theta, \varphi) = & a + b P_2^0(\cos(\theta - \theta')) \\ & + c P_2^2(\cos \theta) \cos 2(\varphi - \varphi'), \end{aligned} \quad (9)$$

where often 'a' is referred to as 'isotropic' Knight shift and 'b' is called 'axial' Knight shift. Note that $c = 0$ for three-fold or higher symmetry of $\mathbf{A}_f \chi_f$ for rotation of $\mathbf{H}$ in the

x - y plane. The offset angles θ' (φ') vanish if the non-diagonal elements A^{xz}, A^{yz} (A^{xy}) of $\mathbf{A}_f$ are zero. Note that for $\mathbf{H} \parallel \mathbf{x}, \mathbf{y}, \mathbf{z}$, i.e. $(\theta, \varphi) = (90^\circ, 0^\circ), (90^\circ, 90^\circ), (0^\circ, 0^\circ)$, (8) simplifies to (6), that will be used in the data analysis below.

4. Results

In the following we present the experimental results on the anisotropy and the temperature dependence of the μ^+ Knight shift in PrNi_5 , and derive the effective hyperfine coupling $\mathbf{A}_f$ from the experimental data. With PrNi_5 being a hexagonal system, the principle axes of the lattice $(\mathbf{a}, \mathbf{\bar{a}}, \mathbf{c})$ can be chosen as the coordinate frame, for which the susceptibility tensor χ is diagonal with diagonal elements $\chi_c = \chi_{\parallel}$ and $\chi_a = \chi_{\bar{a}} = \chi_{\perp}$.

Figure 1 shows a Fourier transform of a TF μSR spectrum at $T = 23$ K for an arbitrary orientation of $\mathbf{H}$ within the basal plane $\mathbf{a}-\mathbf{\bar{a}}$ of the hexagonal structure. Clearly, three signals of equal intensity are observed besides a small and well resolved signal from the sample holder. The latter is identified by its small shift relative to the vacuum frequency $\nu_0 = \gamma_\mu H / 2\pi$ and its angular independent frequency. The observed angular dependence of the μ^+ Larmor precession frequencies, for rotation of $\mathbf{H}$ in the basal plane $\mathbf{a}-\mathbf{\bar{a}}$ and the $\mathbf{a}-\mathbf{c}$ plane are shown as points in Fig. 2a and Fig. 2b, respectively. The vacuum frequency ν_0 is marked by a horizontal line. The large Knight shift anisotropy points to large contributions of the dipolar fields to the total internal field at the μ^+ . The solid curves in Fig. 2a are fits to the data, using the equation $\nu(\varphi) / \nu_0 - 1 = a' + c \cos 2(\varphi - \varphi')$ (compare Eq. 9). The fitted curves describe the data very well and yield equal a' and c for all three signals, with relative offset angles $\varphi' = 0^\circ, 60^\circ, 120^\circ$. The angular dependence of the precession frequencies observed by rotation of $\mathbf{H}$ in the $\mathbf{a}-\mathbf{c}$ plane, where the two signals labelled II in Fig. 2a coincide, is shown as points in Fig. 2b. The curves in Fig. 2b are fits

Fig. 1. Fourier transform of a TF μSR spectrum on PrNi_5 in the external magnetic field $H = 3328$ Oe ($\nu_0 = 45.105$ MHz) at $T = 23$ K for the orientation $\varphi = 52^\circ$ (compare Fig. 2a) of $\mathbf{H}$ within the basal plane $\mathbf{a}-\mathbf{\bar{a}}$. The shaded peak is the signal from the copper sample holder

Fig. 2a, b. Angular dependence of the μ^+ Larmor precession frequencies observed in PrNi_5 at $H = 3328 \text{ Oe}$ and $T = 23 \text{ K}$, labelled I and II for identification; **a** H rotated in the basal plane $a\bar{a}$, three signals of equal intensity are observed; **b** H rotated in the a - c plane, $\theta = 90^\circ$ corresponds to $\phi = 0^\circ$ in (a); two signals are observed, the signal with lower frequency (open circles) has twice the intensity of the other one. Solid curves are fits of pure second order angular dependences to the data (see text)

to the data, using the equation $\nu(\theta)/\nu_0 - 1 = a + bP_2^0(\cos\theta)$ (compare 9). At $\theta = 0^\circ$, i.e. $H\|c$, all three signal merge into one. The overall behavior of the Knight shift anisotropy proves that the implanted μ^+ occupy a single crystallographic interstitial site with at least three (or $3n$, $n = 1, 2, 4$) equivalent sites per unit cell. Moreover, the observation of a pronounced ϕ -dependence of the precession frequencies shows that the symmetry *with respect to each μ^+ site* cannot be threefold or higher ('axial') for rotation about an axis parallel to the c -axis, because in this case the ϕ -dependence would vanish as can be deduced from (8). The precise determination of the interstitial site occupied by the μ^+ from these results is presented in the following section. It requires a quantitative analysis of the Knight shift anisotropy.

