Quantized Hyperfine Field at an Implanted μ^+ Site in PrPb_3 : Interplay between Localized f Electrons and an Interstitial Charged Particle

T. U. Ito,^{1,2} W. Higemoto,² K. Ohishi,^{2,*} N. Nishida,¹ R. H. Heffner,^{2,3} Y. Aoki,⁴ A. Amato,⁵
T. Onimaru,⁶ and H. S. Suzuki⁷

¹*Department of Physics, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan*

²*Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan*

³*Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

⁴*Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan*

⁵*Laboratory for Muon-Spin Spectroscopy, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland*

⁶*Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8530, Japan*

⁷*National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan*

(Received 28 October 2008; published 3 March 2009)

The local effect of an interstitial hydrogenlike particle on localized f electrons was studied in PrPb_3 by means of μ^+ spin rotation and relaxation. Spontaneous μ^+ spin precession with harmonic frequencies was observed for the first time in f electron compounds. We demonstrate that the signal is derived from a coupling between the μ^+ spin and the hyperfine-enhanced nuclear spin of nearest neighbor (NN) ^{141}Pr with Ising-like anisotropy. The signal also suggests a marked suppression of spin dynamics of the NN ^{141}Pr in comparison with that of the bulk ^{141}Pr . These facts strongly indicate modification of the f electronic state due to the interstitial charged particle.

DOI: 10.1103/PhysRevLett.102.096403

PACS numbers: 71.70.Ch, 76.75.+i

The behavior of ^1H impurities in rare-earth (RE) based compounds and the influence on their surroundings are crucial issues for practical materials science. ^1H is the most common impurity which affects the quality of samples. In fact, ^1H is sometimes deliberately loaded into a material to improve functions of the base compound [1], or to store ^1H itself at interstitial sites of the crystal [2]. In RE-containing materials the electronic state of the RE ion should be sensitive to the ^1H impurity because the positive charge of the ^1H creates an additional crystalline-electric-field (CEF) potential which affects electromagnetic properties of the nearby RE ions. A detailed understanding of the effects of ^1H impurities in RE-based compounds is therefore important for industrial applications as well as for fundamental science.

One of the most efficient techniques to investigate microscopic properties of interstitial ^1H is positive muon-spin rotation and relaxation ($\mu^+\text{SR}$), which probes the local magnetic environment around an interstitial μ^+ , a light isotope of ^1H . In this Letter, we report $\mu^+\text{SR}$ measurements in PrPb_3 to clarify the local effect of the interstitial μ^+ on the localized $4f$ electrons. PrPb_3 has physical properties appropriate for this purpose: (i) a simple cubic structure (space group $Pm\bar{3}m$), (ii) a well-defined CEF level scheme with small excitation energies, (iii) a non-magnetic Γ_3 CEF ground state (GS) in a CEF potential with O_h symmetry. In ^{141}Pr -based compounds with a non-magnetic GS, a strong intraionic hyperfine coupling between the ^{141}Pr nuclear spin I and the $4f$ electrons causes an effective nuclear dipolar moment typically 10 ~ 100 times larger than the bare nuclear value. This enables one to monitor the $4f$ electronic state in zero applied field (ZF)

by observing the local field caused by the hyperfine-enhanced (HE) nuclear dipolar moment. Here we report the first observation of spontaneous μ^+ spin precession with harmonic frequencies in the paramagnetic state, which indicates a coupling between the μ^+ spin S and I with Ising-like anisotropy. We discuss the interplay between μ^+ and the localized $4f$ electrons on the basis of the anomalous μ^+ spin precession and a strongly anisotropic μ^+ Knight shift.

Single crystal samples of PrPb_3 were grown by the Bridgman method. The $\mu^+\text{SR}$ measurements were carried out at the M15 and M20B beam lines, TRIUMF, Canada, the πM3 beam line, PSI, Switzerland, and the πA port, muon science laboratory (MSL), KEK, Japan. The single crystals with (001) cleavage plane were mounted on a sample holder. ZF- $\mu^+\text{SR}$ measurements were performed with the spin-polarized μ^+ along the [001] direction. For the transverse field (TF) $\mu^+\text{SR}$ measurements, a magnetic field of 2 T was applied along the [001] direction with an initial μ^+ spin polarization $P(t=0)$ perpendicular to the [001] direction.

