μ⁺ diffusion in cubic f-electron compounds observed by high transverse field μ⁺SR

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Abstract. Positive muon (μ⁺) diffusion was observed in cubic f-electron compounds PrPb₃ and SmAg₂In by means of the μ⁺ spin rotation (μ⁺SR) method in high transverse field applied along the [001] direction. The applied field splits one crystallographic site into two magnetically inequivalent sites. The μ⁺ diffusion between these magnetically different sites drastically influences the μ⁺SR frequencies, so that two lines are gradually merged into one line at increasing temperature due to the motional narrowing effect. The μ⁺ hopping rate Ω derived from the μ⁺SR line shape follows the Arrhenius law, namely, Ω = Ω₀ exp(−U/kₜB T) in both cases. The preexponential factor Ω₀ suggests that the dominant mechanism of μ⁺ diffusion is classical over-the-barrier hopping in PrPb₃ for 140<T<200 K and phonon-assisted quantum tunneling in SmAg₂In for 40<T<70 K.

1. Introduction
The diffusion of positive muons (μ⁺) in condensed matter has been investigated for many years using the μ⁺ spin rotation/relaxation (μ⁺SR) technique. These μ⁺SR studies have provided deep insight into quantum diffusion of a light charged particle at low temperatures, as well as a hopping process at high temperatures [1, 2]. These processes are closely related to hydrogen dynamics in materials since the μ⁺ can be regarded as a light isotope of ¹H. Knowledge of μ⁺ diffusion is therefore important, not only for fundamental science, but also for industrial applications.

Information about motion of the μ⁺ can be deduced from the dynamical properties of the hyperfine field that the μ⁺ feels in materials. The dynamical nature of the hyperfine field is often investigated by monitoring narrowing of a single μ⁺SR line caused by the μ⁺ motion between equivalent interstitial sites. For precise determination of the μ⁺ hopping rate, the local field at an interstitial site must be constant in magnitude and static within the μ⁺SR time-window over the temperature range of interest. However, this condition frequently breaks down in f-electron
compounds, in which magnetism of lanthanide or actinide ions causes a temperature-dependent \(\mu^+\) spin relaxation. In such cases, the high transverse field (TF) \(\mu^+\)SR method is useful for investigation of the \(\mu^+\) dynamics.

The high TF-\(\mu^+\)SR study of the \(\mu^+\) diffusion is based on the observation of nuclear spin diffusion by NMR [3]. A high TF applied along a certain crystal axis induces a magnetic moment at the ion which leads to symmetry lowering at the probe site. The magnetic environment of the probe site can split into more than two different environments even if the probe site is crystallographically unique. Diffusion of the probe between the magnetically inequivalent sites drastically influences the NMR or \(\mu^+\)SR lines in frequency space, where multiple lines are gradually merged into one line with increasing temperature due to the motional narrowing effect.

The first high TF-\(\mu^+\)SR investigation of the \(\mu^+\) diffusion in \(f\)-electron compounds was performed by Alexandrowicz et al. in PrIn\(_3\) which has a cubic AuCu\(_3\)-type structure; high sensitivity of this technique to the \(\mu^+\) diffusion was demonstrated [4]. In this pioneering paper it was suggested that isomorphic PrPb\(_3\) is a candidate system potentially amenable for such experiments. In this paper, we report experimental results using high TF-\(\mu^+\)SR in PrPb\(_3\), as well as successful observation of \(\mu^+\) motion in SmAg\(_2\)In, which has a cubic Heusler-type crystal structure.

2. Experiment

Single-crystalline samples of PrPb\(_3\) and SmAg\(_2\)In were grown by the Bridgeman method. The \(\mu^+\)SR measurements were carried out using the HiTime spectrometer at the M15 beam line, TRIUMF, Canada. A single-crystalline sample with a (001) plane surface was mounted on a sample holder. A magnetic field was applied along the [001] direction and the positive muons were implanted into the sample with an initial \(\mu^+\) spin polarization perpendicular to the [001] direction. The magnitude of the applied field was 2 T for PrPb\(_3\) and 6 T for SmAg\(_2\)In.