Results on the temperature dependence of the Knight shifts K_i ($i = a, \bar{a}, c$) of the individual signals labelled I and II in Fig. 2 for all three principal orientations of the external field are shown as points in Fig. 3a-c. All data were corrected for bulk demagnetization and Lorentz fields. The corrections $K_{\text{dem},L}$ are determined from the equation $K_{\text{dem},L} = 4\pi(1/3 - N)\rho_{\text{molar}}\chi_{\parallel\perp}$ (where ρ_{molar} is the molar density, given in $[\text{mol}/\text{cm}^3]$ and $\chi_{\parallel\perp}$ is the bulk molar susceptibility for the corresponding orientations. The demagnetization factors N are estimated from the ratio of the height and diameter of the samples [16], where

Fig. 3a-c. Temperature dependence of the Knight shifts K_f observed in PrNi_5 , labels I and II as in fig. 2; **a** $H\|a$; the signal II with negative shift (open circles) has twice the intensity as signal I; **b** $H\|\bar{a}$; the signal II with the smaller shift (filled circles) has twice the intensity of signal I; **c** $H\|c$; only one signal is observed. The data are corrected for demagnetization and Lorentz fields and for the temperature independent contribution K_0 . Broken curves: behavior expected for linear scaling of the shifts with the bulk susceptibility, see text

the magnetic field was applied perpendicular to the symmetry axis of the cylinder used for the measurement in $H\|a$ (resulting in $N = 0.47$) or perpendicular to the flat face of the sliced samples used for the measurements in $H\|\bar{a}$ and $H\|c$ (resulting in $N \approx 0.8$). At the corresponding maximum bulk susceptibility the demagnetization shifts $K_{\text{dem},L} = -0.31\%$, -1.15% and -0.37% had to be subtracted from the total shift (compare Fig. 3a-c). Since redundant data points were available for samples of different shapes, a consistency check of the applied demagnetization corrections was possible, yielding good agreement. In addition to these corrections, the temperature independent contribution K_0 to the total Knight shift, as discussed below, was subtracted. Therefore, Fig. 3a-c display the sole f electron contribution to the Knight shift, K_f . The dashed curves in Fig. 3 (see further below for details)

represent the predicted Knight shifts assuming linearscaling between the shifts and the bulk susceptibility, normalized for the high temperature region $50 \text{ K} < T < 150 \text{ K}$. The observed temperature dependence of the Knight shifts K_f for H parallel to the basal plane (points in Fig. 3a,b) reveal clearly that the expected linear scaling of the Knight shift with the susceptibility is not observed at low temperatures. In contrast to the bulk susceptibility in the basal plane $\chi_{\perp}$, that exhibits a pronounced maximum around 15 K and a van Vleck type saturation at $T \rightarrow 0$ [12, 14, 17], the corresponding Knight shifts partly exhibit essentially no saturation down to lowest temperatures. The linear scaling at higher T is best demonstrated by the plot of the splitting $\Delta K = |K_i(I) - K_i(II)|$ between the two signals observed for $H \parallel a$ and $H \parallel \bar{a}$ (compare figs. 3a,b) as a function of the corresponding bulk susceptibility $\chi_{\perp}$, as shown in Fig. 4a. In addition we present the Knight shift for $H \parallel c$ as a function of $\chi_{\parallel}$ in Fig. 4b. Clearly, a linear scaling of ΔK is observed only in a limited temperature range $30 \text{ K} \leq T \leq 150 \text{ K}$. At $T \leq 30 \text{ K}$ the observed splitting ΔK is distinctly larger than extrapolated for both orientations of H parallel to the basal plane. From the linear region the slope $d\Delta K/d\chi_{\perp} = 0.325 (5) \text{ mol/emu}$ is determined, reflecting the anisotropy of the Knight shift due to the dipolar fields. At temperatures $T > 150 \text{ K}$ the splitting is strongly reduced, pointing to the onset of μ^+ diffusion at that temperature, producing jumps between magnetically inequivalent sites, consistent with

results from μSR depolarization rate measurements on LaNi_5 and LaNi_5H_6 [18, 19]. For $H \parallel c$ a reduction of K_c is not expected in case of μ^+ diffusion since all μ^+ sites are magnetically equivalent.

From the intercept of the extrapolated line in Fig. 4a with the susceptibility axis, corresponding to the extrapolation $1/T \rightarrow 0$ ($\chi_{4f} \rightarrow 0$), one obtains the non- $4f$ contribution to the susceptibility

$$\chi_0 = 0.0025(5) \text{ emu/mol.}$$

This value agrees quite well with $\chi_0 = 0.002 \text{ emu/mol}$ derived from susceptibility measurements on PrNi_5 and LaNi_5 [14, 20]. From K_c at χ_0 a Knight shift value

$$K_0 = 250 (\pm 100) \text{ ppm}$$

is derived (see Fig. 4b). For comparison, in LaNi_5 a value of $K_0 = -5 (\pm 5) \text{ ppm}$ has been observed previously [21].

