Li-ion diffusion in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiTi_2O_4 battery materials detected by muon spin spectroscopyJun Sugiyama,^{1,2,*} Hiroshi Nozaki,¹ Izumi Umegaki,¹ Kazuhiko Mukai,¹ Kazutoshi Miwa,¹ Susumu Shiraki,³ Taro Hitosugi,³ Andreas Suter,⁴ Thomas Prokscha,⁴ Zaher Salman,⁴ James S. Lord,⁵ and Martin Månsson⁶¹*Toyota Central Research and Development Laboratories Inc., Nagakute, Aichi 480-1192, Japan*²*Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan*³*Advanced Institute for Materials Research, Tohoku University, Sendai, Miyagi 980-8577, Japan*⁴*Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*⁵*ISIS Muon Facility, Rutherford Appleton Laboratory, Didcot, Oxfordshire, OX11 0QX, United Kingdom*⁶*Department of Materials and Nanophysics, KTH Royal Institute of Technology, Electrum 229, SE-16440 Kista, Sweden*

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Lithium diffusion in spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiTi_2O_4 compounds for future battery applications has been studied with muon spin relaxation ($\mu^+\text{SR}$). Measurements were performed on both thin-film and powder samples in the temperature range between 25 and 500 K. For $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and above about ~ 200 K, the field distribution width (Δ) is found to decrease gradually, while the field fluctuation rate (ν) increases exponentially with temperature. For LiTi_2O_4 , on the contrary, the $\Delta(T)$ curve shows a steplike decrease at ~ 350 K, around which the $\nu(T)$ curve exhibits a local maximum. These behaviors suggest that Li^+ starts to diffuse above around 200 K for both spinels. Assuming a jump diffusion of Li^+ at the tetrahedral $8a$ site to the vacant octahedral $16c$ site, diffusion coefficients of Li^+ at 300 K in the film samples are estimated as $(3.2 \pm 0.8) \times 10^{-11} \text{ cm}^2/\text{s}$ for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $(3.6 \pm 1.1) \times 10^{-11} \text{ cm}^2/\text{s}$ for LiTi_2O_4 . Further, some small differences are found in both thermal activation energies and Li-ion diffusion coefficients between the powder and thin-film samples.

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I. INTRODUCTION

In order to improve the safety and the volumetric charge density of the current Li-ion batteries, novel battery materials have been under intense investigation. Although several new compounds have been found for cathode and electrolyte materials of advanced batteries, there are only very few candidates for anode materials [1,2], other than the current graphite related compounds. Among the small number of candidates, lithium-titanium-oxide spinel, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($=(\text{Li})_{8a}[\text{Li}_{1/3}\text{Ti}_{5/3}]_{16d}\text{O}_4$, where $8a$ and $16d$ mean the tetrahedral and octahedral site, respectively), is thought to be the most promising alternative [3–6] to graphite. This is due to its stability, durability, high rate capabilities, and despite its insulating nature, relatively high working voltage (1.562 V versus Li/Li^+) and low capacity. That is, the theoretical capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is 175 mAh/g, while that for graphite (C_6Li) is 372 mAh/g. Furthermore, the change in lattice constants during charge and discharge reaction, i.e., the Li intercalation and deintercalation reaction, $\text{Li}_4\text{Ti}_5\text{O}_{12} + 3\text{Li}^+ + 3e^- \rightleftharpoons \text{Li}_7\text{Ti}_5\text{O}_{12}$, are very small, leading to virtually no stress [4]. Therefore $\text{Li}_4\text{Ti}_5\text{O}_{12}$ becomes an attractive anode material for future all solid-state batteries.

A stoichiometric spinel LiTi_2O_4 ($=(\text{Li})_{8a}[\text{Ti}_2]_{16d}\text{O}_4$) was also reported to show a reversible Li-intercalation and deintercalation reaction with a lower working voltage (1.338 V versus Li/Li^+) [3] than for $\text{Li}_4\text{Ti}_5\text{O}_{12}$. In addition, the metallic nature of LiTi_2O_4 , which undergoes a superconducting phase below $T_c \sim 13$ K [7], is preferable for an anode material. However, the LiTi_2O_4 phase is known to be unstable in air [8], and therefore, at present, LiTi_2O_4 is a less popular choice than $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as future anode material.

For current Li-ion batteries using a liquid electrolyte as well as future all solid-state batteries, it is widely believed that the interface between the cathode and electrolyte and/or between anode and electrolyte plays a key role in determining the performance and safety of the complete battery device [9]. This is because the Li^+ ions must diffuse across these interfaces during each charge and discharge cycle. However, prior to studying Li-diffusion across the interfaces, it is important to first understand the behavior in each individual component, particularly for $\text{Li}_4\text{Ti}_5\text{O}_{12}$, since there are no reliable measurements of the Li^+ ions diffusion coefficient (D_{Li}) in this compound [10–14].

Tracer diffusion measurements showed that $D_{\text{Li}} = 2.2 \times 10^{-6} \text{ cm}^2/\text{s}$ at 900°C [10] ($\sim 10^{-18} \text{ cm}^2/\text{s}$ at 300 K) and Li-NMR indicated an extremely slow jump rate in the temperature range between 295 and 400 K [11]. However, in reality, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibits a relatively fast reversible Li-intercalation and deintercalation reaction even at ambient temperature [15,16]. Here, we wish to point out that NMR is very sensitive to localized magnetic moments. Therefore it is extremely difficult to measure a spin-lattice relaxation rate ($1/T_1$) due to Li diffusion in materials containing magnetic ions and/or localized moments [17]. Indeed, first-principles calculations predict a relatively high D_{Li} for LiTi_2O_4 , i.e., $D_{\text{Li}} \sim 10^{-10} \text{ cm}^2/\text{s}$ at ambient temperature [13], whereas there are no predictions for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ due to the presence of multiple Li sites with slightly different local environments in the lattice [14].

