Contribution to Special Issue Dedicated to Paul Heitjans

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How Li diffusion in spinel $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ is seen with $\mu^\pm\text{SR}$

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Abstract: The diffusive behavior in a spinel-type Li^+ ion battery material, $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$, has been studied with positive and negative muon spin rotation and relaxation ($\mu^\pm\text{SR}$) measurements in the temperature range between 200 and 400 K using a powder sample. The implanted μ^+ locates at an interstitial site near O^{2-} ion so as to form a O–H like bond, while the implanted μ^- is mainly captured by an oxygen nucleus, resulting in the formation of muonic oxygen. This means that local magnetic environments in $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ were investigated from the two different sites in the lattice, i.e., one is an interstitial site for $\mu^+\text{SR}$ and the other is an oxygen site for $\mu^-\text{SR}$. Since both $\mu^+\text{SR}$ and $\mu^-\text{SR}$ detected an increase in the fluctuation rate of a nuclear magnetic field for temperatures above 200 K, the

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origin of this increase is clearly confirmed as Li diffusion. Assuming a random walk process with the hopping of thermally activated Li^+ between a regular Li site and the nearest neighboring vacant octahedral sites, a self-diffusion coefficient of Li^+ was found to range above $10^{-11} \text{ cm}^2/\text{s}$ at temperatures above 250 K with an activation energy of about 0.06 eV.

Keywords: Li diffusion; Li ion battery materials; muon spin rotation and relaxation.

1 Introduction

In order to understand the operational processes of battery materials, it is crucial to understand the diffusive nature of ions in these materials, because the transport of ions is the fundamental mechanism behind their operation. Nuclear magnetic resonance (NMR) has been widely used for such a purpose [1–3], through the observation of nuclear magnetic fields in these materials. Recently, the positive muon spin rotation and relaxation ($\mu^+\text{SR}$) technique [4, 5] was found to be a good tool for detecting ion diffusion in solids [6]. Unlike in NMR, where the polarization is dependent on an externally applied high magnetic field, the initial muon spin polarization is aligned antiparallel to its momentum due to parity violation of a muon creation reaction [7]. As a result, $\mu^+\text{SR}$ senses the internal magnetic field in materials without the need of any external magnetic field, i.e., even in zero field (ZF).

This leads to the following two important features: the first one is that $\mu^+\text{SR}$ distinguishes the nuclear magnetic field from the electron magnetic field by simply applying a weak longitudinal field (LF) [8]. Here, “weak” means the field is comparable to the field distribution width formed by surrounding nuclear magnetic moments at the muon site, which typically ranges between 5 and 10 Oe, and “longitudinal field” means the magnetic field is parallel to the initial muon spin polarization. Such weak LFs decouple the contribution from a nuclear magnetic field on the μ^+ spin, while the effect of weak LF on the contribution from the electron magnetic field is negligibly small. Consequently, $\mu^+\text{SR}$ provides information on ion diffusion even in materials that include paramagnetic ions [9, 10]. This is an attractive feature for studying Li^+ [11–21], Na^+ [10, 22, 23], and K^+ [24] diffusion in cathode materials for an ion battery, because these materials always contain transition metal ions to keep charge neutrality during ion insertion and extraction reactions.

Another feature that makes $\mu^+\text{SR}$ an attractive probe is its sensitivity, which in principle is temperature independent, since the muon spin polarization is an intrinsic feature of the technique, whereas the effect of an external field on aligning nuclear spins is suppressed by thermal excitation, resulting in the decrease of NMR

sensitivity with temperature. Therefore, μ^+ SR is a very important tool to study ion dynamics at high temperatures.

Despite the above features, the information obtained with μ^+ SR is sometimes ambiguous. Whereas the implanted μ^+ is presumed to be static at low temperatures in its interstitial site (where its electrostatic potential is in a local minimum), in any solid there is a chance that the μ^+ will start to diffuse above certain temperatures. This means that the observed diffusive behavior could be caused by not only ion diffusion but also μ^+ diffusion. In order to confirm the diffusing species, μ^+ or ion, we have initiated series of μ^- SR experiments on battery materials [25–27]. Here, μ^- SR is the “anti-technique” of μ^+ SR by not using μ^+ but negative muons (μ^-) [28–31].