From the plots of the individual Knight shifts K_i ($i = a, \bar{a}, c$) of the signals I and II versus the corresponding susceptibility (not shown for $H \parallel a, \bar{a}$), the slopes $A^{ii} = dK_i/d\chi_i$ for all orientations can be determined only to limited accuracy due to the small extension of the linear region $50 \text{ K} \leq T \leq 150 \text{ K}$. For signal I we obtain the hyperfine coupling tensor

$$\mathbf{A}_f(I) = \begin{pmatrix} 0.225 & 0 & 0 \\ 0 & -0.210 & 0 \\ 0 & 0 & -0.150 \end{pmatrix} \frac{\text{mol}}{\text{emu}}.$$

The errors are 0.010 mole/emu. The non-diagonal elements are zero as we conclude from the fact that the offset angles θ' and φ' are zero for signal I (compare Eq. 9). For the signals II the above $\mathbf{A}_f$ is valid after rotation by $\pm 60^\circ$ about the z -axis. The calculation leads to the hyperfine tensor

$$\mathbf{A}_f(II) = \begin{pmatrix} -0.101 & 0.188 & 0 \\ 0.188 & 0.116 & 0 \\ 0 & 0 & -0.150 \end{pmatrix} \frac{\text{mol}}{\text{emu}}.$$

The calculated diagonal elements are in agreement with the experimentally observed values for the signals II , $A^{xx} = -0.100 (10) \text{ mol/emu}$ and $A^{yy} = 0.115 (10) \text{ mol/emu}$, respectively, showing that the two data sets obtained for $H \parallel a$ and $H \parallel \bar{a}$ are consistent.

Following Sect. 3, the experimentally observed effective hyperfine coupling tensor $\mathbf{A}_f$ can now be decomposed into the contact contribution $\mathbf{A}_{\text{con}} = A_{\text{con}} \mathbf{E}$, with $A_{\text{con}} = -0.045 \text{ mol/emu}$, and a traceless part, corresponding to the dipolar coupling tensor $\mathbf{A}_{\text{dip}}$,

$$\mathbf{A}_{\text{dip}} = \begin{pmatrix} 0.270 & 0 & 0 \\ 0 & -0.165 & 0 \\ 0 & 0 & -0.105 \end{pmatrix} \frac{\text{mol}}{\text{emu}}.$$

These results are also listed in the top of Table 1. Using the experimental values for the hyperfine coupling $\mathbf{A}_f$, the extrapolation of a linear scaling of the Knight shift with the $4f$ -susceptibility $\chi_f = \chi_{\parallel, \perp} - \chi_0$ to lower temperatures, assuming temperature independent hyperfine coupling, is shown in Fig. 3a-c as dashed curves. They demonstrate

Fig. 4 a Splitting $\Delta K = |K(I) - K(II)|$ between the signals I and II observed for $H \parallel \bar{a}$ (open squares) and $H \parallel a$ (filled circles, compare Fig. 3a,b) versus the bulk susceptibility $\chi_{\perp}$; b Knight shift K_c as a function of $\chi_{\parallel}$. The temperature is an implicit parameter. The straight lines are fits to the linear regions $50 \text{ K} \leq T \leq 150 \text{ K}$

the pronounced deviations of the measured Knight shifts from the expected behavior at $T < 50$ K. Before we explain this phenomenon, we will first discuss the determination of the position of the interstitial μ^+ from the Knight shift anisotropy in the next section, because the knowledge of the μ^+ site is a prerequisite for the quantitative analysis of the Knight shifts at $T < 50$ K.

At the end of this section we would like to stress that the presented results, obtained on three new samples that were prepared independently, are perfectly consistent. However, the current results on the Knight shift anisotropy at any given temperature are in disagreement with earlier results obtained with a supposedly well characterized sample [22]. For example, whereas the angular pattern in the present Fig. 2b exhibits just two frequencies (signals), the angular pattern obtained under seemingly similar conditions in the earlier study (Fig. 1 in [22]) exhibits a total of three major and two minor frequencies (signals), which were assigned to several different μ^+ sites, none of which is coinciding with the present site assignment. While the discrepancies on the anisotropy remain unsettled (the original ‘early crystal’ is no longer available), essentially all of the presently observed features related to the temperature dependence of the Knight shifts, including the non-scaling with bulk susceptibility and the non-saturating behavior at low temperatures were reported qualitatively also with the ‘early crystal’. As will be shown further below, at least the three major signals observed in the earlier work may be understood in terms of the present μ^+ -site assignment by assuming a misorientation of the rotation axis during the early measurements.

5. Determination of the μ^+ site

In the following we describe the determination of the μ^+ interstitial site from the Knight shift anisotropy. PrNi_5 is of CaCu_5 type structure (see Fig. 4 in [17]), the space group is $P6/mmm$. All types of sites within a crystal of a certain symmetry may be classified by the number of these sites per unit cell (multiplicity) followed by the Wyckhoff letter. Classification lists can be found e.g. in [23].

