Pressure dependence of magnetic transition temperature in Li[Li\(_x\)Mn\(_{2-x}\)]O\(_4\) (0 \(\leq x \leq 1/3\)) studied by muon-spin rotation and relaxation

Kazuhiko Mukai\(^1\), Danile Andreica\(^2\), Yutaka Ikedo\(^3\), Hiroshi Nozaki\(^1\), Martin Månsson\(^4\), Alex Amato\(^5\), and Jun Sugiyama\(^1\)

\(^1\)Toyota Central Research and Development Laboratories, Inc., 41-1 Yokomichi, Nagakute, Aichi 480-1192, Japan
\(^2\)Faculty of Physics, Babes-Bolyai University, 400084 Cluj-Napoca, Romania
\(^3\)Muon Science Laboratory, Institute of Materials Structure Science, KEK, 1-1 Oho, Tsukuba, Ibaraki 305-0001, Japan
\(^4\)Laboratory for Solid State Physics, ETH Zürich, Zürich CH-8093, Switzerland
\(^5\)Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institut, Villigen CH-5232, Switzerland

(Received 9 January 2013; accepted 22 January 2013; published online 4 February 2013)

In order to study a change in electrochemical, structural, and magnetic properties for lithium manganese oxide spinels Li[Li\(_x\)Mn\(_{2-x}\)]O\(_4\) (LMO) with 0 \(\leq x \leq 1/3\), muon-spin rotation and relaxation (\(\mu\)SR) spectra were recorded under pressure (\(P\)) up to 2.1 GPa. At ambient \(P\), \(P = 0.1\) MPa, the antiferromagnetic or spin-glass-like transition temperature \((T_\text{m})\) at \(P = 0.1\) MPa monotonically decreases with increasing \(x\). On the contrary, the slope of the \(T_\text{m}\) vs. \(P\) (\(dT_\text{m}/dP\)) rapidly increases from 0.9(1) K/GPa at \(x = 0\) to 1.4 K/GPa at \(x = 0.1\), then drops to 0.7(1) K/GPa at \(x = 0.15\), and finally keeps constant \((\sim 0.4\) K/GPa) with further increasing \(x\). Considering the structural change of LMO with \(x\), the decrease in the distance between Mn ions \((d_{\text{Mn-Mn}})\) is likely to play an essential role for determining \(T_\text{m}\) under \(P\). According to cyclic voltammetry on LMO, the peak current at both anodic and cathodic directions shows the maximum at \(x = 0.1\), indicating the highest diffusivity of Li\(^+\) ions \((D_{\text{Li}})\) at \(x = 0.1\). © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4790377]

I. INTRODUCTION

A spinel-type lithium manganese oxide Li[Li\(_x\)Mn\(_{2-x}\)]O\(_4\) (LMO) with 0 \(\leq x \leq 1/3\) has attracted much attention as a positive electrode material of lithium-ion batteries (LIB), due to a reversible Li extraction and insertion reaction.\(^6\) At room temperature (\(T\)), LMO has a cubic structure with a space group of \(Fd\bar{3}m\), in which Li\(^+\) ions occupy both tetrahedral \(8a\) and octahedral \(16d\) sites, while Mn\(^{3+/4+}\) ions sit in the octahedral \(16d\) site [see Fig. 1(a)]. Since the average valence of Mn ions increases from +3.5 at \(x = 0\) to +4 at \(x = 1/3\), the theoretical capacity based on a redox reaction of Li[Li\(_x\)Mn\(_{2-x}\)]O\(_4\) \(\rightarrow\) yLi\(^+\) + ye\(^-\) + Li\(_{1-y}\)[Li\(_{x}\)Mn\(_{2-x}\)]O\(_4\) \((y = 1-3x)\) increases with increasing \(x\). Although the electrochemical performance of LMO depends on an oxygen deficiency, particle size/ morphology, and surface condition of the particle, there is a general agreement that the presence of a small amount of Li\(^+\) ions at the \(16d\) site improves the cyclability and rate capability of LMO.\(^2\)\(^6\)