The implanted μ^- is captured by a nucleus and forms a stable muonic atom. The muonic atoms, apart from the ones based on the diffusing species, is immobile until the decomposition temperature of the material. In other words, by means of μ^+ SR, we are able to see the internal magnetic field from different viewpoints: at the atomic position in the lattice with μ^- SR and at the interstitial sites with μ^+ SR. It should be noted that a μ^- SR spectrum requires about 36 times higher counts than that of μ^+ SR to obtain the same statistical precision, since the spin polarization of μ^- is down to about 1/6 of its initial polarization during the atomic capture process by a nucleus [32,33]. It is thus only reasonable to use the expensive and difficult μ^- SR technique in order to determine the diffusing species, while the details of the diffusion processes are best determined by μ^+ SR.

A combined μ^+ SR work has confirmed Li^+ diffusion in an olivine-type LiMnPO_4 above around 200 K [26] and in a spinel-type $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($= \text{Li}^+ [\text{Li}_{1/3} \text{Ti}_{5/3}^{4+}] \text{O}_4$) above around 250 K [34]. Here, we have studied the diffusive nature in another spinel-type battery material, $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ ($= \text{Li}^+ [\text{Ni}_{1/2}^{2+} \text{Mn}_{3/2}^{4+}] \text{O}_4$, see Figure 1), which has a different cation distribution from that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, by means of μ^+ SR. This is because $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ is highly attractive as a cathode material for an all solid-state battery [35–38], due to the fact that the charge and discharge reactions occur at about 4.7 V (vs. Li/Li^+) and such voltage is almost independent of the Li content [39]. Our previous μ^+ SR study on a powder and film samples of $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ revealed the occurrence of Li diffusion at temperatures above around 250 K [40].

2 Experimental

A powder sample of $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ was purchased from Toshima Manufacturing, Ltd. The μ^- SR time spectra were measured on the decay muon beam line ARGUS [42, 43] at ISIS pulsed neutron and muon source of Rutherford Appleton Laboratory in UK. Approximately 22 g powder sample was placed in a copper container with a sample space of 30 mm diameter and 15 mm depth, made

Figure 1: The crystal structure of cubic spinel $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ drawn with VESTA [41]. Li^+ ions occupy the tetrahedral (8a) site, while Ni and Mn ions occupy the octahedral (16d) site. O^{2-} ion is located in each corner of the tetrahedron and octahedron. Dark grey spheres represent a vacant 16c site.

of 1 mm thick Cu plate [see Figure 2(a)]. A cap of the container was made of 3 mm thick Cu plate, which also works as a degrader to adjust the range of μ^- s. The copper container was then set onto the end of the He-flow cryostat (Ministat, Oxford Instruments). The momentum of the μ^- beam was adjusted to 70 MeV/c to maximize the number of μ^- stopped in the sample, as shown in Figure 2(b). The μ^- SR spectrum was measured at 200, 300, and 400 K with up to 50 Mevents for transverse field (TF) μ^- SR and 200 Mevents for zero field (ZF) and 150 Mevents for longitudinal field (LF) μ^- SR at a counting rate of 17 Mevents/h. Here TF [LF] means the applied magnetic field was perpendicular [parallel] to the initial μ^- spin polarization.

The μ^+ SR time spectra were measured on the surface muon beam line EMU [43, 45] at ISIS. Approximately 2 g powder sample from the same batch as for the μ^- SR measurements was packed into a standard ISIS titanium cell. The window of the cell was made of a titanium foil with 20 μm thickness. The cell was then mounted onto the Al plate of a closed cycle refrigerator-type cryofurnace in the temperature range between 50 and 500 K. The counting rate was about 100 Mevents/h. The experimental techniques are described in more detail elsewhere [4, 5]. The obtained μ^+ SR data was analyzed with musrfit [46].

3 Results

While the μ^- SR study is the main focus of this paper, to put these results into context our discussion will start with the μ^+ SR measurements that were carried out on the same system.