We first discuss the μ^+ Knight shift, which provides insight into the μ^+ localization site, local susceptibility, and the coupling between S and the $4f$ dipolar moment. The TF- $\mu^+\text{SR}$ signal in the paramagnetic state consists of two components with the intensity ratio of 1:2, suggesting that the local environment at the μ^+ site splits into two magnetically inequivalent locations. Among possible interstitial sites, only the $3d$ site at (0.5, 0, 0) is consistent with this splitting. This site is located at the midpoint of two nearest neighbor (NN) Pr ions, as depicted in the inset of Fig. 1. The 1/3 (2/3) signal with a frequency $f_{\parallel}$ ($f_{\perp}$)

FIG. 1 (color online). The temperature dependence of the μ^+ Knight shift in a magnetic field $\mu_0 H = 2$ T applied along the [001] direction. The inset shows the μ^+ localization site.

corresponds to the site with fourfold symmetry around the [001] axis ([100] and [010] axes).

The μ^+ Knight shift $K_{\parallel,\perp}$ was derived from $K_{\parallel,\perp} = (f_{\parallel,\perp} - f_0)/f_0 - K_{L,\text{dem}}$, where f_0 is a zero-shift frequency, $K_{L,\text{dem}}$ is a correction term for the Lorentz and demagnetization fields (see a preliminary report [3] for details). Figure 1 shows the extremely anisotropic nature of the shifts $K_{\parallel} \gg K_{\perp}$. We now rewrite the Knight shift as a rank-2 tensor $\hat{K}$. Hereafter, coordinate axes are set to be along primitive vectors of the simple cubic lattice so that $\hat{K}$ becomes a diagonal tensor. When the μ^+ is located at the site with fourfold symmetry around the z axis, the diagonal components K_{ii} conform to $K_{xx} = K_{yy} = K_{\perp}$ and $K_{zz} = K_{\parallel}$. Following the treatment in Ref. [4], we decompose $\hat{K}$ as

$$\hat{K} = (\hat{A}_{\text{NN}}^{\text{dip}} + \hat{A}^c)\hat{\chi}_{\text{NN}} + \hat{A}_{\text{1-NN}}^{\text{dip}}\hat{\chi}, \quad (1)$$

where $\hat{A}^{\text{dip}}$ s are classical-dipolar-coupling tensors, $\hat{A}^c$ is an isotropic contact-hyperfine-coupling tensor, $\hat{\chi}$ s are ionic susceptibilities, and subscripts NN and 1-NN designate the NN Pr ions and the remaining further Pr ions, respectively. We assume that the μ^+ influences only the NN Pr ions, so $\hat{\chi}_{\text{1-NN}}$ is replaced by an intrinsic susceptibility tensor $\hat{\chi}$ in Eq. (1). This assumption seems reasonable since the μ^+ is located further away from the Pr ions than their ligands, except for the NN Pr ions. The contact term for the 1-NN Pr ions was omitted for simplicity.

When $\hat{\chi}_{\text{NN}}$ is identical to $\hat{\chi}$, Eq. (1) reduces to $\hat{K} = (\hat{A}^{\text{dip}} + \hat{A}^c)\hat{\chi}$, where $\hat{A}^{\text{dip}} = \hat{A}_{\text{NN}}^{\text{dip}} + \hat{A}_{\text{1-NN}}^{\text{dip}}$. In such a case, $\hat{A}^c$ is the only unknown variable in Eq. (1) since $\hat{\chi}$ is known from Ref. [5] and $\hat{A}^{\text{dip}}$ is purely geometric and calculable. We obtained the solid lines in Fig. 1 for $\hat{A}^c = 0$ and the dashed lines for $\hat{A}^c$ set to satisfy $K_{\perp} \sim 0$. The significant deviation from the observed $\hat{K}$ suggests a breakdown of our assumptions, implying (i) μ^+ -induced modification in $\hat{\chi}_{\text{NN}} (\neq \hat{\chi})$, and/or (ii) temperature-dependent and anisotropic $\hat{A}^c$ which has been invoked to explain μ^+ Knight shift in several f electron systems [6,7]. By only measuring $\hat{K}$, the dominant factor cannot be pinpointed in the present

case. Fortunately, it turns out that the following ZF- μ^+ SR results provide crucial information to resolve this point.