The structural and magnetic nature of LMO is also known to change drastically by a small amount of \(x\).\(^7\)\(^12\) The \(x = 0\) compound exhibits a structural phase transition from a high-\(T\) cubic \((Fd\bar{3}m)\) phase to a low-\(T\) orthorhombic \((Fdd\bar{2})\) phase at \(\sim 285\) K \((=T_\text{T})\), which is induced by a cooperative Jahn-Teller (JT) transition due to the Mn\(^{3+}\) ions with \(S = 2\).\(^7\) Differential calorimetry analyses\(^8\) indicated that, as \(x\) increases from 0, \(T_\text{T}\) rapidly decreases down to \(\sim 214\) K at \(x = 0.035\), and finally disappears with further increasing \(x\). Moreover,\(^7\) Li-NMR,\(^9\) neutron scattering,\(^10\) and muon-spin rotation and relaxation (\(\mu\)SR)\(^11\)\(^12\) measurements clarified that the \(x = 0\) compound shows an antiferromagnetic (AF) transition at \(T_\text{N} \sim 60\) K, while the compound with \(x \geq 0.05\) indicates a spin-glass-like transition below \(T_f \sim 25\) K. Here, \(\mu\)SR is very sensitive to local magnetic environment and is a powerful technique for investigating both static and dynamic magnetic fields generated by nuclear- and electronic-magnetic moments.\(^13\)

Since the deviations from stoichiometry in LiCoO\(_2\)\(^14\)\(^15\) and LiNiO\(_2\)\(^16\) also alter their electrochemical, structural, and magnetic properties, an in-depth-understanding of the lightly substituted LMOs that could lead to the further development of LIB materials. However, the roles of the Li\(^+\) ions at the \(16d\) site in LMO are still not fully understood, because the substitution of Li\(^+\) ions for Mn\(^{3+}\) ions produces multiple variations in the LMO crystal lattice, e.g., decreases the cubic lattice parameter \((a_0)\), modifies the ratio of Mn\(^{3+}\)/Mn\(^{4+}\) ions, and changes the oxygen positional parameter \((\nu)\). Note that, for the \(x = 0\) compound at room \(T\), it is reported to be \(\sim 0.385,\(^2\)\) resulting in the distortion of the oxygen sub-lattice [see Fig. 1(b)]. We have, therefore, performed a systematic high-pressure (HP) \(\mu\)SR studies on LMO with 0 \(\leq x \leq 1/3\) up to the pressure \((P)\) of 2.1 GPa. This is because \(P\) is one of the crucial parameters for determining structural and physical properties via the shrinkage of lattice parameters. In this paper, we report the \(P\) dependence of magnetic transition temperature \((dT_\text{m}/dP)\) of LMO, and discuss the relation between \(dT_\text{m}/dP\) and the diffusivity of Li\(^+\) ions in LMO.
II. EXPERIMENTAL METHOD

Powder samples of LMO with \( x = 0, 0.05, 0.1, 0.15, 0.2, \) and 1/3 were prepared by a two-step solid-state reaction technique as reported previously.\(^{12,17}\) The reaction mixture of \( \text{LiOH}_2\text{H}_2\text{O} \) and \( \text{MnOOH} \) was well mixed with a mortar and pestle, and pressed into a pellet of 23 mm diameter and \( \sim 5 \text{ mm thickness} \). The pellet was heated at 1273 K under air for 12 h, then crushed and repressed into a pellet again, and finally oxidized under air for 24 h at 973 K for \( x = 0, 923 \text{ K for } x = 0.05, 873 \text{ K for } x = 0.1, 848 \text{ K for } x = 0.15, \) and 823 K for \( x = 0.2 \). For \( x = 0.3 \), the pellet was oxidized under air for 24 h at 923 K, 873 K, 823 K, and 773 K, successively, without cooling down to room \( T \). The obtained powders were characterized by a powder X-ray diffraction (XRD) measurement at the synchrotron radiation facility of SPring-8, Japan and an inductively coupled plasma-atomic emission spectrometer (ICP-AES, CIROS 120, Rigaku Co., Ltd., Japan).