3.1 μ^+ SR

Figure 3 shows the μ^+ SR time spectra recorded in wTF with $H = 20$ Oe at selected temperatures in order to understand the magnetic nature of the $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$

Figure 2: (a) A copper container filled with a black powder sample of $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ for a μ^- SR experiment. The size of the sample space is 30 mm diameter and 15 mm depth. (b) The variation of the depth profile of the muons in the copper container filled with the sample by five different implantation momentum. The profile was simulated with SRIM [44].

sample. At 150 K, the spectrum exhibits a clear oscillation with a full asymmetry due to wTF, which means that the whole volume of the sample is in a paramagnetic state. As the temperature decreases from 150 K, the oscillating asymmetry decreases with decreasing temperature and then almost disappears below 100 K. In order to extract the μ^+ SR parameters, the wTF- μ^+ SR spectrum is fitted by a combination of an exponentially relaxing cosine oscillation due to wTF and an exponentially relaxing non-oscillatory signal, due to the 1/3 tail arising from the distribution of static electronic components in the powder sample when in an AF ordered state.

$$A_0 P_{\text{TF}} = A_{\text{TF}} \cos(2\pi f_{\text{TF}} t + \phi_{\text{TF}}) \exp(-\lambda_{\text{TF}} t) + A_{\text{tail}} \exp(-\lambda_{\text{tail}} t), \quad (1)$$

where A_0 is the initial asymmetry determined by the wTF measurements at high temperatures and P_{TF} is the muon spin polarization function in wTF. A_{TF} , f_{TF} , ϕ_{TF} and λ_{TF} are the asymmetry, muon spin precession frequency, initial phase, and relaxation rate due to the applied TF. Here, $f_{\text{TF}} = \gamma_{\mu}/2\pi \times 20 \text{ Oe} = 13.554 \text{ kHz/}$

$0\text{e} \times 20\text{ Oe} \sim 0.27\text{ MHz}$. The A_{tail} component corresponds to the signal from the magnetic ordered phase, in which the internal AF field is parallel to the initial muon spin polarization.

Figure 4 shows the temperature dependencies of the four wTF- μ^+ SR parameters, i.e., A_{TF} , A_{tail} , λ_{TF} , and λ_{tail} . The $A_{\text{TF}}(T)$ curve exhibits a step-like change at around 105 K, which indicates the appearance of a very large internal magnetic field compared with wTF at low temperatures. From the middle point of the step-like change in the $A_{\text{TF}}(T)$ curve, T_N is determined as 104.2(5) K using a Sigmoid function. A relatively wide transition ($\Delta T_N = 41\text{ K}$) indicates a random distribution of Ni and Mn at the octahedral site in the spinel lattice [40,47], where $\Delta T_N = T^{90\%} - T^{10\%}$ with $A_{\text{TF}}(T^{90\%}) = 0.9[A_{\text{TF}}(200\text{ K}) - A_{\text{TF}}(30\text{ K})] + A_{\text{TF}}(30\text{ K})$ and $A_{\text{TF}}(T^{10\%}) = 0.1[A_{\text{TF}}(200\text{ K}) - A_{\text{TF}}(30\text{ K})] + A_{\text{TF}}(30\text{ K})$. A non-zero A_{TF} well below T_N is caused by the muons stopped outside of a sample, such as, the Ti sample holder and/or the surrounding experimental setup. This is because A_{TF} is almost temperature independent below T_N . The $\lambda_{\text{TF}}(T)$ curve, on the other hand, shows a critical behavior above T_N , as expected.

As temperature decreases from 200 K, A_{tail} starts to increase below 130 K and approaches a predicted value for the 1/3 tail signal below 90 K, where A_{tail} well below T_N is predicted as $[A_{\text{TF}}(200\text{ K}) - A_{\text{TF}}(30\text{ K})]/3$. Besides the vicinity of T_N , λ_{tail} is small and almost temperature independent. These features are consistent with those for the 1/3 tail signal.

Figure 5 shows the ZF- and two LF- μ^+ SR spectra recorded at 150, 300, and 425 K, i.e., in a paramagnetic state. As temperature increases, the μ^+ SR spectrum indicates a clear change from a low-temperature static behavior to a high-temperature dynamic behavior. The μ^+ SR spectra were therefore fitted with a combination of an exponentially relaxing dynamic Kubo-Toyabe function (G^{DGKT})

Figure 3: Weak transverse field (wTF) μ^+ SR time spectra for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ recorded at 50, 100, 110, 120, and 150 K. Solid lines represent the best fit using Eq. (1).