The ZF- μ^+ SR spectra at several temperatures are shown in Fig. 2(a). Surprisingly, periodic recoveries of the asymmetry, indicated by the arrows, are found below $T \lesssim 15$ K. Figure 2(b) shows results of fast Fourier transform (FFT) on the ZF- μ^+ SR signals after subtraction of a zero-frequency component. This reveals that the original spectra consists of five oscillatory components (six, when the zero-frequency component is counted). The μ^+ spin precession frequencies f_i are shown in Fig. 3 as functions of temperature. The frequencies monotonically increase with decreasing temperature, and the lowest frequency f_1 reaches ~ 3.4 MHz at 1 K, which corresponds to a hyperfine field (HF) of ~ 0.025 T at the μ^+ site, much larger than the bare nuclear dipolar field. However, no magnetic ordering is expected since the Γ_3 GS is nonmagnetic. These facts indicate that the HF principally originates from the $4f$ dipolar moments induced by the intraionic hyperfine interactions. A linear relation between the f_i s and f_1 is shown in the inset of Fig. 3. Slopes obtained from the linear fits indicate that the f_i s are integral multiples of the f_1 . This means that the HF at the μ^+ is quantized. The quantum nature and the number of splittings imply a coupling between S with $S = 1/2$ and a small number of I s with $I = 5/2$.

The periodic structure in the ZF signals gradually disappears below ~ 1 K, probably as the temperature approaches 0.4 K, where an antiferroquadrupolar (AFQ) ordering with a long ordered structure occurs [8]. This behavior may be related to the AFQ ordering and its precursive phenomenon, which changes the HE nuclear magnetism through modifications of the $4f$ electronic state.

We are now ready to construct a phenomenological model to describe the ZF- μ^+ SR results. It is known that a strong coupling between a μ^+ spin and a small number of nearby nuclear spins causes spontaneous μ^+ spin precession even in the paramagnetic state. This has been observed in some fluorides in which an entangled state of the nuclear

FIG. 2. (a) ZF- μ^+ SR spectra. The base lines are shifted by 0.1 as the temperature increases. The solid curves are the best fits with Eq. (7). (b) FFT spectra of the ZF- μ^+ SR signals.

FIG. 3 (color online). The spontaneous μ^+ spin precession frequencies as functions of temperature. The inset is the f_i versus f_1 plot ($i > 1$). The solid lines represent the linear fits.

spins, $^{19}\text{F}-\mu^+-^{19}\text{F}$, is realized [9]. In the case of μ^+ in PrPb_3 , two Pr ions and an interstitial μ^+ form a collinear spin configuration $^{141}\text{Pr}-\mu^+-^{141}\text{Pr}$. Therefore, we consider the following spin Hamiltonian: $H = H_{SI} + H_{II} + H_{\text{quad}}$, where H_{SI} and H_{II} express spin interactions between S and I s, and between I s, respectively, and H_{quad} is a Hamiltonian for the nuclear quadrupolar interaction under the electric field gradient created by the μ^+ . We hereafter distinguish the two NN Pr with subscripts 1 and 2.