3. \(\mu^+\)SR line shape in PrPb\(_3\) and analysis

The \(\mu^+\)SR line shape in PrPb\(_3\) in the paramagnetic state is shown in Fig. 1 (left). Two lines with peaks at \(\omega_1\) and \(\omega_2\) with the intensity ratio of 2:1 were observed in the temperature range below \(\sim 160 \text{ K}\). Here the implanted \(\mu^+\) is almost stationary at an interstitial site, within the \(\mu^+\)SR time-window. This low temperature behavior has been previously reported in Ref. [5, 6]. Among possible interstitial sites, only the \(d\) site at \((0.5, 0, 0)\) is consistent with this splitting. This site is located at the midpoint of two Pr ions, as depicted in the inset of Fig. 1 (left). The two lines are gradually merged into one line with increasing temperature as a result of the motional narrowing.

The \(\mu^+\) hopping rate \(\Omega\) between the two magnetic sites can be extracted from the \(\mu^+\)SR line shape with the Anderson-Weiss approach, assuming a Markov-type hopping process [7]. The \(\mu^+\)SR line shape is expressed using the notation of Ref. [3] as follows,

\[
I(\omega') = \frac{L^3 + 3L^2\Omega + \frac{4}{3}\delta^3\Omega + L[\omega' - \frac{2}{5}\delta\omega' + \delta^2 + \frac{3}{5}\Omega^2]}{L^4 + (\omega'^2 - \delta^2)^2 + 3L^3\Omega + \Omega L(3\omega'^2 + 2\delta\omega' + 3\delta^2) + \frac{1}{4}\Omega^2(3\omega' + \delta)^2 + L^2[2(\omega'^2 + \delta^2) + \frac{9}{5}\Omega^2]},
\]

where \(\omega_0 = (\omega_1 + \omega_2)/2\), \(\delta = (\omega_2 - \omega_1)/2\), \(\omega' = \omega - \omega_0\), \(L\) is the intrinsic Lorentzian linewidth of the signals at \(\omega_{1,2}\) in the absence of hopping. It should be noted that this theory requires that the \(\mu^+\)SR frequencies \(\omega_1\) and \(\omega_2\) expected for static \(\mu^+\) are to be used in the motional narrowing regime at high temperatures. We estimated these values from low temperature data, assuming a linear relation between the peak frequencies and the susceptibility \(\chi\). The result of linear fits to the peak frequencies between 130 K and 150 K is shown in Fig. 1 (right) with solid lines. Using values for \(\omega_1\) and \(\omega_2\) derived from these linear functions, we fitted the \(\mu^+\)SR line shape data with Eq. 1 and obtained satisfactory results, as shown in Fig. 1 (left) by the solid curves.
Figure 1. Left: the $\mu^+$SR line shape in PrPb$_3$ under a field of 2 T applied along the [001] direction. The solid curves are the best fits with Eq. 1. The inset shows a schematic view of a unit cell and representative $\mu^+$ sites. The thick arrows represent the magnetic moments induced by the external field at the Pr site along the field direction. Right: the $\mu^+$SR frequencies as functions of the susceptibility $\chi$. The solid lines $\omega_1(T)$ and $\omega_2(T)$ represent the linear fits to the data between 130 K and 150 K. The dotted line corresponds to $\omega_0(T) = (\omega_1 + \omega_2)/2$.

In all of the fits $L$ was fixed to be 0.142 $\mu$s$^{-1}$, which was determined from the data at 130 K. The only free parameter $\Omega$ was obtained as a function of temperature, and is discussed in Sec. 5.

4. $\mu^+$SR line shape in SmAg$_2$In and analysis

The $\mu^+$SR line shape in SmAg$_2$In in the paramagnetic state is shown in Fig. 2 (left). Two lines with peaks at $\omega_1$ and $\omega_2$ with the intensity ratio of 1:2 were observed in the $\mu^+$ localization regime below $\sim 42.8$ K. Note that the intensity ratio is opposite to that of the signal in PrPb$_3$. Among possible interstitial sites, only the $d$ site at (0.25, 0.25, 0) is consistent with this splitting. This site is located at the face center of the cube constructed by four Sm and four In atoms at the corners, and one Ag atom at the center, as depicted in the inset of Fig. 2 (left). The same site was suggested in isomorphic PrAg$_2$In from the spin relaxation rate in zero applied field [8]. The two lines are gradually merged into one line at increasing temperature, as was observed in PrPb$_3$.