The electrochemical reactivity for LMO was examined in a non-aqueous lithium cell. In preparing the electrode, polyvinylidene fluoride (PVdF) dissolved in N-methyl-2-pyrrolidone (NMP) solution was used as a binder. The black viscous slurry consisting of 88 wt. % LMO powder, 6 wt. % acetylene black, and 6 wt. % PVdF was cast on an aluminum foil (\( \phi \) 16 mm) with blade. The electrode was dried under vacuum at 393 K for 12 h in order to evaporate the NMP. Lithium metal pressed on a stainless steel plate (\( \phi \) 19 mm) was used as a counter electrode. Two sheets of porous polyethylene membrane (TonenGeneral Sekiyu K. K., Japan) were used as a separator. The electrolyte was 1 M LiPF\(_6\) dissolved in ethylene carbonate (EC)/dimethyl carbonate (DEC) (1/1 by volume ratio) solution (Kishida Chemical Co., Ltd., Japan). In order to obtain the steady-state voltammograms, the charge and discharge test for five cycles was first done in the voltage range between 3.0 and 4.2 V at constant current density of 0.15 mA cm\(^{-2}\) at 298 K. Then, cyclic voltammetry (CV) was carried out in the voltage range between 3.0 and 4.5 V at scan rate of 0.1 mV s\(^{-1}\) (HZ-5000, Hokuto Denko Co., Ltd., Japan).

Weak-transverse-field (wTF-) \( \mu \)SR experiment was performed using high momentum muons on the \( \mu \)E1 decay muon beam line (GPD) at the Paul Scherrer Institut, Switzerland. The piston-cylinder-cell made of Cu-Be\(_2\) alloy [Fig. 2(a)] was used to apply \( P \) up to 1.4 and 2.8 GPa at room \( T \). About six disks of the pressed sample [Fig. 2(b)] were stacked in the sample space (5.2 mm diameter and 20 mm height) of the cell. The 1:1 mixture of \( n \)-pentane and isoamyl alcohols was used as a \( P \) medium in order to apply hydrostatic \( P \) to the sample. The actual \( P \) at low-\( T \) was monitored by the superconducting transition \( T \) of a piece of indium wire located at the bottom of the sample cell, by ac-susceptibility (\( \gamma \)) measurements, and then estimated to be 1.2 and 2.1 GPa. wTF-\( \mu \)SR spectra were recorded in the \( T \) range between 10 and 70 K with an applied magnetic field \( H_{\text{wTF}} = 50 \text{ G} \). The details of the experimental setup and techniques are described elsewhere.\(^{18} \)

III. RESULTS

Figure 3 shows a typical example of the wTF-\( \mu \)SR spectra for the LMO sample with \( x = 0 \) at \( T = 10 \) and 70 K at \( P = 0.1 \text{ MPa} \), in order to display a change in the muon asymmetry \( A_{\text{wTF}} \) with decreasing \( T \). The wTF-\( \mu \)SR spectra for all the LMO samples were well fitted by a simple exponentially relaxing cosine function,

\[
A_0 P(t) = A_{\text{wTF}} \exp(-\lambda_{\text{wTF}} t) \cos(\omega_p t + \phi),
\]

where \( A_0 \) is the initial muon decay asymmetry, \( P(t) \) is the muon spin polarization function, \( A_{\text{wTF}} \) is the asymmetry from both sample and body of the HP cell, \( \lambda_{\text{wTF}} \) is the relaxation rate, \( \omega_p \) is the muon Larmor frequency, and \( \phi \) is the initial phase of the muon pression. Although \( T_{m} \) for the LMO samples varies with \( x \) as illustrated later in Fig. 5(a), \( A_{\text{wTF}} \) decreases from \( \sim 0.25 \) (\( = A_{\text{wTF}}^{0.05} \)) at 70 K to \( \sim 0.2 \) (\( = A_{\text{wTF}}^{0.2} \)) at 10 K (Fig. 3). According to the previous \( \mu \)SR study on LMO using surface muon beam,\(^{11,12}\) the whole volume of the LMO sample was found to enter into a magnetic phase below \( T_{m} \), for instance, \( T_N = 61 \text{ K} \) for \( x = 0 \), \( T_J = 29 \text{ K} \) for \( x = 0.1 \), and \( T_J = 24 \text{ K} \) for \( x = 0.2 \). Thus, the decrease in \( A_{\text{wTF}} \) by \( \sim 0.05 \) evidences a magnetic transition of the LMO samples.