As argued in Sect. 4 only one interstitial site that appears $3n$ times per unit cell is occupied by the μ^+ . Thus all ‘axial’ symmetric sites, that are sites of type $(0, 0, z)$ and $(1/3, 2/3, z)$, can be safely discarded. For all other interstitial sites we performed dipolar field calculations, using (7) and (9) and summarizing over all $4f$ moments within a Lorentz sphere of radius 25 Å, where the summation has converged already to better than 0.5% . From the results of these calculations it follows that only sites of type $3f$, $6i$ and $6j$ are of the right symmetry to produce a pattern in the angular dependence of the Knight shift similar to the one observed. All sites with multiplicity larger than six can be ruled out as μ^+ sites, since due to their low symmetry the dipolar fields from the f moments would produce more signals than actually observed in the angular dependence. The remaining interstitial sites $6k$, $6l$, $6m$ would produce patterns in the angular dependence that are shifted by $\varphi' = 30^\circ$ for rotation of H in the basal plane or of strongly different amplitudes for rotation of H in the a - c plane compared to the observed ones.

The precise determination of the actual μ^+ site is now possible by a comparison of the experimentally observed dipolar field tensor $\mathbf{A}_{\text{dip}}$ (see Table 1) with calculated values for the interstitial sites $3f(1/2, 0, 0)$, $6i(1/2, 0, z)$ and $6j(x, 0, 0)$. Note that for the two latter types of site we have free parameters z and x , respectively. Some calculated dipolar field values are listed in Table 1. By comparison, the experimentally observed dipolar fields are found to be in agreement *only* with a μ^+ localization at a site of $6i$ -type $(1/2, 0, z)$ with $z = 0.21$. (Note that in the previous publication [13], with the knowledge of only two elements of $\mathbf{A}_{\text{hf}}$, the $3f$ site was proposed as being consistent with symmetry arguments.)

To check for the influence of a possible local lattice expansion (contraction) around the μ^+ on the site determination we performed additional dipolar field calculations, allowing for a (radial) displacement δr up to 0.25 Å of the two Pr ions next to the $6i$, $3f$ and $6j$ sites and thus for a reduction the (dominant) contribution of these ions to the dipolar fields. We found that no choice of the parameters $\delta r, x, z$ other than $\delta r = 0$ (± 0.05 Å), $x = 0, z = 0.21$ (± 0.02) could reproduce the observed dipolar coupling $\mathbf{A}_{\text{dip}}$.

We also considered the possibility of localized moments on the Ni, as suggested from spin polarized band structure calculations [24]. One calculates large dipolar fields per unit Ni moment, e.g. at the site $(0.5, 0, 0.21)$:

$$\mathbf{A}_{\text{dip}}(I, \text{Ni}) = \begin{pmatrix} -2.024 & 0 & 0 \\ 0 & -0.012 & 0 \\ 0 & 0 & 2.036 \end{pmatrix} \frac{\text{mol}}{\text{emu}}.$$

We estimate that only a very small local moment susceptibility of Ni of less than 2% of that of Pr would be consistent with the experimentally observed dipolar fields at $T > 50$ K. Assuming a Curie-Weiss behavior of the Ni-susceptibility this results in an upper limit for the effective Ni moment of $\mu_{\text{Ni}} \leq 0.6 \mu_B$, larger than the value $\mu_{\text{Ni}} = 0.2 \mu_B$, resulting from a selfconsistent solution of the

Table 1. Experimental and calculated hyperfine coupling parameters for the μ^+ sites allowed from symmetry. They are scaled by a factor $1/N_A$ compared to eq. (3) to obtain molar values

	A^{aa}	A^{aa} mol/emu*	A^{cc}
experimental:			
A_{dip}^{ii}	0.225	− 0.210	− 0.150
A_{dip}^{ii}	− 0.045	− 0.045	− 0.045
A_{dip}^{ii}	0.270	− 0.165	− 0.105
errors:		(± 0.010)	
calculated:			
A_{dip}^{ii} at site			
$3f(1/2, 0, 0)$	0.378	− 0.183	− 0.195
$6j(0.45, 0, 0)$	0.406	− 0.198	− 0.208
$6m(0.13, 0.26, 1/2)$	− 0.261	− 0.064	0.325
$12n(0.47, 0, 0.092)$	0.361	− 0.183	− 0.178
$6i(1/2, 0, z)$			
$z = 0.088$ [26]	0.355	− 0.179	− 0.176
$z = 0.21$	0.268	− 0.164	− 0.104

*for SI units: $1 \text{ mol/emu} = 0.5585 \text{ T}/\mu_B$

mentioned band structure calculations. Thus from our results the existence of small localized moments on the Ni cannot be ruled out. However, the estimated upper limit for a Ni contribution is too small to explain the observed deviations from a linear scaling of the Knight shifts with the bulk susceptibility at $T < 50$ K. Moreover, it has to be noted that even large localized moments on the Ni could not account for the observed behavior. From the calculated $A_{\text{dip}}(\text{Ni})$ it follows that dipolar fields due to moments on the Ni should affect the shift of signal *I* much stronger for $H \parallel a$ or $H \parallel c$ than for $H \parallel \bar{a}$, in strong contrast to the observation (compare Fig. 3). In addition, the appearance of localized Ni moments would be in contradiction with the observation of a temperature independent Pauli susceptibility in LaNi_5 [20], that is believed to characterize the Ni $3d$ electron system also in PrNi_5 [14].