On the other hand, we have demonstrated that the muon spin relaxation ($\mu^+\text{SR}$) technique is able to detect changes in the nuclear dipole field due to Li-ion diffusion, even under the coexistence of paramagnetic moments in the sample [18–23]. Here, we report the first results of $\mu^+\text{SR}$ measurements on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiTi_2O_4 films and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder in the temperature range between 10 and 500 K. We have observed

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FIG. 1. (Color online) The relationship between the distribution of the implanted muons in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film [i.e., normalized stopping distribution (N_{SD})] and the energy of the muon beam (E_{μ}^{imp}). The distribution was simulated by the computer program TRIMSP, in which we used the density of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as 3.29 g/cm^3 and that of MgAl_2O_4 as 3.65 g/cm^3 .

clear evidence for Li-diffusive behavior above 200 K for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and above 250 K for LiTi_2O_4 .

II. EXPERIMENTAL

Both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (111) and LiTi_2O_4 (111) films were grown on a spinel MgAl_2O_4 (111) substrate with a $1 \times 1 \text{ cm}^2$ area using pulsed laser deposition (PLD) at the Advanced Institute for Materials Research of Tohoku University. The thickness of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film was 190 nm, while that of the LiTi_2O_4 was 220 nm. The preparation and characterization of the two films are described in more detail elsewhere [24]. A powder sample of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was also prepared by a conventional solid-state reaction technique between TiO_2 (anatase) and $\text{LiOH} \cdot \text{H}_2\text{O}$ at 750°C for 12 h in an air flow.

The μ^+ SR spectra for the films were measured using the low-energy μ^+ (LEM) beam at $S\mu\text{S}$ of PSI in Switzerland, and the powder sample was measured using a surface muon beam, MuSR, at ISIS of RAL in United Kingdom. At PSI, four nominally identical film samples, covering a $2 \times 2 \text{ cm}^2$ area, were glued onto a Ni-coated Al or stainless steel plate, which was then mounted on a cryostat or oven, respectively. The implanted beam energy (E_{μ}^{im}) was 17.5 keV, for which the μ^+ stops at an average depth of about 100 nm (see Fig. 1). The temperature range for LEM- μ^+ SR measurements was between 10 and 320 K for a cryostat and 300 and 500 K for an oven. The details of LEM- μ^+ are described elsewhere [25–28].

At ISIS, a $\sim 2\text{-g}$ powder sample was pressed into a disk with 23-mm diameter and 1-mm thickness, and packed into an Au O-ring sealed titanium cell. The window of the cell was made of a Kapton film with 50- μm thickness. The cell was mounted onto the Al plate of a He flow-type cryofurnace in the temperature range between 50 and 450 K. The details of setup and experimental procedure of μ^+ SR are described elsewhere [29,30].

III. RESULTS

A. $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Figure 2 shows the zero-field (ZF-) and longitudinal-field (LF-) μ^+ SR spectra for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film obtained at 150

FIG. 2. (Color online) The ZF and LF- μ^+ SR spectra for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film obtained at (a) $T = 150 \text{ K}$ using a cryostat and (b) $T = 400 \text{ K}$ using an oven at $S\mu\text{S}$ of PSI. Solid lines represent the best fit using Eq. (1).

and 400 K. Here, ZF means a zero external field and LF means an external field parallel to the initial muon-spin polarization. The different response of the muon spin relaxation to LF at 150 and 400 K clearly shows that the internal magnetic field at the muon site (H_{int}) is static at 150 K, but dynamic at 400 K. This indicates that either Li^+ or μ^+ starts to diffuse between 150 and 400 K. The ZF- and LF-spectra were fitted simultaneously by a combination of a dynamic Gaussian Kubo-Toyabe (KT) function [$G^{\text{DGKT}}(\Delta, \nu, t, H_{\text{LF}})$] multiplied by an exponential relaxation function caused by a fluctuating H_{int} due to ion diffusion and $3d$ moments [31], respectively. In addition, an offset background (BG) signal was used for the fraction of muons stopped in the sample holder, which is made of Ni-coated Al (for the 150 K data) or Ni-coated stainless steel (for the 400-K data),

$$A_0 P(t) = A_{\text{KT}} \exp(-\lambda t) G^{\text{DGKT}}(\Delta, \nu, t, H_{\text{LF}}) + A_{\text{BG}}. \quad (1)$$

Here, A_0 is the initial ($t = 0$) asymmetry, A_{KT} and A_{BG} are the asymmetries associated with sample and background, respectively. λ is the exponential relaxation rate, Δ is the static width of the local field distribution at the disordered sites, and ν is the field fluctuation rate. The latter contains the main dynamic information related to the ion diffusion. When $\nu = 0$ and $H_{\text{LF}} = 0$, $G^{\text{DGKT}}(t, \Delta, \nu, H_{\text{LF}})$ is a static Gaussian KT function $G_{\text{zz}}^{\text{KT}}(t, \Delta) = \frac{1}{3} + \frac{2}{3}(1 - \Delta^2 t^2) \exp(-\frac{1}{2} \Delta^2 t^2)$ in ZF. Technically, since the spectra exhibit a fast relaxing behavior in an early time domain (below $0.2 \mu\text{s}$) due to the muons stopped in a ferromagnetic Ni coating, we fitted the spectra with Eq. (1) in the time domain between 0.4 and $12.3 \mu\text{s}$ using MUSRFIT [32].