Figure 4: The temperature dependencies of (a) the weak transverse field asymmetry (A_{TF}) and tail asymmetry (A_{tail}) (b) their exponential relaxation rates (λ_{TF} and λ_{tail}) for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$. The data were obtained by fitting the wTF- μ^+ SR spectrum with Eq. (1). A red solid line in (a) represents the best fit by a Sigmoid function and a blue dotted line indicates the predicted $A_{\text{tail}} = [A_{\text{TF}}(200 \text{ K}) - A_{\text{TF}}(30 \text{ K})]/3$. The color of the symbol for the TF signal is slightly changed at temperatures below 90 K, since the wTF- μ^+ SR signal comes from not the sample but from the Ti sample holder (see text).

from the sample and a time independent background signal from the Ti sample holder:

$$A_0 P_{\text{LF}}(t) = A_{\text{KT}} G^{\text{DGKT}}(t, \Delta, \nu, H_{\text{LF}}) \exp(-\lambda_{\text{KT}} t) + A_{\text{BG}}, \quad (2)$$

where P_{LF} is the muon spin polarization function in ZF and LF. A_{KT} and A_{BG} are asymmetries of the two signals, Δ is the field distribution width, ν is the field fluctuation rate, and λ_{KT} is the exponential relaxation rate. For $\nu = 0$ and $H_{\text{LF}} = 0$ (i.e., ZF), $G^{\text{DGKT}}(t, \Delta, \nu, H_{\text{LF}})$ becomes a static Gaussian Kubo-Toyabe function ($G_{\text{zz}}^{\text{KT}}$) given by [48]:

$$G_{\text{zz}}^{\text{KT}}(t, \Delta) = \frac{1}{3} + \frac{2}{3} (1 - \Delta^2 t^2) \exp\left(-\frac{1}{2} \Delta^2 t^2\right), \quad (3)$$

which represents the time variation of the muon spin polarization due to the internal magnetic field formed by randomly oriented static nuclear dipoles with Gaussian distribution. Since the implanted muons *feel* both a nuclear magnetic field formed mainly by ^6Li , ^7Li , and ^{55}Mn and a magnetic field caused by localized $3d$ electrons of Ni^{2+} ($3d^8$) and Mn^{4+} ($3d^3$) [36, 39, 49], an exponential is multiplied with G^{DGKT} [50] in Eq. (2).

In the paramagnetic state, the TF- μ^+ SR spectrum is also fitted with an Abragam equation [51, 52] using Δ^+ and ν^+ and exponential relaxation function $\exp(\lambda_{\text{KT}}^+ t)$ as:

Figure 5: The temperature variation of the ZF- and two LF- μ^+ SR spectra recorded at (a) 150 K, (b) 300 K, and (c) 425 K. The applied LF's were 5 and 10 Oe. Green solid lines represent the best fit using Eq. (2).

$$\begin{aligned}
 A_0 P_{\text{TF}}(t) &= A_{\text{TF}} \cos(2\pi f_{\text{TF}} t + \phi_{\text{TF}}) G^A e^{-\lambda_{\text{KT}} t} \\
 &\quad + A_{\text{BG}} \cos(2\pi f_{\text{TF}} t + \phi_{\text{TF}}), \\
 G^A(t) &= \exp \left[-2 \frac{\Delta^2}{v^2} (e^{-tv} - 1 + tv) \right]
 \end{aligned} \tag{4}$$

Combining with Eq. (2), the TF-, ZF-, and LF- μ^+ SR spectra were fitted using common A_{KT} , A_{BG} , and A_{TF} at temperatures between 150 and 425 K, while Δ^+ , v^+ , and λ_{KT}^+ are common at each temperature.

Figure 6 shows the temperature dependencies of the μ^+ SR parameters obtained by fitting the TF-, ZF-, and two LF- μ^+ SR spectra with Eqs. (4) and (8). Here, a superscript of each symbol, i.e., “+” means that the data obtained from μ^+ SR

measurements. The field distribution width (Δ^+), which roughly corresponds to the spin-spin relaxation rate ($1/T_2$), is found to be almost temperature independent.