Considering a coupling with the HE nuclear dipolar moment μ_{hf} , we first formulate H_{SI} as $-\gamma_\mu \hbar S \cdot \hat{a}(\mu_{\text{hf},1} + \mu_{\text{hf},2})$, where γ_μ is the muon gyromagnetic ratio, and $\hat{a}$ is the hyperfine coupling tensor defined for each μ^+ -Pr coupling. The μ_{hf} is rewritten with the ^{141}Pr Knight shift tensor $\hat{K}_I$ as $\gamma_I(1 + \hat{K}_I)\hbar$, where γ_I is the gyromagnetic ratio of the bare ^{141}Pr nucleus. Assuming that the principal value of $\hat{K}_I$ is much larger than 1, we obtain the following expression,

$$H_{SI} \sim -\gamma_\mu \gamma_I \hbar^2 S \cdot \hat{a} \hat{K}_I (I_1 + I_2). \quad (2)$$

Although the above form includes an unknown tensor $\hat{a} \hat{K}_I$, it will turn out to be approximately proportional to the μ^+ Knight shift $\hat{K}$. The $\hat{K}$ is dominated by the coupling to the two NN Pr ions, so $\hat{K} \sim 2\hat{a} \hat{\chi}_{\text{NN}}$. The $\hat{K}_I$ is proportional to $\hat{\chi}_{\text{NN}}$ through the following relation,

$$\hat{K}_I = \frac{a_J}{g_J \mu_B \gamma_I \hbar} \hat{\chi}_{\text{NN}}, \quad (3)$$

where a_J is the intraionic hyperfine coupling constant between I and the total angular momentum J of the $4f$ electrons, and $g_J = 4/5$ is the Lande g factor. Substituting $\hat{K}_I$ from Eq. (3) into Eq. (2) and using $\hat{K} \sim 2\hat{a} \hat{\chi}_{\text{NN}}$ yields,

$$H_{SI} \sim -\frac{a_J \gamma_\mu \hbar}{2g_J \mu_B} S \cdot \hat{K} (I_1 + I_2). \quad (4)$$

As shown in Fig. 1, the $\hat{K}$ is strongly anisotropic below the temperature at which the spontaneous μ^+ spin precession

appears, and it is reasonable to set $K_\perp = 0$. Hence, Eq. (2) reduces to,

$$H_{SI} \sim -\hbar \omega_f S_\parallel (I_{1,\parallel} + I_{2,\parallel}), \quad (5)$$

where $\omega_f = a_J \gamma_\mu K_\parallel / (2g_J \mu_B)$, and $S_\parallel$, $I_\parallel$ are spin components parallel to the local symmetry axis. This result implies an Ising-like anisotropy of the S - I coupling, which has not been reported so far in cubic systems.

The H_{II} and H_{quad} should be invariant under the symmetry operation of the system. We will not discuss these terms further since they do not affect the following outcome as long as this condition is satisfied.

With $P(0) \parallel [001]$, the time evolution of the μ^+ spin polarization $P(t) = P(t) \cdot P(0)$ is expressed as follows,

$$P(t) = \sum_{j=x,y,z} \frac{1}{3} \text{Tr}[\rho e^{iH_j t/\hbar} \sigma_z e^{-iH_j t/\hbar}], \quad (6)$$

where σ_z is the z component of the Pauli spin matrices and $\rho = (1 + \sigma_z)/[2(2I + 1)^2]$ is the density matrix which describes the spin state at $t = 0$. It should be noted that explicit forms of the spin Hamiltonian H_j depend on an angle between $P(0)$ and the local symmetry axis. The subscript j is a label to indicate a spin configuration with the local symmetry axis parallel to the x , y , z axis.

Calculating $P(t)$ according to Eq. (6) and multiplying it by the total asymmetry A yields the following function with oscillatory components including five harmonic frequencies with a fundamental frequency $\omega_f/2\pi$, i.e.,

$$AP(t) = \frac{A}{27} [5\cos(\omega_f t) + 4\cos(2\omega_f t) + 3\cos(3\omega_f t) + 2\cos(4\omega_f t) + \cos(5\omega_f t) + 3] e^{-\lambda_\perp t} + \frac{A}{3} e^{-\lambda_\parallel t}, \quad (7)$$