Figure 3 shows the temperature dependencies of the μ^+ SR parameters both for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film and powder sample together with the susceptibility ($\chi = M/H$) of the powder sample. Note that from a first look the overall results for the film sample are very similar to those for the powder

FIG. 3. (Color online) The temperature dependencies of (a) the field distribution width (Δ), (b) the field fluctuation rate (ν), (c) the exponential relaxation rate of the KT signal (λ), and (d) magnetic susceptibility ($\chi = M/H$) for the film and powder sample of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The data were obtained by fitting the time spectrum with Eq. (1). The magnetization (M) for the powder sample was measured with a field cooling mode under $H = 10 \text{ kOe}$ using a SQUID magnetometer (MPMS, Quantum Design).

sample. Both Δ and ν are almost temperature independent between 20 and 200 K, then Δ gradually decreases with increasing temperature (see also Sec. IV C). In parallel, ν starts to increase for $T \geq 200 \text{ K}$, reaches a maximum around $T_{\text{max}} = 400 \text{ K}$, and then decreases for higher temperatures. This is a typical behavior for Li-ion battery materials, which show a relatively fast Li diffusion, such as, Li_xCoO_2 [18] and $\text{Li}_x\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [23]. The maximum in the $\nu(T)$ curve means that the diffusion becomes too fast to be visible by $\mu^+\text{SR}$ above T_{max} . In fact, by studying the ν/Δ ratio at T_{max} we can discern a first difference between the powder ($\nu/\Delta \sim 3$) and thin-film ($\nu/\Delta \sim 5$) samples. Such differences will be further discussed in greater detail below.

FIG. 4. (Color online) The temperature variation of (a) ZF- and (b) wTF- $\mu^+\text{SR}$ spectrum for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder sample. In (a), each data point is shifted by 0.025 for clarity of display. The data were obtained at ISIS of RAL.

Although the exponential relaxation rate (λ) is zero at high temperatures λ starts to increase for $T \leq 200 \text{ K}$ for both thin-film and powder samples. In order to demonstrate such behavior, Fig. 4 shows the temperature variation of ZF- and weak transverse field (wTF)- $\mu^+\text{SR}$ spectra for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder sample. Here, TF means an external magnetic field applied perpendicularly to the initial muon-spin and “weak” means that the external field is very small compared with the internal magnetic field caused by the d electrons. At 50 K, the ZF-spectrum exhibits an exponential relaxing behavior in an early time domain below about $1 \mu\text{s}$, while a Gaussian relaxation is observed in the spectrum obtained at 200 and 225 K. The change in the spectrum with temperature is more remarkable for wTF measurements. That is, the wTF spectrum at 50 K is damped faster than that at 200 K, indicating the presence of an additional relaxation process besides nuclear magnetism. We wish to note that the initial asymmetry of the wTF spectrum at 50 K is the same to that at 200 K. Indeed, for the case that a small amount of a magnetic phase appears in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample, we attempted to fit the ZF and LF spectra using Eq. (1) with $\lambda = 0$ plus an exponentially relaxing signal for the magnetic phase:

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

where $\lambda = 0$, A_{M} is the asymmetry of the magnetic phase and λ_{M} is the relaxation rate. However, such a fit was less reliable than the fit using Eq. (1). This suggests that the whole volume of the sample enters into a phase with nonzero λ at low temperatures, i.e., $A_{\text{M}} = 0$.

The $\chi(T)$ curve [Fig. 3(d)] shows a clear increase below around 60 K, indicating the appearance of localized moments too, although the increase in χ is very small. We attribute the sharp increase in λ below 100 K to the localized moments of

$\text{Li}_4\text{Ti}_5\text{O}_{12}$. However, all Ti ions are expected to be in a 4+ state with $S = 0$ in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ lattice, if the composition of the samples is stoichiometric. Therefore such localized moments are most likely due to the decrease in Li at the Ti sites during the synthesis and film deposition. That is, the correct formula of the present $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample is thought to be given by $\text{Li}[\text{Li}_{(1-\delta)/3}\text{Ti}_{(5+\delta)/3}]\text{O}_4$ ($\equiv \text{Li}_{4-\delta}\text{Ti}_{5+\delta}\text{O}_{12}$). And, the localized Ti^{3+} moments most likely to show a spin-glass like freezing below about 60 K [33]. Considering the fact that $\mu^+\text{SR}$ provides intrinsic magnetic information on a sample, the whole volume of both thin-film and powder samples is naturally assigned as a $\text{Li}_{4-\delta}\text{Ti}_{5+\delta}\text{O}_{12}$ phase.

Such increase in χ below 60 K was also observed for another batch of powder $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples, including the powder (ENERMIGHT®) purchased from Ishihara Sangyo Kaishya, LTD. Since the $\lambda(T)$ curve for the film sample is identical to that of the powder sample, the Li deficient $\text{Li}[\text{Li}_{(1-\delta)/3}\text{Ti}_{(5+\delta)/3}]\text{O}_4$ phase is found to be stable under the present deposition and synthesis conditions, although it is at present very difficult to correctly estimate δ . To make such an estimation, very careful x-ray and/or neutron diffraction measurements as well as advanced data analysis are most likely needed.