The field fluctuation rate, ν^+ , which corresponds roughly to the spin-lattice relaxation rate, increases almost monotonically with increasing temperature, being consistent with Li diffusion. Further confirmation for Li diffusion is given in Section 3.2. On the contrary, λ_{KT}^+ decreases with increasing temperature. Since λ_{KT}^+ is caused by the fluctuation of $3d$ localized moments, such decrease is explained by a Curie-Weiss behavior of magnetization for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ [39].

In the above fit, each asymmetry is assumed to be temperature independent, because the fractions of muons stopped in the sample and the Ti cell are, in principle, independent of temperature.

3.2 $\mu^+\text{SR}$

When considering the positive muon results, we cannot rule out the possibility that the muon may start to diffuse in the sample at some temperature. To be certain we

Figure 6: The temperature dependencies of the $\mu^+\text{SR}$ parameters for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$: (a) the field distribution width (Δ^+), (b) the field fluctuation rate (ν^+) and the exponential relaxation rate (λ_{KT}^+), and (c) the three asymmetries (A_{TF}^+ , A_{KT}^+ , and A_{BG}^+). “+” of each symbol means that the data was obtained from $\mu^+\text{SR}$ measurements. Δ^+ , ν^+ , A_{TF}^+ , and A_{BG}^+ were obtained by fitting the TF-, ZF- and LF- $\mu^+\text{SR}$ spectra with Eq. (2). Note that Δ^+ corresponds roughly to a spin-spin relaxation rate ($1/T_2$), while ν^+ corresponds roughly to a spin-lattice relaxation rate ($1/T_1$). More correctly, $1/T_1$ would be the relaxation rate of the nuclear moments that contribute to Δ^+ , not the relaxation rate of the μ^+ spin.

are studying the change in the nuclear magnetic field from a “fixed view point” we have also measured the μ^- SR spectrum for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ using the same sample to that for μ^+ SR. Figure 7 shows the time histogram of the TF- μ^- SR spectrum with $\text{TF} = 50$ Oe recorded at 300 K. Here, forward [backward] means upstream [downstream] detector positions with respect to the sample position and the incoming muon beam direction. Since the decay asymmetry is very small and the lifetime of the μ^- depends upon the nucleus on which it is captured by, the histogram of μ^- SR was fitted by a combination of four different lifetimes ($\tau_{i=1-4}$). Note that, for μ^+ SR, the time histogram includes only one component, i.e., μ^+ with $\tau = 2.19703$ μs :

$$N(t) = \sum_{i=1}^{n=4} N_i e^{-t/\tau_i} [1 + A_i e^{-\lambda_i t} \cos(\omega_i t + \phi_i)], \quad (5)$$

where N_i is a normalization constant at $t = 0$ for the i -th muon lifetime (τ_i), i.e., muonic O (μ^- O) with $\tau_1 = \tau_{\text{O}} = 1.7954$ μs [53], muonic Li (μ^- Li) with $\tau_2 = \tau_{\text{Li}} = 2.188$ μs [53], muonic Mn (μ^- Mn) with $\tau_3 = \tau_{\text{Mn}} = 0.2325$ μs [53], and an unknown component with $\tau_4 = 26.8(6)$ μs , A_i is the muon decay asymmetry for each process, $\omega_i = 2\pi f_i$ is the angular frequency of the μ^- spin precession caused by the applied TF, and ϕ_i is the initial phase. Since $\tau_4 \gg \tau_{\mu} = 2.19703$ μs , the τ_4 component is caused by other particles, such as e^- , e^+ and/or neutrons perhaps created by a decay reaction of the muonic atoms. However, the contribution of the τ_4 component is negligibly small for $t < 10$ μs .