where the first (second) term corresponds to the spin configuration with the symmetry axis perpendicular (parallel) to the z axis. Note that the exponential relaxation functions in Eq. (7) with the relaxation rates $\lambda_{\perp,\parallel}$ were inserted in the theoretical function to express a transverse (longitudinal) relaxation for the first (second) term which appears in the real spectra. Excellent fits are obtained for the time-domain data below 14 K, as shown in Fig. 2(a) by the solid curves. The relative amplitude of the oscillatory components shown in Fig. 2(b) is also reproduced well. On the other hand, if we assume $K_\parallel = 2K_\perp$, which is realized in the case of $\hat{\chi}_{\text{NN}} = \hat{\chi}$ and $\hat{A}_c = 0$, more than five oscillatory components with anharmonic frequencies should appear. This fact indicates that the Ising-like anisotropy is necessary to reproduce the harmonic frequencies in the ZF- μ^+ SR spectra.

A value for a_J is available from the present μ^+ SR data through $a_J = 2g_J \mu_B / \gamma_\mu \times (\omega_f / K_\parallel)$. The ratio $\omega_f / K_\parallel$ was estimated to be 82.9 rad/s from the linear slope in the $\omega_f/2\pi$ ($= f_1$) versus $K_\parallel$ plot shown in Fig. 4, so that we obtained $a_J/k_B = 105$ mK, which is remarkably large compared to the other trivalent RE ions [10]. The present

FIG. 4. The fundamental frequency $\omega_f/2\pi$ ($=f_1$) versus the $K_{||}$ in a field of 2 T. The solid line indicates a linear fit.

result thus provides microscopic evidence for the HE nuclear magnetism of ^{141}Pr . Note that our value for a_J is about 2 times larger than that in Ref. [10]. This discrepancy might be ascribed to an incomplete theoretical formulation, where we used $\hat{K}_I \propto \hat{\chi}_{\text{NN}}$, defined in a uniform field, to describe the HE nuclear dipolar moment in ZF. In the uniform field, the Pr ion feels a molecular field from surrounding Pr moments polarized along the field direction and $\hat{\chi}_{\text{NN}}$ should include the molecular field effect. On the other hand, the Pr moments in ZF are randomly oriented and the effect of exchange interactions among the Pr moments should be different from the molecular field in the uniform field. The molecular field coefficient estimated from the magnetization is $-2.56 \text{ T}/\mu_B$ [5] which causes suppression of the field-induced dipolar moment, consistent with the overestimation of a_J .

The observation of a spontaneous μ^+ spin precession indicates that the spin fluctuation rate τ_c^{-1} of the NN Pr ions is much lower than 1 MHz. By contrast, the intrinsic spin fluctuation rate $|J_{\text{nuc}}|/h \sim 36 \text{ MHz}$ is estimated from $T_c = |J_{\text{nuc}}|I(I+1)/3k_B$ [11], with the nuclear ordering temperature $T_c \sim 5 \text{ mK}$ [12], where $|J_{\text{nuc}}|$ is the nuclear exchange constant. The marked reduction of τ_c^{-1} strongly suggests that the anisotropy in $\hat{K}$ is principally due to that in $\hat{\chi}_{\text{NN}}$, which suppresses the ^{141}Pr HE nuclear spin dynamics. It should also be noted that previous arguments regarding the μ^+ -induced perturbation on localized f electronic states are based on the significant deviation from $\hat{K}$ - $\hat{\chi}$ scaling at low temperatures [4,13]. However, such a behavior also appears in NMR and μ^+ Knight shifts in several f electron systems, and is ascribed to a temperature-dependent hyperfine coupling [6,7,14], or to development of a local susceptibility attributed to the heavy electrons [15,16]. In this sense, an ambiguity exists in the interpretation of previous μ^+ SR data. The present observation thus provides the first experimental fact clearly illustrating that the localized f electronic state is modified by the local effects of an interstitial charged particle.