B. LiTi_2O_4

Figure 5 shows the temperature dependencies of Δ , ν , and λ for the LiTi_2O_4 film. As the temperature is increased from

FIG. 5. (Color online) The temperature dependencies of (a) Δ , (b) ν , and (c) λ for the LiTi_2O_4 film. The data were obtained by fitting the time spectrum using Eq. (1). The scales of both axes in (a)–(c) are the same to those in Fig. 3 for comparison.

50 K, the $\Delta(T)$ curve shows a small steplike downturn at 325 K, around which the $\nu(T)$ curve shows a maximum. In approximate similarity to previous samples, ν is almost zero until 250 K, then increases exponentially, reaches a maximum at $T_{\text{max}} = 320$ K, and then decreases again. Note that $\nu/\Delta \sim 3$ at the maximum, which is lower than for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ films. The reason for the different temperature dependencies of Δ and ν in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiTi_2O_4 will be discussed later.

Although λ increases monotonically for $T \leq 300$ K, the magnitude of λ at 50 K is about 1/6 of that for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film. This is consistent with a Pauli paramagnetic nature of metallic LiTi_2O_4 . In addition, for LiTi_2O_4 , χ was reported to increase by 18% when going from 250 to 30 K [34]. This effect is probably connected to the presence of a narrower electronic d -band structure.

C. Activation energy for Li-ion diffusion

Figure 6 shows the relationship between ν and inverse temperature for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiTi_2O_4 . The increase in ν above 200 K is clearly explained by a thermal activation process, as expected for Li diffusion. The activation energy E_a was estimated by fitting $\nu(T)$ to an Arrhenius-like behavior $\nu = \nu_0 + A \exp(-E_a/k_B T)$, which gives $E_a = 0.12(2)$ eV for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film [0.09(2) eV for the powder] and 0.17(6) eV for the LiTi_2O_4 film. Here, ν_0 is temperature independent and k_B is the Boltzmann constant. The estimated E_a for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is at least in the correct order of magnitude compared to that reported for the hopping of Li^+ from the $8a$ to $16c$ site by Li-NMR [35], that is, 4.2 kJ/mol ($=0.043$ eV), and 5.2 kJ/mol ($=0.054$ eV) for the reverse hopping from the $16c$

FIG. 6. (Color online) The relationship between ν and inverse temperature for (a) the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film and powder and (b) the LiTi_2O_4 film. The numbers in (a) and (b) represent the thermal activation energy E_a estimated by fitting the data with $\nu = \nu_0 + A \exp(-E_a/k_B T)$ in the temperature range between 50 and 350 K. For LiTi_2O_4 , since $\nu_0 = 0$ below 200 K, we fitted the data in the temperature range between 200 and 325 K.

to $8a$ sites. The rather large discrepancy is to be expected from the already mentioned problems with studying these processes by the NMR technique in the presence of localized moments [36]. However, it is more interesting to compare the results between the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder and thin-film samples. Even though the data in Fig. 6(a) look rather similar, the actual fit of the Arrhenius equation reveals that E_a for the film is approximately 40% higher than for the powder. Further, it is also clear that for the two thin-film samples, LiTi_2O_4 displays a 45% higher activation energy than $\text{Li}_4\text{Ti}_5\text{O}_{12}$. These observations and possible reasons will be further discussed below.

IV. DISCUSSION

A. Li^+ and μ^+ site(s) in the spinel lattice

In the following discussion, we ignore the previously mentioned effect of δ on the diffusive nature in $\text{Li}_{4-\delta}\text{Ti}_{5+\delta}\text{O}_{12}$, because δ is estimated to be very small. Concerning the ion distribution in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel lattice, $(\text{Li}^+)_{8a}[\text{Li}_{1/3}^{+}\text{Ti}_{5/3}^{4+}]_{16d}\text{O}_4^{2-}$, the tetrahedral $8a$ site is occupied only by Li^+ ions, while 1/6 of the octahedral $16d$ sites are shared by Li^+ and the remaining 5/6 by Ti^{4+} ions. The other octahedral $16c$ sites are fully vacant (see Fig. 7). The reversible Li intercalation and deintercalation reaction is represented by [4,6]

For the present μ^+ SR measurements, there are no additional Li^+ ions that are intercalated into the lattice by the electrochemical reaction described in Eq. (3). Therefore the Li^+ ions at the $8a$ site are expected to hop to the vacant $16c$ site. For the spinel LiTi_2O_4 , a similar hopping process should be applicable since it clearly belongs to the same crystallographic framework as $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

FIG. 7. (Color online) The monoclinic supercell for first-principles calculations of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The optimized lattice parameters are $a = 10.4850 \text{ \AA}$, $b = 6.0277 \text{ \AA}$, $c = 14.9396 \text{ \AA}$, and $\beta = 89.6036^\circ$.

TABLE I. The electrostatic potential E and field distribution width Δ of the possible muon sites in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiTi_2O_4 predicted by DFT calculations with GGA and dipole field calculations. The value of E is relative to the lowest value near O^{2-} . The atomic position of the site with the lowest E is (0.19481, 0.00000, 0.10924) for $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and (0.28786, 0.28786, 0.09388) for LiTi_2O_4 , which are consequently deduced to be the muon stopping sites for the respective compounds.