Figure 4 shows the \( T \) dependence of the normalized wTF asymmetry (\( N_{\text{wTF}} \)) for the LMO samples with (a) \( x = 0 \), (b) \( x = 0.1 \), and (c) \( x = 0.2 \) at \( P = 0.1 \text{ MPa}, 1.2 \text{ GPa}, \) and 2.1 GPa. Here, \( N_{\text{wTF}}(T) \) is calculated by
\[
N_{ATF} = \frac{A_{wTF}(T)}{A_{min}^{wTF}} \frac{C_0}{A_{max}^{wTF}} - \frac{C_0}{A_{min}^{wTF}},
\]
and is roughly proportional to the volume fraction of paramagnetic (PM) phases in the sample. In other words, when \(N_{ATF} = 1\), the whole sample is in a PM state, while when \(N_{ATF} = 0\), the whole sample is in a magnetic phase, such as ferromagnetic, ferrimagnetic, AF, or spin-glass-like phase.

As seen in Fig. 3, the \(N_{ATF}\) for the \(x = 0\) sample at \(P = 0.1\) MPa starts to decrease from 1 at \(T = 40\) K and reaches 0 at \(T = 25\) K, indicating that the whole volume of the sample enters into the AF phase below 25 K. The magnetic transition temperature at which \(N_{ATF} = 0.5\) \(T_{mid}^m\) is \(35.6(3)\) K. Note that \(T_{mid}^m\) for \(x = 0\) is \(25\) K lower than the previous results on the \(x = 0\) compounds studied by neutron scattering and \(\muSR\) measurements. However, synchrotron XRD measurements for the present \(x = 0\) sample exhibit the structural phase transition from the high-\(T\) cubic \((Fd\bar{3}m)\) phase to low-\(T\) orthorhombic \((Fddd)\) phase at 285 K (not shown), which is a characteristic of stoichiometric \(\text{LiMn}_2\text{O}_4\). Also, as shown later in Fig. 6(a), a small cathodic peak around 3.3 V is clearly observed for the \(x = 0\) sample, confirming the stoichiometric Li/Mn ratio. Since \(T_N\) is very sensitive to \(x\) at the vicinity of \(x = 0\), the difference between the present \(T_m\) and \(T_N\) is probably due to a small compositional difference of Li ions at the 16\(d\) site. In other words, magnetic measurements such as \(wTF-\muSR\) and neutron scattering are more sensitive.
to the stoichiometry of LiMn$_2$O$_4$ compared to XRD and electrochemical measurements.

As shown in Figs. 4(b) and 3(c), $T_{\text{mid}}^m$ at $P = 0.1$ MPa decreases with increasing $x$, that is, $T_{\text{mid}}^m = 30.2(2)$ K for $x = 0.1$ and $T_{\text{mid}}^m = 23.9(2)$ K for $x = 0.2$. It is clearly found that $T_{\text{mid}}^m$ for all the LMO samples increases with $P$; the $N_{\text{ATF}}(T)$ curves simply shift towards the higher $T$ side. Furthermore, a linear relationship between $T_{\text{mid}}^m$ and $P$ is found up to 2.1 GPa (see the insets in Fig. 4).

Figure 5(a) shows the $T_{\text{mid}}^m$ obtained at $P = 0.1$ MPa and 2.1 GPa as a function of $x$ in LMO. $T_{\text{mid}}^m$ decreases with increasing $x$ regardless of $P$, but the slope $(dT_{\text{mid}}^m/dP)$ around $x = 0.1$ seems to be larger than those for other LMO samples. Indeed, as illustrated in Fig. 5(b), $dT_{\text{mid}}^m/dP$ has the maximum at $x = 0.1$, i.e., as $x$ increases from 0, $dT_{\text{mid}}^m/dP$ rapidly increases from 0.9(1) K/GPa to 1.4(1) K/GPa at $x = 0.1$, then drops to 0.7(1) K/GPa at $x = 0.15$, and finally approaches almost constant value ($\sim 0.4$ K/GPa) with further increasing $x$. Although there has been few reports on the HP-$\mu$SR studies for other spinel oxides, the $dT_{\text{mid}}^m/dP$ value for LMO is about 30%–50% to that for Co$_3$O$_4$ ($\sim 2.2$ K/GPa),