The position of the actual μ^+ site is sketched in Fig. 5. Note that from our results we cannot derive any information about a possible displacement of Ni ion next to the μ^+ . The μ^+ is located within the plane defined by a triangle of Ni ions with its center at $(1/2, 0, 0.12)$. Strong repulsive forces from the Pr^{3+} next to the μ^+ seem to be responsible for the shift of the μ^+ to $z > 0.12$. We may compare our observation with the results of hydrogen site determinations in LaNi_5 . The sites $3f$, $6i$ and in addition $12n$ have been considered as hydrogen sites in LaNi_5D_3 , the exact position of D apparently depending on the concentration δ [25]. Our results would correspond to the limit of zero hydrogen concentration. The observed μ^+ site is close to the $6i$ site found to be occupied by 75% of the D in the intermediate phase LaNi_5D_3 [26], where $z = 0.088$ was observed at ambient and higher temperatures. The occupancy of the second site $6m$ was observed to be much lower than 25% in the α -phase of LaNi_5D_3 ($\delta < 0.4$), namely 6% at room temperature in a sample with $\delta = 0.08$ [27]. This tendency is in agreement with our observation of only one μ^+ site at $T \leq 150$ K. Deuterium site determinations by neutron scattering in the α -phase could not unambiguously locate the D [28, 29]. From our results we can specifically rule out the occupation of the

Fig. 5 The location of the μ^+ site with respect to its nearest Pr and Ni neighbors. The given coordinate frame (x, y, z) is used for the description of the μ^+ perturbed susceptibility (see text). Note that it is defined by the relative geometry of the μ^+ and the neighbouring ions, being identical with $(a, \bar{a}, c)$ for μ^+ at $(1/2, 0, 0.21)$ and rotated by $\pm 60^\circ$ relative to $(a, \bar{a}, c)$ for μ^+ at $(1/2, 1/2, 0.21)$ and $(0, 1/2, 0.21)$

$12n$ site by μ^+ that was proposed as possible D site in one of these works [28]. The larger z observed for μ^+ in PrNi_5 compared to the D site in LaNi_5D_3 [26] may be due to differences in the repulsive forces from neighboring atoms due to the high hydrogen loading in LaNi_5D_3 . The large difference of the masses of μ^+ and D by a factor of 18 in addition could give rise to different widths of the zero point motions in the typically asymmetric trapping potential, leading to an additional shift of the equilibrium position of the μ^+ relative to that of D.

6. Explanation of the low temperature Knight shift

In the following we discuss the strong deviations from the expected linear scaling of the Knight shifts with the bulk susceptibility at $T < 50$ K (see Fig. 3a-c). Since the $4f$ contribution to the Knight shift for the principal orientations is simply given by $K_i = A_{ii}^f \chi_i$ (Eq. 4), the origin of the unusual behavior could in principle be traced back to a change of the hyperfine coupling and/or to a modification of the atomic susceptibility tensor χ_f . We will argue that the observed behavior cannot be explained by a change of the hyperfine coupling $A_f = A_{\text{dip}} + A_{\text{con}} \mathbf{E}$. First, the dipolar contribution A_{dip} is determined by the lattice geometry and the μ^+ interstitial site and therefore temperature independent [30]. Secondly, a change of the isotropic contact coupling A_{con} that could appear because of the depopulation of excited CEF levels of the Pr^{3+} ions, would lead to deviations from the extrapolated behavior of *equal size* for all signals observed for $H \parallel a, \bar{a}$. The splitting between the signals *I* and *II* in this case should further scale linearly with the bulk susceptibility, in strong contrast to the observation (see Fig. 4). In addition, for $H \parallel c$, the deviations from the extrapolated behavior should be negative like for the other orientations of the external field, again in contrast to the observation (see Fig. 3c).

Hence the only possible conclusion from the observations is that *the local susceptibility monitored by the μ^+ becomes different from the bulk susceptibility*. The magnetic susceptibility of at least the two Pr^{3+} ions next to the μ^+ (labeled 'nn'-Pr in the following) is altered due to the presence of the μ^+ itself. Assuming constant hyperfine coupling, the modified susceptibility is directly reflected in the observed Knight shifts. The situation is most transparent for the signal *I* for which the external field is parallel (perpendicular) to the direction x in the coordinate frame defined in Fig. 5 for $H \parallel a$ ($H \parallel \bar{a}$). Clearly, the muon induces an *anisotropy within the basal plane* at $T < 50$ K. To obtain a quantitative determination of the influence of the muon we have calculated the magnetic susceptibility of the two nn-Pr ions from the experimental Knight shifts for all three principal orientations assuming

- the μ^+ site $(1/2, 0, 0.21)$,
- a temperature independent A_f as given at the top of Table 1,
- that A_{con} is produced only by the two nn- Pr^{3+} ions, and
- that only the susceptibility of the two nn- Pr^{3+} ions is affected by the presence of the μ^+ and that all other Pr ions exhibit the unperturbed susceptibility χ_f .