		Measured at 50 K Near O^{2-}		
		Site 16c	Site 8b	
$\text{Li}_4\text{Ti}_5\text{O}_{12}$	E (eV)	0	+0.91	+3.09
	$\Delta(10^6 \text{ s}^{-1})$	0.165(8)	0.252	0.334
LiTi_2O_4	E (eV)	0	+0.55	+3.26
	$\Delta(10^6 \text{ s}^{-1})$	0.136(4)	0.237	0.320

The electrostatic potential distribution predicted by DFT calculations with generalized gradient approximation (GGA) [37] suggests that the implanted muons are located near the O^{2-} ions rather than the vacant $16c$ or $8b$ sites for the two spinels (see Table I). For the calculations in $\text{Li}_4\text{Ti}_5\text{O}_{12}$, we used a monoclinic supercell with $a = 10.4850 \text{ \AA}$, $b = 6.0277 \text{ \AA}$, $c = 14.9396 \text{ \AA}$, and $\beta = 89.6036^\circ$ (see Fig. 7). In the optimized lattice, the Li ions at the $16d$ site are distributed to minimize an electrostatic repulsion energy. As a result, every sixth layer along the c axis is occupied only by Li^+ , as in the case of the calculations using a hexagonal unit cell [14]. For LiTi_2O_4 , on the other hand, we used a usual cubic unit cell with $a = 8.5564 \text{ \AA}$.

The complex crystal structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ naturally alters the local structural environments of Li^+ ions even for the same $8a$ site. In fact, there are three different $8a$ sites in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ lattice for the above calculations. Therefore Li diffusion is expected to increase gradually with temperature, being consistent with the progressive changes in Δ and ν [Figs. 3(a) and 3(b)]. In contrast, there is only one Li site in LiTi_2O_4 , resulting in the sudden change in Δ and ν [Figs. 5(a) and 5(b)].

Finally, our recent β -NMR experiment on the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiTi_2O_4 films using a spin-polarized ^8Li beam [38] also reveals that Li^+ ions are diffusing even below 200 K for $\text{Li}_4\text{Ti}_5\text{O}_{12}$, but starts to diffuse above 200 K for LiTi_2O_4 . This clearly supports that the dynamic behavior observed by the present μ^+ SR measurements is mainly caused by Li-ion diffusion.

B. Diffusion coefficient D_{Li} : conventional approach

Assuming that the field fluctuation rate ν corresponds to a hopping rate, i.e., the jump frequency of Li^+ ions between the $16c$ and $8a$ sites, D_{Li} is given by [39]

$$D_{\text{Li}} = \sum_{i=1}^n \frac{1}{N_i} Z_{v,i} s_i^2 \nu, \quad (4)$$

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, $n = 1$, $N_1 = 2$, $Z_1 = 1$, and $s_1 = 1.87 \text{ \AA}$ for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $1.85 \text{ \AA}$ for LiTi_2O_4 . Using the temperature-dependent term for ν in Eq. (4), i.e., $\nu = \nu_0$,

FIG. 8. (Color online) The temperature dependence of D_{Li} for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiTi_2O_4 films estimated with a conventional approach (case 1). Note that points above T_{max} are omitted since their values are too low due to the artificial effect caused by the insufficient time scale of $\mu^+\text{SR}$ at high temperatures and are hereby not valid for obtaining true values of D_{Li} .

we obtain $D_{\text{Li}}(T)$ as shown in Fig. 8. From this, we are able to extract, e.g., $D_{\text{Li}} = (3.2 \pm 0.8) \times 10^{-11} \text{ cm}^2/\text{s}$ for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film [$D_{\text{Li}} = (3.6 \pm 1.1) \times 10^{-11} \text{ cm}^2/\text{s}$ for the LiTi_2O_4 film] at 300 K. These values are consistent with the prediction from first-principles calculations [12,13] as well as electrochemical measurements [15,16]. However, the current results are seven orders of magnitude (!) higher than what was previously presented from tracer diffusion measurements [10], which revealed that $D_{\text{Li}} \sim 10^{-18} \text{ cm}^2/\text{s}$ at 300 K. Though, such discrepancy is very easily explained since these data were actually obtained at very high temperatures, around $T = 900^\circ\text{C}$, and then extrapolated to obtain a value for D_{Li} at room temperature. This is in general not only unreliable, but in addition, recent neutron diffraction measurements [40] show the presence of Li also at the 32e site for $T \geq 700^\circ\text{C}$. This indicates the appearance of a structural phase transition and a new migration pathway from 8a to 16c through 32e at high temperatures. Therefore it is highly unsuitable to extract D_{Li} at 300 K from data obtained above 700°C .

Our current results also show a higher diffusion rate than previously published Li-NMR investigations [11], which show extremely slow jump rates as well as much larger activation energies. This is most likely related to the well-known problems in studies of ion diffusion for samples containing localized moments, e.g., the case of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [Fig. 3(d)]. On the contrary, thanks to the unique feature of $\mu^+\text{SR}$ to detect a nuclear magnetic field in paramagnetic materials, along with the possibility to measure slow diffusion mechanisms within a reasonable experimental time frame, $\mu^+\text{SR}$ yields reliable and reproducible intrinsic values of D_{Li} for both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiTi_2O_4 compounds.