$$I_p = 0.4463 \left( \frac{F^3}{RT} \right)^{1/2} n^{3/2} AD^{1/2} C v^{1/2},$$

where $F$ is the Faraday constant, $R$ is the gas constant, $T$ is the absolute temperature, $n$ is the number of electrons involved in an electrode reaction, $A$ is the reaction surface area, $C$ is the bulk concentration, and $v$ is the scan rate. Since the weight of positive electrode is uniformed to be $\sim 22$ mg for all the LMO cells, the diffusivity of Li$^+$ ions $(D_{\text{Li}})$ is thought to have a maximum at $x = 0.1$.

**IV. DISCUSSION**

**A. $x$ dependence of $dT_{\text{mid}}^m/dP$**

As shown in Figs. 4 and 5(a), $T_{\text{mid}}^m$ increases with $P$ in the whole $x$ range. It should be noted that at ambient $P$, the O-Mn-O bond angles do not change with $x$, but the distance between Mn ions $(d_{\text{Mn-Mn}})$ decreases almost linearly with $x$. This is because $a_c$, at $P = 0.1$ MPa and $T = 300$ K, decreases monotonically with $x$, whereas $u$ remains almost constant ($\sim 0.387$) in the whole $x$ range [Fig. 5(c)]. Although we have no data for the change in $a_c$ with $P$ in the low-$T$, according to the previous results for a structural analysis of LiMn$_2$O$_4$ as a function of $P$, $a_c$ at 350 K decreases monotonically with a slope $(da_c/dP) \sim 0.01$ Å/GPa up to $\sim 2$ GPa$^{21}$ In addition, XRD and Raman studies under $P$ on the other spinel oxides such as NiMn$_2$O$_4$, ZnFe$_2$O$_4$, and Zn$_2$TiO$_4$ suggest that $a_c$ linearly decreases with $P$, while $u$ is independent of $P$. Therefore, the positive dependence of $T_{\text{mid}}^m$, for the LMO is likely to be attributed to the decrease in $d_{\text{Mn-Mn}}$. That is, since the MnO$_6$ octahedra are compressed by $P$, the crystal electric field is enhanced by $P$, leading to larger splitting of the 3d orbitals than that at $P = 0.1$ MPa.

In contrast to the linear relationship between $x$ and $T_{\text{mid}}^m$ at $P = 0.1$ MPa, a broad maximum in the $dT_{\text{mid}}^m/dP(x)$ curve
indicates that at least two opposite effects contribute to determine $T_{m}^{md}$ under $P$ [Figs. 5(a) and 5(b)]. If we assume that the decrease in $d_{Mn-Mn}$ governs $T_{m}^{md}$ under $P$, the $dT_{m}^{md}/dP(\chi)$ curve suggests that the change in $d_{Mn-Mn}$ under $P$ is the largest at the $x = 0.1$ composition, namely, the $x = 0.1$ sample is the softest in the whole $x$ range. Although the origin of $P$ dependence on $d_{Mn-Mn}$ (or $T_{m}^{md}$) is currently unclear, the decrease in $a_{x}$ with $x$ naturally inhibits the decrease in $d_{Mn-Mn}$ under $P$. On the other hand, the cooperative JT distortion disappears with $x$, although our $\mu$SR studies on LMO clarifies that a short-range cooperative JT distortion exists even at the $x = 0.15$ composition.\(^{11}\) Since the Mn$^{3+}$-Mn$^{4+}$ and Mn$^{4+}$-Mn$^{4+}$ ions are strongly bound in the cooperative JT distortion phase, the increase in $x$ would release the couplings between Mn$^{3+}$ (or Mn$^{4+}$) ions. This consideration is consistent with our recent XRD studies on LMOs; as $x$ increases from 0, the thermal expansion coefficient, which correlates the bond strength between Mn ions, slightly increases up to $x = 0.1$, then levels off with further increasing $x$.\(^{25}\)