The last two assumptions are well justified by the fact that the distance d from the μ^+ site (1/2, 0, 0.21) to the two next-nearest neighbor Pr ions is already a factor of 1.7 larger than to the nn-Pr. First, since A_{con} is mediated by the RKKY interaction that falls off with $1/d^3$, the contact contribution is expected to be dominated by the nn-Pr ions. The oscillatory behavior of the RKKY interaction may modify this simple picture, but we will see that a relaxation of the third assumption produces only minor changes in the quantitative results. Secondly, the fourth assumption is reasonable because the influence of the μ^+ on the susceptibility of the other Pr ions should be much smaller than on that of the nn-Pr ions. In addition a possible change of the susceptibility of these other Pr ions will have only a minor effect on the dipolar fields at the μ^+ site that are dominated by the contribution from the nn-Pr ions.

The above assumptions allow to decompose the contribution from the nn-Pr ions to the hyperfine coupling A_f from that of all other ions except nn-Pr (labelled '1-nn' in the following) within the Lorentz sphere. The Knight shifts of signal *I* for the principal orientations ($i = a, \bar{a}, c = x, y, z$) can then be rewritten as

$$\begin{aligned} K_a(I) &= (A_{\text{dip,nn}}^{xx} + A_{\text{con}}) \chi_x + A_{\text{dip,(1-nn)}}^{xx} \chi_{f,\perp}, \\ K_{\bar{a}}(I) &= (A_{\text{dip,nn}}^{yy} + A_{\text{con}}) \chi_y + A_{\text{dip,(1-nn)}}^{yy} \chi_{f,\parallel}, \\ K_c(I) &= (A_{\text{dip,nn}}^{zz} + A_{\text{con}}) \chi_z + A_{\text{dip,(1-nn)}}^{zz} \chi_{f,\parallel}, \end{aligned} \quad (10)$$

where the subscripts nn (or 1-nn) denote, that the respective dipolar field contribution was taken from nearest neighbor Pr ions (or all except nearest neighbors) only. Note that A_{dip} is dominated by the nn contribution with diagonal elements $A_{\text{dip,nn}}^{ii} = (0.314, -0.185, -0.129)$ mol/emu, whereas $A_{\text{dip,(1-nn)}}^{ii} = (-0.046, 0.021, 0.025)$ mol/emu and $A_{\text{con}} = -0.045$ mol/emu. In (10) we have introduced a new atomic susceptibility tensor with diagonal elements (χ_x, χ_y, χ_z) characterizing the perturbed susceptibility of the nn-Pr ions. Note that we use the coordinate frame (x, y, z) defined by Fig. 5 and related to the relative geometry of the μ^+ and the neighboring Pr ions. Using (10) and the measured χ_f , we calculated the perturbed susceptibility for all three principle orientations from the Knight shifts K_i for signal *I*. The results are shown in Fig. 6 (filled circles and triangles). The second data set in Fig. 6 (open circles) is derived from the Knight shifts observed for the signal *II*, for which equations similar to (10) can be derived by rotation of the tensor $A\chi$ by $\varphi = 60^\circ$:

$$\begin{aligned} K_a(II) &= \frac{1}{4} (A_{\text{dip,nn}}^{xx} + A_{\text{con}}) \chi_x + \frac{3}{4} (A_{\text{dip,nn}}^{yy} + A_{\text{con}}) \chi_y \\ &\quad + \left(\frac{1}{4} A_{\text{dip,(1-nn)}}^{xx} + \frac{3}{4} A_{\text{dip,(1-nn)}}^{yy} \right) \chi_{f,\perp}, \\ K_{\bar{a}}(II) &= \frac{3}{4} (A_{\text{dip,nn}}^{xx} + A_{\text{con}}) \chi_x + \frac{1}{4} (A_{\text{dip,nn}}^{yy} + A_{\text{con}}) \chi_y \\ &\quad + \left(\frac{3}{4} A_{\text{dip,(1-nn)}}^{xx} + \frac{1}{4} A_{\text{dip,(1-nn)}}^{yy} \right) \chi_{f,\perp} \end{aligned} \quad (11)$$

We checked that a relaxation of the third assumption discussed above introduces only minor changes in the calculated susceptibility. If one would assume A_{con} to be determined completely by the non-nn-Pr ions, it would be added to $A_{\text{dip,(1-nn)}}^{ii}$ instead to $A_{\text{dip,nn}}^{ii}$ in (10).

Fig. 6 The magnetic susceptibility of the two Pr^{3+} ions next to the μ^+ for all three principal orientations (x, y, z), as defined in Fig. 5. They are calculated from the observed Knight shifts for signal *I* (filled circles/squares) and *II* (open circles/squares) for $H \parallel a$ and $H \parallel \bar{a}$ and from the single signal for $H \parallel c$ (filled triangles) under the assumptions discussed in the text. The dashed curves are the corresponding bulk susceptibility ($\chi_{\perp, \parallel}$). The solid curves are results from a three parameter CEF field fit explained in the text

Then one would obtain e.g. $\chi_x(T = 10\text{K}) = 0.067$ emu/mol and $\chi_x(T = 10\text{K}) = 0.32$ emu/mol, not too different from the values displayed in Fig. 6 ($\chi_x = 0.063$, $\chi_y = 0.28$ emu/mol).