C. Diffusion coefficient D_{Li} : alternate approach

It is well known that μ^+ “sees” a static magnetic field with a muon-spin precession frequency ranging up to a few hundred megahertz. Therefore one can consider that Δ is independent of temperature even when Li^+ starts to diffuse. In fact, such situation possibly looks suitable for LiTi_2O_4 (Fig. 5). In order to deduce if such assumption allows for a better description of the current results, we have performed an additional series

FIG. 9. (Color online) The temperature dependencies of (a) Δ and (b) the reduced χ^2 (χ^2/N , where N is the degree of freedom), and (c) the relationship between Δ and inverse temperature for the powder sample of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. For the case 2, we fixed $\Delta = 0.1641 \times 10^6 \text{ s}^{-1}$ in the whole temperature range measured. The number in (c) represents E_a .

of fits to the data. Contrary to previous fits (case 1) where Δ was treated as a free T -dependent parameter, we have in this alternate approach (case 2) a fixed Δ . For the latter, we used $\Delta = 0.1641 \times 10^6 \text{ s}^{-1}$, which is the average value of Δ for $T \leq 150 \text{ K}$ [case 1, see also Fig. 3(a)]. The result is shown in Fig. 9(a) where ν is found to monotonically increase with temperature and does not display a maximum at T_{max} anymore (as in case 1). To judge which of the two cases produce the most reliable fit, we have compared χ^2/N (N is the degree of freedom), which is an indicator for fitting reliability. As seen in Fig. 9(b), χ^2/N is much worse for case 2 above the onset of diffusion. In fact, as seen in Fig. 10, for case 2 the best obtainable fit does not even remotely reproduce the obtained spectra at 300 K.

To further investigate case 2, we also attempted to fit the data using a slightly modified function:

$$A_0 P(t) = A_{\text{KT1}} \exp(-\lambda t) G^{\text{DGKT}}(\Delta, \nu, t, H_{\text{LF}}) + A_{\text{KT2}} \exp(-\lambda_{\text{KT2}} t) + A_{\text{BG}}, \quad (5)$$

where the A_{KT2} is the asymmetry for the muons sensing the internal magnetic field with $\nu \gg \Delta$. However, such fit also did not manage to reproduce the measured spectra. Therefore we can clearly judge that Eq. (1) using a free Δ parameter

FIG. 10. (Color online) The ZF- and LF- μ^+ SR spectra for the powder sample of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ obtained at (a) 150, (b) 300, and (c) 300 K in ISIS. Solid lines represent the best fit with Eq. (1) using a temperature-dependent Δ (case 1) and a temperature-independent Δ (case 2). At 150 K, $\Delta = 0.1641 \times 10^6 \text{ s}^{-1}$ for both cases, while, at 300 K, $\Delta = 0.1286 \times 10^6 \text{ s}^{-1}$ for case 1 and $\Delta = 0.1641 \times 10^6 \text{ s}^{-1}$ for case 2.

(case 1) is the most reliable approach to fit the current data. Even though, for reference, we have also calculated the diffusion coefficient (D_{Li}) and extracted the thermal activation energy (E_a) for case 2. The results are shown in Fig. 9(c) and Table II. It should be noted that even though there are some differences between cases 1 and 2, the resulting changes

TABLE II. The diffusion coefficient D_{Li} and its thermal activation energy E_a for powder and film samples of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and a film sample of LiTi_2O_4 estimated using two different fitting conditions. The first is when Δ is a free fitting parameter dependent on temperature (case 1), while the other is when Δ is fixed to mean value independent of temperature (case 2). Note that case 1 is clearly judged to be the most reliable. However, for completeness, we also show the values of D_{Li} and E_a for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiTi_2O_4 using the case 2 scenario.

Sample	Case	D_{Li} at 300 K ($10^{-11} \text{ cm}^2/\text{s}$)	E_a (eV)
$\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder	1	2.29 ± 0.11	0.09 ± 0.02
	(2)	6.94 ± 0.12	0.161 ± 0.005
$\text{Li}_4\text{Ti}_5\text{O}_{12}$ film	1	3.2 ± 0.8	0.12 ± 0.02
	(2)	4.9 ± 1.1	0.16 ± 0.03
LiTi_2O_4 film	1	3.6 ± 1.1	0.17 ± 0.06
	(2)	6 ± 3	0.15 ± 0.08

in D_{Li} and E_a are still several orders of magnitude smaller than the irregularities found in the values obtained from other experimental techniques (see Sec. I). This further emphasizes the robustness of obtaining absolute intrinsic values for these important diffusion parameters through μ^+ SR.

D. Powder versus thin-film results

As already stated, characterizing ion diffusion using the μ^+ SR technique has proven to be a reliable tool, especially compared to other techniques that present results scattered over several order of magnitude. Obtaining such reliable data also allow us to extract and compare values of intrinsic material parameters on a new level. This possibility is here especially interesting for comparing the results from the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder versus thin-film samples. Above, it was shown that the activation energy changes by as much as 40% between the powder and the thin film. We are now able to discern that there are also small changes in the diffusion coefficient. Our present data show, for instance, a 30% increase in D_{Li} for the films at $T = 300 \text{ K}$ (see Table II). This is indeed a rather subtle effect but a potentially interesting result and especially discussing what the underlying reason might be.

One of the main differences between the powder sample and the film is that the latter nominally is fully single crystalline. This would mean that ion diffusion in such a film could appear without any interference from grain boundaries/interfaces, which is not the case for the powder samples. In line with the discussion above regarding interface issues and limitations in battery performance [9], this could explain the higher Li-ion diffusion rate in the thin-film sample.

Another possible explanation could be related to dimensionality. In most research areas, when drastically reducing the physical size of the investigated system, unexpected but useful phenomena might occur and open completely new fields, e.g., quantum computing. The area of battery devices is not an exception and lately the field of nanostructured materials for energy applications is experiencing a very fast development where new reports of improved ionic transport properties and device performances due to nanotuning are presented almost every day [41]. Here, one difference between our samples is, of course, that in our powder the grain size is on the order of a few to several micrometers, while the thin film has a much reduced dimension (190 nm) along one particular crystallographic (111) axis. Such reduced dimensionality and higher ion diffusion rate is in agreement with previous reports on nanosized battery materials [41].