As a first approximation, A_i is non-zero only for the main component, i.e., μ^- O and negligible for the other elements. This is because both Li and Mn have nuclear spins and will therefore form hyperfine-coupled states with the μ^- , leading to a precession at a dramatically different frequencies compared with the applied

Figure 7: The time histogram of the TF- μ^- SR spectrum in $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ for the (a) forward counter and (b) backward counter. Red open circles represent the experimental data, green solid lines represent the fit result using Eq. (5), and blue solid lines represent the histograms of the four muonic-atom lifetimes.

value. Furthermore, A_i is less than 1/6 of A_0 for $\mu^+\text{SR}$ (typically 0.24) due to the reduction of spin polarization, $A_i < 0.04$ ($= 0.24/6$) $\ll 1$. Therefore, it is reasonable to fix $A_i = 0$ for the other minor elements to estimate each N_i using Eq. (5). Due to a short lifetime of muonic nickel ($\mu^-\text{Ni}$, $\tau_{\text{Ni}} = 0.1569 \mu\text{s}$ [53]) together with a relatively small amount of $\mu^-\text{Ni}$ compared with that of $\mu^-\text{Mn}$, it was impossible to fit the histogram with a combination of five different lifetime components.

The relative asymmetric counting efficiency can be estimated for each element and are listed in Table 1. It is noted that both $\alpha_{\text{Li}} = N_{\text{Li}}^{\text{B}}/N_{\text{Li}}^{\text{F}}$ and $\alpha_4 = N_4^{\text{B}}/N_4^{\text{F}}$ are smaller than $\alpha_0 = N_0^{\text{B}}/N_0^{\text{F}}$. As a result, the asymmetry spectrum based on α_0 , which is defined by Eq. (6), is naturally distorted in late time domain.

$$A_0P(t) \sim \frac{N^{\text{B}}(t) - \alpha_0 N^{\text{F}}(t)}{N^{\text{B}}(t) + \alpha_0 N^{\text{F}}(t)}. \tag{6}$$

In fact, the TF-, ZF-, and two LF- $\mu^-\text{SR}$ spectra for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ exhibit a sudden decrease with time particularly below around $8 \mu\text{s}$, regardless of external magnetic field (see Figure 8). This is well explained by the effect of the τ_4 component on the $\mu^-\text{SR}$ spectra, because the τ_4 component with $\alpha_{\tau_4}/\alpha_0 = 0.67$ becomes predominant in a late time domain. In addition, each spectrum is distorted in an early time domain due to the effect from $\mu^-\text{Mn}$. Besides these distortions, the ZF- and LF- $\mu^-\text{SR}$ spectra show a decoupling behavior, which evidences the observation of a nuclear magnetic field with $\mu^-\text{SR}$.

Therefore, as seen in Figure 9, the TF-, ZF-, and two LF- $\mu^-\text{SR}$ spectra were fitted in the time domain between 0.8 and $6 \mu\text{s}$ with a combination of an exponentially relaxing cosine oscillation and an exponentially relaxing non-oscillatory signal for the TF-spectrum, and with a combination of an exponentially relaxing dynamic Kubo–Toyabe signal and an exponentially relaxing non-oscillatory signal for the ZF- and LF-spectra. In addition, the following three parameters, i.e., A_{TF} , A_{TFe} , and

Table 1: Parameters of the TF- $\mu^-\text{SR}$ histograms for the $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ sample obtained by fitting with Eq. (5), where τ_0 , τ_{Li} , and τ_{Mn} were fixed to the values reported in Ref. [53]. Since it is extremely difficult to determine short τ components using data at early times because of the difficulty for determining a correct time zero (t_0) of the pulsed μ^+ beam, the histograms were fitted only in the time domain between 0.4 and $16 \mu\text{s}$.

n	Component	τ (μs)	$N_i^{\text{F}}/N_0^{\text{F}}$	$N_i^{\text{B}}/N_0^{\text{B}}$	$\alpha_i \equiv N_i^{\text{B}}/N_i^{\text{F}}$	α_i/α_0
1	O	$\tau_0 = 1.7954$ [53]	1	1	$\alpha_0 = 1.062(5)$	1
2	Li	$\tau_{\text{Li}} = 2.188$ [53]	0.014(2)	0.010(2)	$\alpha_{\text{Li}} = 0.8(3)$	0.7(2)
3	Mn	$\tau_{\text{Mn}} = 0.1569$ [53]	1.05(2)	1.33(4)	$\alpha_{\text{Mn}} = 1.34(6)$	1.26(6)
4	?	$\tau_4 = 26.8(6)$	0.00110(2)	0.00073(2)	$\alpha_4 = 0.71(3)$	0.67(3)

Figure 8: The TF-, ZF-, and two LF- μ^- SR spectra for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ recorded at 300 K. The applied TF was 50 Oe, and the applied LF were 20 and 50 Oe.