B. Correlation between $dT_{m}^{md}/dP$ and $D_{Li}$

Considering the crystal structure of LMO (see Fig. 1), only the Li$^+$. ions at the $8a$ site seem to participate in the electrochemical reaction of Li$_{1-x}$[Li$_{0.2}$Mn$_{0.8}$]O$_{4}$ ($y = 1 - 3x$) in the $y$ range between 0 and 1. Actually, the observed capacity in the voltage range between 3.0 and 4.2 V at low current $0.15$ mA cm$^{-2}$ decreases with increasing $x$. However, CV demonstrates that the $I_{m}(x)$ [$I_{pc}(x)$] curve, in other words, the $D_{Li}(x)$ curve shows the maximum at $x = 0.1$ (Fig. 6). This means that the Li$^+$ ions at the 16$d$ site play a significant role on the electrochemical kinetics of LMO. Here, it has been established that the local compositional inhomogeneities during solid-state diffusion generate stresses, leading to particle level fracture, degradation of rate capability, and capacity fading of LIB.\(^{26-31}\) This is called as diffusion-induced stress (DIS) and should be minimized in order to increase the rate capability and mechanical durability. The $x$ dependence of $dT_{m}^{md}/dP$ implies that the $x = 0.1$ sample is softest in the whole $x$ range. Since the simulation studies on DIS\(^{26-31}\) suggest that the soft and flexible materials have better rate capability rather than hard and brittle ones, the soft material nature of the $x = 0.1$ sample would decrease the DIS during Li extraction and insertion. In other words, the $x$ dependence of $dT_{m}^{md}/dP$ is thought to be correlated with that of $D_{Li}$.

Finally, we wish to emphasize the unique spatial resolution of $\mu$SR technique. In contrast to dc-$\chi$ measurements, muon reflects the magnetic fields within a few angstrom, and consequently, it is very sensitive to microscopic magnetism and crystal structure.\(^{13}\) Positive muon is most likely to bind to the nearest O$^{2-}$ ion with a typical bond length $d_{\mu-O} = 1.1 \AA$, which feels the nuclear magnetism of Li ions at the $8a$ site [Fig. 1(b)]. Most of the LIB materials except for Li$_{2}$CoO$_{2}$ enter into a magnetic phase below $\sim 100$ K.\(^{11,12,32,33}\) Thus, HP-$\mu$SR study provides microscopic information concerning DIS, although a change in volume during extraction and insertion is currently used for simulating the DIS of LIB materials.\(^{26}\)

V. CONCLUSION

We have found an abnormal the pressure ($P$) dependence of the magnetic transition temperature ($T_{m}^{md}$) for (LMO) by $\mu$SR measurements. That is, although $T_{m}^{md}$ at ambient $P$ monotonically decreases with increasing $x$, a slope of the $T_{m}^{md}$ vs. $P$ shows the maximum at $x = 0.1$. Since cyclic voltammetry also demonstrates the highest diffusivity of Li$^{+}$ ions at $x = 0.1$, the Li$^{+}$ ions at the 16$d$ site, in other words, soft and flexible nature plays an essential role for determining an electrochemical kinetics of LMO. We expect that high-pressure $\mu$SR studies are applicable for studying a diffusion-induced stress of lithium-ion battery materials.

ACKNOWLEDGMENTS

We appreciate Professor T. Ohzuku, Dr. K. Ariyoshi, and Mr. H. Wakabayashi of Osaka City University for preparation of Li[Li$_{0.2}$Mn$_{0.8}$]O$_{4}$ and Mr. Y. Kondo of TCRDL for ICP-AES analyses. $\mu$SR was measured at the Swiss Muon Source, Paul Scherrer Institut (PSI). XRD experiment was performed at the SPring-8, Japan, with the approval of the Japan Synchrotron Radiation Research Institute (Proposal No. 2007A1917). We thank the staff of PSI and SPring-8 for help with the $\mu$SR and XRD measurements. This work was partially supported by Grant-in Aid for Scientific Research (B), Grant No. 19340107 provided by MEXT, Japan. D.A. acknowledges the support from the Romanian UEFISCDI Project No. PN-II-ID-PCE-2011-3-5083 (85/2011).