A third possibility is related to the fact that our thin-film sample is grown on an MgAl_2O_4 (111) substrate [24]. This is because MgAl_2O_4 has an in-plane lattice constant ($a' = 8.08 \text{ \AA}$), which is approximately 4% smaller than the respective one for bulk $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($8.359 \text{ \AA}$). Since our films are rather thin, it could easily result in the presence of compressive strains within the sample. There have been several reports in the area of both fuel cells [42,43] as well as recently in battery materials [44] that indicate a surprisingly strong effect on ion diffusion rates from local strain fields on the atomic scale.

Finally, a fourth option is that there are slight differences in the Li/Ti intermixing, i.e., δ in $\text{Li}_{4-\delta}\text{Ti}_{5+\delta}\text{O}_{12}$, between

powder and thin-film samples. A possible indication for this is seen in the temperature dependence of λ [see Fig. 3(c)] where some slight differences appear below 60 K. However, as already mentioned, very exact determination of δ is needed for both samples, which is very difficult and require the use of additional experimental techniques.

All these four scenarios give possible explanations for the differences we find in the values for E_a and D_{Li} between the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder versus thin-film samples. However, at the current stage, with present data and the very subtle changes between the samples, we are unable to discern which explanation (if any) is the most plausible. Future systematic work concerning tuning of dimensionality, microscopic strains, exact determination of δ , and measurements across interfaces will be of crucial interest in order to find new routes for tuning and optimization in these and other energy related compounds.

V. SUMMARY

We have measured $\mu^+\text{SR}$ spectra for an anode material, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, using highly oriented films and powder samples. At temperatures below 150 K, $\mu^+\text{SR}$ indicates the appearance of localized moments for both samples. This was confirmed by magnetization measurements for many powder samples, suggesting the formation of Ti^{3+} ions due to a slight deviation of the composition during the sample synthesis. Namely, the correct formula of the present $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples is found to be $\text{Li}_{4-\delta}\text{Ti}_{5+\delta}\text{O}_{12}$. At temperatures above 200 K, a diffusive behavior was clearly observed in the temperature dependencies of the field distribution width Δ and

field fluctuation rate ν . Using a jump diffusion model, the diffusion coefficient of Li^+ (D_{Li}) at 300 K is estimated as $(3.2 \pm 0.8) \times 10^{-11} \text{ cm}^2/\text{s}$ for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin films with a thermal activation energy E_a of $0.12 \pm 0.02 \text{ eV}$. Further, some small differences are also found in both thermal activation energies and Li-ion diffusion coefficients between the powder and thin-film samples. However, more accurate and systematic measurements are needed in order to verify and explain such a possible effect.

We have also investigated Li-diffusion in a stoichiometric spinel LiTi_2O_4 film for comparison. The temperature variation of Δ and ν for LiTi_2O_4 is more drastic than that for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ probably due to a regular spinel structure. The diffusion parameters are extracted as $D_{\text{Li}} = (3.6 \pm 1.1) \times 10^{-11} \text{ cm}^2/\text{s}$ and $E_a = 0.17 \pm 0.06 \text{ eV}$, which is still rather similar to the values found for $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

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- [1] R. Marom, S. F. Amalraj, N. Leifer, D. Jacob, and D. Aurbach, *J. Mater. Chem.* **21**, 9938 (2011).
 - [2] M. V. Reddy, G. V. Subba Rao, and B. V. R. Chowdari, *Chem. Rev.* **113**, 5364 (2013).
 - [3] K. Colbow, J. Dahn, and R. Haering, *J. Power Sources* **26**, 397 (1989).
 - [4] T. Ohzuku, A. Ueda, and N. Yamamoto, *J. Electrochem. Soc.* **142**, 1431 (1995).
 - [5] T.-F. Yi, L.-J. Jiang, J. Shu, C.-B. Yue, R.-S. Zhu, and H.-B. Qiao, *J. Phys. Chem. Solids* **71**, 1236 (2010).
 - [6] X. Sun, P. V. Radovanovic, and B. Cui, *New J. Chem.* **39**, 38 (2015).
 - [7] D. Johnston, H. Prakash, W. Zachariasen, and R. Viswanathan, *Mater. Res. Bull.* **8**, 777 (1973).
 - [8] D. Johnston, *J. Low Temp. Phys.* **25**, 145 (1976).
 - [9] K. Xu, *Chem. Rev.* **104**, 4303 (2004).
 - [10] S. Takai, M. Kamata, S. Fujine, K. Yoneda, K. Kanda, and T. Esaka, *Solid State Ionics* **123**, 165 (1999).
 - [11] M. Wilkening, R. Amade, W. Iwaniak, and P. Heitjans, *Phys. Chem. Chem. Phys.* **9**, 1239 (2007).
 - [12] M. Anicete-Santos, L. Gracia, A. Beltrán, J. Andrés, J. A. Varela, and E. Longo, *Phys. Rev. B* **77**, 085112 (2008).
 - [13] J. Bhattacharya and A. Van der Ven, *Phys. Rev. B* **81**, 104304 (2010).
 - [14] B. Ziebarth, M. Klinsmann, T. Eckl, and C. Elsässer, *Phys. Rev. B* **89**, 174301 (2014).
 - [15] G. Wang, D. Bradhurst, S. Dou, and H. Liu, *J. Power Sources* **83**, 156 (1999).
 - [16] S. Panero, P. Reale, F. Ronci, V. Albertini, and B. Scrosati, *Ionics* **6**, 461 (2000).
 - [17] C. P. Grey and N. Dupré, *Chem. Rev.* **104**, 4493 (2004).
 - [18] J. Sugiyama, K. Mukai, Y. Ikeda, H. Nozaki, M. Månsson, and I. Watanabe, *Phys. Rev. Lett.* **103**, 147601 (2009).
 - [19] J. Sugiyama, Y. Ikeda, K. Mukai, H. Nozaki, M. Månsson, O. Ofer, M. Harada, K. Kamazawa, Y. Miyake, J. H. Brewer *et al.*, *Phys. Rev. B* **82**, 224412 (2010).
 - [20] J. Sugiyama, H. Nozaki, M. Harada, K. Kamazawa, O. Ofer, M. Månsson, J. H. Brewer, E. J. Ansaldi, K. H. Chow, Y. Ikeda *et al.*, *Phys. Rev. B* **84**, 054430 (2011).
 - [21] J. Sugiyama, H. Nozaki, M. Harada, K. Kamazawa, Y. Ikeda, Y. Miyake, O. Ofer, M. Månsson, E. J. Ansaldi, K. H. Chow *et al.*, *Phys. Rev. B* **85**, 054111 (2012).
 - [22] J. Sugiyama, K. Mukai, H. Nozaki, M. Harada, M. Månsson, K. Kamazawa, D. Andreica, A. Amato, and A. D. Hillier, *Phys. Rev. B* **87**, 024409 (2013).
 - [23] J. Sugiyama, K. Mukai, M. Harada, H. Nozaki, K. Miwa, T. Shiotsuki, Y. Shindo, S. R. Giblin, and J. Lord, *Phys. Chem. Chem. Phys.* **15**, 10402 (2013).