λ_{TFe} , are common for the TF-, ZF-, and LF- μ^- SR spectra at each temperature, and Δ and ν are common for the ZF- and LF- μ^- SR spectra at each temperature:

$$\begin{aligned} A_0P_{\text{TF}}(t) &= A_{\text{TF}}\cos(2\pi f_{\text{TF}}t + \phi_{\text{TF}})\exp(-\lambda_{\text{TF}}t) \\ &\quad + A_{\text{TFe}}\exp(-\lambda_{\text{TFe}}t), \\ A_0P_{\text{LF}}(t) &= A_{\text{KT}}G^{\text{DGKT}}(t, \Delta, \nu, H_{\text{LF}})\exp(-\lambda_{\text{KT}}t) \\ &\quad + A_{\text{LFe}}\exp(-\lambda_{\text{LFe}}t), \end{aligned}$$

where

$$\begin{aligned} A_{\text{TF}} &= A_{\text{KT}}, \\ A_{\text{TFe}} &= A_{\text{LFe}}, \\ \lambda_{\text{TFe}} &= \lambda_{\text{LFe}}. \end{aligned} \tag{7}$$

The exponentially relaxing non-oscillatory signal (A_{TFe} and A_{LFe}), which is common for the TF-, ZF-, and LF- μ^- SR spectra, is most likely originating from different lifetimes of μ^- between μ^- Li and μ^- O [26], but both μ^- spins are also depolarized by the localized 3d moments. The other possibility for the origin of the A_{TFe} signal is the formation of μ^- Al in the surroundings of the sample. The lifetime difference between μ^- Al and μ^- O could provide a comparable relaxation to the experiment.

Figure 10 shows the temperature dependencies of Δ^- , ν^- , and λ_{KT}^- for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$. A superscript of each symbol, i.e., “-” means that the data obtained from μ^- SR measurements. Although the observed Δ^- slightly increases with temperature, Δ^- is approximately temperature independent and very consistent with the predicted value at the oxygen site in the $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ lattice. Here, the predicted value ($\Delta^-, \text{calc} = 0.314 \mu\text{s}^{-1}$) was obtained by dipole field calculations with Dipelec [54]. Since the slight increase in Δ^- with temperature is difficult to explain, we have attempted to fit the spectra using a common Δ^- [$\Delta^- = 0.30(3) \mu\text{s}^{-1}$] in the whole measured temperature range.

Figure 9: The TF-, ZF-, and two LF- μ SR spectra for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ recorded at (a) 200 K, (b) 300 K, and (c) 400 K in the time domain between 0 and 7 μs . The applied TF was 50 Oe, and the applied LF were 20 and 50 Oe. (b) is the same to Figure 8.

The value of ν^- determined from fitting with Δ^- as a free parameter increases with temperature with a slope $(d\nu^-/dT)$ that is steeper than that of ν^+ . This is likely to be due to a correlation of the fitted parameters. However, when the spectra are fitted using Δ^- instead, the increase in ν^- is comparable to that of ν^+ . Finally, λ_{KT}^- decreases with temperature and the obtained values of λ_{KT}^- is almost equivalent to the ones of λ_{KT}^+ . The fact that $\lambda_{\text{KT}}^- > \lambda_{\text{KT}}^+$ implies the effect of orbital hybridisation

Figure 10: The temperature dependencies of the μ^- SR parameters for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$, (a) the field distribution width (Δ^-), (b) the field fluctuation rate (ν^-), and (c) the exponential relaxation rate (λ_{KT}^-). “-” of each symbol means that the data was obtained from μ^- SR measurements. Δ^{-c} , ν^{-c} , and λ_{KT}^{-c} are the fitting results with a common Δ^- ($\Delta^{-c} = 0.30(3) \mu\text{s}^{-1}$) in the whole temperature range measured. In (a), a dotted line represents $\Delta^{-, \text{calc}}$ at the oxygen site predicted with dipole field calculations. The μ^+ SR results, i.e., Δ^+ , ν^+ , and λ_{KT}^+ are also plotted for comparison.

between $3d$ orbitals of Mn/Ni and $2p$ orbitals of O, on which the μ^- is captured on. In other words, since the localized $3d$ moments are partially shared by the $2p$ orbital through such hybridisation, the μ^- spin captured on O naturally *feels* a large fluctuation compared with the μ^+ spin at the interstitial site. This is also most likely the reason for the observed behavior $\nu^- > \nu^+$.