The most striking property of the calculated perturbed susceptibility tensor for the Pr ions next to the μ^+ is its apparent anisotropy in the basal plane. The susceptibility χ_y , in contrast to the bulk susceptibility $\chi_{\perp}$ and χ_x , does not exhibit any saturation down to the lowest temperatures but rather shows an approximate Curie-Weiss like temperature dependence. The observed anisotropy of the susceptibility in the basal plane introduced by the μ^+ shows that the preferred orientation of the $4f$ moments is perpendicular to the axis connecting the μ^+ with the nn-Pr ions (compare Fig. 5). At the crystallographic equivalent μ^+ sites producing the signal *II* this axis encloses an angle of about 60° (for $H \parallel a$) or 30° (for $H \parallel \bar{a}$) with the external field. Thus, due to the anisotropic susceptibility the dipolar contribution of the nn-Pr ions to the shift of signals *II* are produced by induced moments $\mu_f = \chi_f H$ not parallel to the external field. Moreover, the anisotropy, and with it the angle between H and the induced moments, increases with decreasing temperature. Actually, *this* is the reason for the change of sign in the Knight shift of signal *II* at 20 K for $H \parallel \bar{a}$ (see Fig. 2b), that represents a particular unusual feature of the present experimental results.

With the now complete knowledge of hyperfine parameters and susceptibility we may calculate the Knight shifts for arbitrary orientations. We find that the angular dependence of the three major signals observed in the earlier measurements [22] can be reproduced in detail assuming the orientation of the rotation axis $\theta = 58^\circ$, $\varphi = 2^\circ$, i.e. an orientation about 32° off the specified orientation $\parallel a$. The origin of the two additional signals in the earlier measurements remains unclear.

7. Discussion

The CEF level scheme of PrNi_5 is well established [12, 17, 14]. The hexagonal CEF (with the CEF hamiltonian $\mathcal{H}_{\text{CEF}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^2 O_6^2$) leads to a splitting of the 3H_4 multiplet of the Pr^{3+} -ions with the Γ_4 singlet eigenstate of $\mathcal{H}_{\text{CEF}}$ as the ground state and the Γ_1 singlet as the lowest excited state (see Fig. 7, left). On the basis of this level scheme and the measured molecular field parameter λ the temperature dependence of the bulk magnetic susceptibility χ_f , which is given by $1/\chi_f = 1/\chi_{\text{CEF}} - \lambda$, is well understood [12]. Here, χ_{CEF} is the unenhanced crystal electric field susceptibility calculated with the standard thermodynamic formula and λ describes the enhancement of χ_{CEF} due to the exchange coupling to the neighboring Pr ions. We have shown in the preceding sections that the μ^+ is located between two Pr ions, the atomic susceptibility of which is perturbed by the presence of the μ^+ , implying a muon induced change of the CEF level scheme of these ions. Due to the apparent reduction of the local symmetry by the presence of the μ^+ , additional terms $B_l^m O_l^m$ appear in $\mathcal{H}_{\text{CEF}}$, that are zero in the unperturbed case, allowing for an anisotropy of the susceptibility within the basal plane.

Starting from the well determined molecular field and CEF parameters λ , B_l^m [12], we are able to fit the modified susceptibility by allowing at least the parameters B_2^0 and B_2^2 to vary independently. The exchange coupling is assumed to be *not* perturbed by the μ^+ . In the calculations of the exchange field at the two Pr ion next to a μ^+ we assume that all other Pr ions exhibit the unperturbed susceptibility χ_f (see the assumptions discussed in Sect. 6).

The fit results are shown in Fig. 6 as solid curves. Best agreement of the CEF-fit with the observed temperature dependence of χ_x and χ_y is found for $B_2^0 = +0.555(5)$ meV and $B_2^2 = +0.085(5)$ meV and the other parameters as for the unperturbed case, for which $B_2^0 = 0.51$ meV and $B_2^2 = 0$ have been reported [12]. The fit to the temperature dependence of χ_z is of minor quality, but the absolute value of the susceptibility is well reproduced (note the different scale in the insert as compared to the main figure). No better fits are obtained when allowing the exchange interaction *between* the two Pr next to the μ^+ to vary from the value determined in ref. [12]. Thus no information about an influence of the presence of the μ^+ on this exchange interaction can be derived. The changes of the CEF parameters cause a considerable rearrangement of the CEF field level scheme, as demonstrated in Fig. 7 (right). Most important is the splitting of the Γ_6 doublet, producing a second low lying singlet. This effect is responsible for the large susceptibility χ_x even at the lowest temperatures.