- [24] A. Kumatani, T. Ohsawa, R. Shimizu, Y. Takagi, S. Shiraki, and T. Hitosugi, *Appl. Phys. Lett.* **101**, 123103 (2012).
- [25] E. Morenzoni, F. Kottmann, D. Maden, B. Matthias, M. Meyberg, T. Prokscha, T. Wutzke, and U. Zimmermann, *Phys. Rev. Lett.* **72**, 2793 (1994).
- [26] E. Morenzoni, *Appl. Magn. Reson.* **13**, 219 (1997).
- [27] T. Prokscha, M. Birke, E. Forgan, H. Glückler, A. Hofer, T. Jackson, K. Küpfer, J. Litterst, E. Morenzoni, C. Niedermayer *et al.*, *Hyperfine Interact.* **120-121**, 569 (1999).
- [28] T. Prokscha, E. Morenzoni, K. Deiters, F. Foroughi, D. George, R. Kobler, A. Suter, and V. Vrankovic, *Nucl. Instrum. Methods Phys. Res., Sect. A* **595**, 317 (2008).
- [29] G. M. Kalvius, D. R. Noakes, and O. Hartmann, *Handbook on the Physics and Chemistry of Rare Earths* (North-Holland, Amsterdam, 2001), Vol. 32, Chap. 206, pp. 55–451.
- [30] A. Yaouanc and P. D. de Reotier, *Muon Spin Rotation, Relaxation, and Resonance: Applications to Condensed Matter* (Oxford University Press, Oxford, 2011).
- [31] T. Matsuzaki, K. Nishiyama, K. Nagamine, T. Yamazaki, M. Senba, J. M. Bailey, and J. H. Brewer, *Phys. Lett. A* **123**, 91 (1987).
- [32] A. Suter and B. M. Wojek, *Phys. Procedia* **30**, 69 (2012).
- [33] K. Mukai (unpublished work obtained in Toyota Central Research & Development Labs., Inc., 2015).
- [34] D. P. Tunstall, J. R. M. Todd, S. Arumugam, G. Dai, M. Dalton, and P. P. Edwards, *Phys. Rev. B* **50**, 16541 (1994).
- [35] M. Vijayakumar, S. Kerisit, K. M. Rosso, S. D. Burton, J. A. Sears, Z. Yang, G. L. Graff, J. Liu, and J. Hu, *J. Power Sources* **196**, 2211 (2011).
- [36] M. Månsson and J. Sugiyama, *Phys. Scr.* **88**, 068509 (2013).
- [37] T. Sato, K. Miwa, Y. Nakamori, K. Ohoyama, H.-W. Li, T. Noritake, M. Aoki, S.-i. Towata, and S.-i. Orimo, *Phys. Rev. B* **77**, 104114 (2008).
- [38] J. Sugiyama *et al.* (unpublished work obtained in TRIUMF, 2015).
- [39] R. J. Borg and G. J. Dienes, *An Introduction to Solid State Diffusion* (Academic Press, San Diego, 1988), Chap. 3, pp. 53–77.
- [40] A. Laumann, H. Boysen, M. Bremholm, K. T. Fehr, M. Hoelzel, and M. Holzapfel, *Chem. Mater.* **23**, 2753 (2011).
- [41] A. S. Aricò, P. Bruce, B. Scrosati, J.-M. Tarascon, and W. van Schalkwijk, *Nat. Mater.* **4**, 366 (2005).
- [42] J. L. M. Rupp, *Solid State Ionics* **207**, 1 (2012).
- [43] Q. Chen, A. Braun, A. Ovalle, C.-D. Savaniu, T. Graule, N. Bagdassarov, *Appl. Phys. Lett.* **97**, 041902 (2010).
- [44] M. Månsson *et al.* (unpublished).
- [45] K. Momma and F. Izumi, *J. Appl. Crystallogr.* **41**, 653 (2008).