4 Discussion

Here, we attempt to estimate the self-diffusion coefficient of Li^+ (D_{Li}^{I}) in $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ using the presented μ^+ SR results. We should emphasize that μ^+ SR detects the thermally activated fluctuation of a nuclear magnetic field. As seen in Figure 11, the activation energy (E_a) is estimated as 0.068(5) eV for ν^+ and 0.043(18) eV for ν^{-c} using the data between 200 and 400 K. The former E_a is comparable to the latter E_a within the estimation accuracy, despite a relatively low accuracy of E_a for ν^{-c} due to a small signal in the μ^- SR spectrum. In overall, it is

Figure 11: The relationship between ν and inverse temperature. Solid lines represent the best fit using a thermal activation process: $\nu = \nu_0 \exp[-E_a/(k_B T)]$, in the temperature range between 200 and 400 K, where E_a is an activation energy and k_B is the Boltzmann constant. The right vertical axis is converted into D_{Li}^J using Eq. (8).

clear that ν increases with temperature for both $\mu^\pm\text{SR}$. This indicates Li^+ diffusion in $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ above 200 K.

In order to estimate D_{Li}^J , we need to know the jump pathway of Li^+ in the spinel lattice. The cation distribution of spinel $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ is represented as $(\text{Li}^+)_{8a}[\text{Ni}_{1/2}^{2+}\text{Mn}_{3/2}^{4+}]_{16d}\text{O}_4$, where $8a$ is a tetrahedral site and $16d$ is the octahedral site (see Figure 1). For Li deficient spinels, Li^+ ions are known to diffuse from the regular Li site, i.e., $8a$ site to a $16c$ site, which is the vacant octahedral site, and then to a vacant Li $8a$ site. The most reasonable pathway for D_{Li}^J in $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ is therefore the route from the $8a$ site to the nearest neighboring $16c$ sites.

If we assume that the field fluctuation rate ν^+ corresponds to a hopping rate, i.e., the jump frequency of Li^+ ions between the $8a$ and $16c$ sites, D_{Li}^J is given by [55];

$$D_{\text{Li}}^J = \sum_{i=1}^n \frac{1}{N_i} Z_{v,i} s_i^2 \nu, \quad (8)$$

where N_i is the number of Li sites in the i -th jump path, $Z_{v,i}$ is the vacancy fraction, and s_i is the jump distance. Based on the above consideration, $n = 1$, $N_1 = 4$, $Z_1 = 1$, and $s_1 = 1.77 \text{ \AA}$. Since D_{Li}^J is proportional to ν^+ in Eq. (7), the right vertical axis of Figure 11 is converted to D_{Li}^J . It is clearly found that D_{Li}^J ranges above $10^{-11} \text{ cm}^2/\text{s}$ at temperatures above 250 K for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$. This result is consistent with the previous $\mu^\pm\text{SR}$ report on a powder and film samples of $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ [40].

5 Summary and future

We have measured not only $\mu^+\text{SR}$ but also $\mu^-\text{SR}$ spectra for a spinel-type battery material, $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$, in order to investigate the diffusing species above around 250 K. The observed dynamic behavior both with $\mu^+\text{SR}$ and $\mu^-\text{SR}$ evidenced

Li diffusion. There exists a wide range of cathode materials for a Li-ion battery, which are mainly classified within the following three groups; layered rocksalt-, spinel-, and olivine-type compounds. We have already confirmed Li diffusion with μ^+ SR in the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [34] and $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$, and the olivine LiMnPO_4 [26]. Moreover, for a typical layered rocksalt-type compound, Li_xCoO_2 , the estimated D_{Li}^{J} determined with μ^+ SR [6] is consistent with the value predicted by first principles calculations [56], and the onset temperature of the Li-diffusion determined with μ^+ SR is in good agreement with the Li-NMR result [57]. Therefore, μ SR is safely applicable for measuring Li diffusion in Li-ion battery materials.

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