The influence of the μ^+ on the CEF on the Pr^{3+} ions may have two origins. First a local lattice expansion around the μ^+ and a corresponding displacement of neighboring Pr and Ni ions and secondly the formation of the electron cloud screening the muon charge, that implies a local charge redistribution and that provides a source of an additional electric field gradient (EFG). As discussed already in Sect. 5, a possible local lattice expansion does not displace the Pr ions next to the μ^+ by more than 0.05 Å. The Ni ions however may experience larger displace-

Fig. 7: CEF level scheme for PrNi_5 (left, [12, 14, 17]); CEF level scheme that gives the best fit to the observed susceptibility of the Pr ions next to the muon (right); the CEF states Γ_3 (≈ 150 K) and $\Gamma_5^{(2)}$ (≈ 335 K) are omitted for clearness

ments. By a comparison of point charge CEF calculations for the unperturbed lattice and for lattices exhibiting local lattice expansions around an interstitial μ^+ we checked that the observed changes of the CEF parameters cannot be explained by displacements of the point charges associated with Pr or Ni ions next to the μ^+ of reasonable size ($\delta r < 0.25$ Å).

We therefore checked if the observed changes of the CEF parameters may be described on the basis of a point charge model for the interstitial muon. The actual charge distribution close to the muon consists of its positive charge and an electron cloud screening this charge. In a jellium model the charge density is an oscillating function of the distance to the muon [31], hence at certain distances the muon may appear even overscreened. Therefore, in the point charge calculations we simply placed an effective charge Z_{eff} on the muon site and calculated the associated CEF parameters associated with the EFG produced at the Pr ions by this charge. In the following we limit our discussion on the second order terms B_2^m . (We checked that the following conclusions are qualitatively not affected by this restriction.) For μ^+ at $(1/2, 0, 0.21)$ one obtains $B_2^0 = Z_{\text{eff}} \times (-0.09)$ meV and $B_2^2 = Z_{\text{eff}} \times 0.35$ meV (and a nonzero B_4^2 , that has only minor influence on the susceptibility). From the observed muon induced changes of the CEF parameters, $B_2^0(\text{perturbed}) - B_2^0(\text{unperturbed}) = +0.045$ meV and $B_2^2(\text{perturbed}) - B_2^2(\text{unperturbed}) = +0.085$ meV, one would derive effective charges at the muon site of different sign, namely $Z_{\text{eff}} = -0.5e$ from B_2^0 and $Z_{\text{eff}} = +0.25e$ from B_2^2 , respectively. Clearly, a simple point charge picture does not apply. We conclude that the actual charge distribution in the screening cloud around the μ^+ may not be replaced by a simple point charge. In addition, also the on-site contribution to the CEF at the Pr^{3+} that is produced by the charge distribution within the electronic shell of the Pr ion [24] may be modified. Unfortunately, to our knowledge, no comparable result on RENi_5H_8 from other techniques is available in the literature. Therefore additional experimental investigations as well as theoretical

calculations of the effect of interstitial hydrogen on the CEF at neighboring Pr ions are highly desirable.

8. Conclusion

In the present work we were able to determine the localization of the 'light hydrogen isotope' μ^+ in PrNi_5 , corresponding to a determination of the hydrogen/deuterium site in the limit of infinite dilution, a task that can be hardly accomplished by other techniques. Moreover, we observed a strong μ^+ induced change of the susceptibility of the Pr^{3+} ions next to the interstitial μ^+ and were able to describe it by a modified crystal electric field at these ions. As the positive muon is electronically equivalent to the proton these results can be viewed as a quantitative determination of the effect of a hydrogen like impurity on the crystal electric field *in the limit of zero impurity concentration*. To our knowledge the present μSR work represents the first experimental result of that kind.

On the basis of our observation we may speculate, that the magnetic properties of hydrided $\text{PrNi}_5\text{H}_\delta$ could be quite different from that of pure PrNi_5 , mainly due to the effect of the interstitial H on the CEF at the Pr^{3+} ions. A tendency towards a large low temperature susceptibility, as suggested by our results, together with the ferromagnetic coupling between the Pr ions could probably lead to ferromagnetic order in $\text{PrNi}_5\text{H}_\delta$, as it is observed in other RENi_5 (e.g., $\text{RE} = \text{Gd}, \text{Er}, \text{Dy}, \text{Tm}$) compounds. It is important to note at this point that by μSR depolarization studies in zero external field [32, 33] it has been found that the spin dynamics of the Pr^{4f} electronic moments is slowed down to a quasistatic behavior at $T \leq 20$ K. The results of the present work strongly suggest that the observed extremely large widths of the static magnetic field distribution at these temperatures are related to the μ^+ -induced modification of the low temperature susceptibility of the neighboring Pr ions. We therefore conclude that it is crucial to take into account the possibility of a muon induced change of the CEF at the RE ions in all μSR studies of other RE intermetallics. However, this possibility has as yet been considered only in the discussion of a very few μSR investigations (see discussion in [13] and refs. therein).

In conclusion, we think that the determination of the effect of a hydrogen like impurity on the CEF as presented in this work may serve as a new approach for understanding the effect of hydrogen absorption on the magnetic properties of host compounds on an atomic level.

We are grateful to I. Felner (Jerusalem) for providing the susceptibility data on the investigated samples and to A. Furrer (ETH Zürich) for useful discussions and making available to us the program for CEF calculations. Part of this research was supported by the Israel Science Foundation (Israel Academy of Science).

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