In this case the $\mu^+$SR line shape is expressed as

$$I(\omega') = \frac{L^3 + 3L^2\Omega + \frac{3}{2}\delta^2\Omega + L[\omega' + \frac{3}{2}\delta\omega' + \delta^2 + \frac{3}{2}\Omega^2]}{L^4 + (\omega'^2 - \delta^2)^2 + 3L\Omega + L(3\omega'^2 - 2\delta\omega' + 3\delta^2) + \frac{3}{4}\Omega^2(3\omega' - \delta)^2 + L^2[2(\omega'^2 + \delta^2) + \frac{3}{4}\Omega^2]}.$$  

(2)

As before, the $\mu^+$SR frequencies $\omega_1$ and $\omega_2$ used in the motional narrowing regime were estimated from the linear relation between the peak frequencies and $\chi$ in the localization regime. The result of linear fits to the peak frequencies between 20 K and 42.8 K is shown in Fig. 2 (right) by the solid lines. Using values for $\omega_1$ and $\omega_2$ derived from these linear functions, we fitted the $\mu^+$SR line shape data with Eq. 2, and obtained the satisfactory results as shown in Fig. 2 (left) by the solid curves. In these fits $L$ was fixed to be 0.133 $\mu$s$^{-1}$, which was determined from the data at 42.8 K. The only free parameter $\Omega$ was obtained as a function of temperature, and is discussed in Sec. 5.
5. Results and Discussion

The $\mu^+$ hopping rate $\Omega$ in PrPb$_3$ and SmAg$_2$In derived from the analytic treatment of the $\mu^+$SR line shape is shown by the Arrhenius plot in Fig. 3. The apparent linear behavior suggests that the $\Omega$ follows a thermal activation-type temperature dependence, namely,

$$\Omega(T) = \Omega_0 \exp \left( -\frac{U}{k_B T} \right). \tag{3}$$

Satisfactory fits were obtained using this equation as shown in Fig. 3 with solid lines. This indicates that classical over-the-barrier hopping or phonon-assisted quantum tunneling should be dominant in the present cases; even in the latter case the $\Omega(T)$ approximately follows Eq. 3 when $T < U/k_B$. The preexponential factor $\Omega_0$ and the potential barrier $U$ are shown in Table 1, together with a parameter $U$ for PrIn$_3$ obtained in Ref. [4].

The value of $\Omega_0$ is useful to discriminate between the classical over-the-barrier hopping and the phonon-assisted quantum tunneling by comparing the value expected for a zero-point vibrational frequency of the $\mu^+$ in a potential well, which is typically in the order of $10^{13}$ s$^{-1}$ [9]. In the case of PrPb$_3$, the $\Omega_0$ value is comparable to this value, indicating that the classical over-the-barrier hopping is dominant above 140 K. On the other hand, the $\Omega_0$ value for SmAg$_2$In is considerably smaller than this characteristic value. This suggests that the phonon-assisted quantum tunneling comes into play in SmAg$_2$In in the temperature range between 40 K and 70 K, although the zero-point vibrational frequency of the $\mu^+$ in this compound has not been accurately determined. The low value of $U/k_B$ also supports this interpretation.

6. Summary

The $\mu^+$ diffusion was observed in cubic $f$-electron compounds PrPb$_3$ and SmAg$_2$In by means of the high TF-$\mu^+$SR technique in magnetic fields applied along the [001] direction. The $\mu^+$ diffusion between magnetically inequivalent sites drastically influences the $\mu^+$SR frequencies,
Figure 3. The Arrhenius plot of the $\mu^+$ hopping rate $\Omega$ in PrPb$_3$ (left) and SmAg$_2$In (right). The solid lines are the best fits with Eq. 3.

Table 1. The $\mu^+$ hopping parameters in PrPb$_3$, PrIn$_3$, and SmAg$_2$In.

|          | $\Omega_0$ [s$^{-1}$] | $U/k_B$ [K] |
|----------|------------------------|-------------|
| PrPb$_3$ | $2.3\pm0.8\times10^{13}$ | 3093$\pm$60 |
| PrIn$_3$ [4] | $-$ | 3260$\pm$45 |
| SmAg$_2$In | $7.1\pm1.5\times10^{10}$ | 694$\pm$11 |

where two lines are gradually merged into one line at increasing temperature due to the motional narrowing effect. The $\mu^+$ hopping rate $\Omega$ derived from the $\mu^+$SR line shape follows the Arrhenius law, namely, $\Omega = \Omega_0 \exp(-U/k_B T)$ in both cases. The preexponential factor $\Omega_0$ suggests that the dominant mechanism of $\mu^+$ diffusion is the classical over-the-barrier hopping in PrPb$_3$ for $140<T<200$ K and the phonon-assisted quantum tunneling in SmAg$_2$In for $40<T<70$ K.

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