Finally, we discuss the μ^+ -induced change in the CEF level scheme. Here we consider only low-lying Γ_3 and Γ_4

states with an excitation energy $\Delta_0 = 14.7 \text{ K}$ [5] for simplicity. The symmetry of CEF potential is lowered from cubic O_h to tetragonal C_{4v} due to the μ^+ [4]. The Γ_3 doublet and Γ_4 triplet split into nonmagnetic singlets $\Gamma_3^{(1)}$ and $\Gamma_3^{(2)}$, and a $\Gamma_{4\pm}^{(1)}$ doublet and a $\Gamma_4^{(2)}$ singlet with magnetic degrees of freedom, where we adopted the notation used in Ref. [5]. The low-temperature behavior in $\hat{K}$ indicates that the magnetic anisotropy at low temperatures is dominated by the Van Vleck term and a new CEF GS is still nonmagnetic. Since a nonzero matrix element of $J_{||}$ is found only between $\Gamma_3^{(1)}$ and $\Gamma_4^{(2)}$ states, the modified level scheme should contain the $\Gamma_3^{(1)}$ singlet as the GS. Meanwhile, $\langle \Gamma_3^{(1)} | J_{||} | \Gamma_4^{(2)} \rangle \neq 0$. An excitation energy Δ of the $\Gamma_4^{(2)}$ ($\Gamma_{4\pm}^{(1)}$) state must be smaller (larger) than Δ_0 to reproduce the anisotropy in $\hat{\chi}_{\text{NN}}$ since the Van Vleck term is reciprocally dependent on Δ . Furthermore, the large enhancement of $\hat{\chi}_{\text{NN},||}$ implies that the μ^+ -induced energy shift is comparable in magnitude to Δ_0 . This result suggests a possible drastic change of local magnetic state around ^1H impurities in RE-based intermetallics with $\Delta \leq \Delta_0$.

We thank staff of the muon facilities for experimental assistance, as well as Professors H. Shiba, H. Ishii, K. Nishiyama, Drs. S. Kambe, Y. Tokunaga, H. Sakai, H. Chudo, and T.D. Matsuda for helpful discussions. This work was supported by a Grant-in-Aid for Scientific Research on Priority Area “Skutterudite”, Ministry of Education, Culture, Sports, Science and Technology, Japan, KEK-MSL Inter-University Program for Oversea Muon Facilities, and 21st Century COE Program at Tokyo Tech “Nanometer-Scale Quantum Physics.”

*Present address: Advanced Meson Science Laboratory, RIKEN, Wako 351-0198, Japan.

- [1] J. N. Huiberts *et al.*, Nature (London) **380**, 231 (1996).
- [2] K. Kadir *et al.*, J. Alloys Compd. **257**, 115 (1997).
- [3] T. U. Ito *et al.*, J. Magn. Magn. Mater. **310**, 743 (2007).
- [4] T. Tashma *et al.*, Phys. Rev. B **56**, 9397 (1997).
- [5] T. Tayama *et al.*, J. Phys. Soc. Jpn. **70**, 248 (2001).
- [6] A. Schenck *et al.*, Phys. Rev. Lett. **93**, 257601 (2004).
- [7] F. De Lorenzi *et al.*, Physica (Amsterdam) **326B**, 581 (2003).
- [8] T. Onimaru *et al.*, Phys. Rev. Lett. **94**, 197201 (2005).
- [9] J. H. Brewer *et al.*, Phys. Rev. B **33**, 7813 (1986).
- [10] B. Bleaney, in *Quantum Electronics (Proceedings of the Third International Congress)* (Columbia University Press, New York, 1964).
- [11] K. Ishida *et al.*, Phys. Rev. B **71**, 024424 (2005).
- [12] S. Abe *et al.*, Physica (Amsterdam) **329–333B**, 637 (2003).
- [13] R. Feyerherm *et al.*, Z. Phys. B **99**, 3 (1995).
- [14] T. Ohama *et al.*, J. Phys. Soc. Jpn. **64**, 2628 (1995).
- [15] K. Ohishi *et al.*, J. Phys. Chem. Solids **68**, 2068 (2007).
- [16] N. J. Curro *et al.*, Phys. Rev. B **70**, 235117 (2004).