

A ${}^7\text{Li}$ nuclear magnetic resonance study on spinel $\text{LiMn}_2\text{O}_{4-\delta}$

Akihiko Koiwai *, Jun Sugiyama, Tatsumi Hioki, Shoji Noda

Toyota Central Research and Development Laboratories, 41-1 Yokomichi, Nagakute, Aichi 480-11, Japan

Accepted 13 November 1996

Abstract

A ${}^7\text{Li}$ nuclear magnetic resonance (${}^7\text{Li}$ -NMR) study was carried out to investigate the magnetic properties of powder samples of LiMn_2O_4 and $\text{LiMn}_2\text{O}_{3.9}$ in the temperature range between 160 and 400 K. Lowering the temperature from 400 K to ~ 300 K, the width of the ${}^7\text{Li}$ -NMR line was found to increase monotonically, then increased rapidly at temperatures below 260 K for LiMn_2O_4 and 290 K for $\text{LiMn}_2\text{O}_{3.9}$. Combining these results with those of differential scanning calorimetry (DSC) analyses, the transition temperature (T_C) was determined to be ~ 250 K for LiMn_2O_4 and ~ 290 K for $\text{LiMn}_2\text{O}_{3.9}$. This indicated that the magnitude of T_C of $\text{LiMn}_2\text{O}_{4-\delta}$ depends on the oxygen deficiency (δ). In addition, at temperatures below T_C , the NMR line seemed to decompose into two Gaussian peaks; it was a symmetrical singlet at temperatures above T_C . Thus, it is deduced that there are two possible sites for the lithium ions in the sample at temperatures below T_C , and one equivalent site above T_C . © 1997 Elsevier Science S.A.

Keywords: Nuclear magnetic resonance study; Lithium; Manganese; Structural phase transition; Oxygen deficiency

1. Introduction

It has been found that LiMn_2O_4 spinel undergoes a structural phase transition from a cubic $Fd\bar{3}m$ phase to a tetragonal $I4_1/amd$ phase [1,2]. The transition temperature (T_C) was reported at ~ 280 K from a differential scanning calorimetry (DSC) analysis [1] and at ~ 230 K from an elastic measurement [2]. This structural phase transition is interesting in connection with the performance of lithium secondary batteries using LiMn_2O_4 as the cathode material. Nevertheless, to the authors' knowledge, there are few data concerning the changes in physical properties for LiMn_2O_4 during the phase transition; at present, even the magnitude of T_C is not clear.

Furthermore, LiMn_2O_4 has been found to release oxygen in a reducing atmosphere at temperatures above 873 K [3–5]. For the oxygen deficient $\text{LiMn}_2\text{O}_{4-\delta}$ spinels, as δ increases from zero, the cubic phase changes into the tetragonal phase at $\delta=0.07$ [5], even at ambient temperature. Therefore, not only electronic and magnetic properties but also the magnitude of T_C are altered by oxygen deficiency. In this paper, we report on DSC analyses and ${}^7\text{Li}$ -NMR experiments of LiMn_2O_4 and $\text{LiMn}_2\text{O}_{3.9}$ to investigate the physical properties of both samples in the 160–400 K temperature range.

2. Experimental

Polycrystalline samples of LiMn_2O_4 and $\text{LiMn}_2\text{O}_{3.9}$ were synthesized by a solid-state reaction technique using reagent-grade Li_2CO_3 and MnO_2 powders. In order to control the oxygen content of the samples, the calcined powders were annealed at 1073 K for 24 h in an O_2/Ar gas mixture flow, and then quenched to 273 K. The preparation, characterization and physical properties of the $\text{LiMn}_2\text{O}_{4-\delta}$ samples are reported in detail elsewhere [5,6].

A differential scanning calorimetry (DSC) analysis was carried out using a power compensation method (Perkin-Elmer, DSC-7) in the 113–423 K temperature range. The ${}^7\text{Li}$ -NMR measurements were performed in a spin echo pulse sequence mode using a Fourier-transform NMR spectrometer (Bruker, MSL-300). The measurements were carried out in the 160–400 K temperature range under a magnetic field of $H=7$ T. About 150 mg of a powder sample was placed in a zirconia tube, mounting on the top of the NMR probe. In order to control the temperature of the sample, the sample was static and was set into the N_2 gas flow. The temperature of the sample was determined directly from the temperature of the N_2 gas flow. The measurement accuracy of the sample temperature was estimated to be ± 5 K from a ${}^1\text{H}$ -NMR study on the melting point of water. The resonance frequency for free ${}^7\text{Li}$ nuclei was determined from the ${}^7\text{Li}$ -NMR line of 1 M LiOH aqueous solution at ambient temperature.

* Corresponding author.

3. Results

3.1. DSC

Fig. 1(a) and (b) shows the DSC curves for the $\text{LiMn}_2\text{O}_{4-\delta}$ samples with $\delta=0$ and $\delta=0.10$ in the 175–375 K temperature range. For the LiMn_2O_4 sample, as temperature was raised from 113 K with a rate of 5 K/min, the DSC curve exhibited an endothermic peak at 249 ± 3 K (see Fig. 1(a)). In contrary, an exothermic peak was observed at 244 ± 3 K in the DSC curve measured on cooling (see Fig. 1(b)). Both peaks are attributed to the phase transition between the cubic and tetragonal phases; thus, the magnitude of the transition temperature (T_C) for LiMn_2O_4 was determined to be 247 ± 3 K; since a difference between the magnitudes of T_C observed on cooling and on heating (ΔT_C) was 5 ± 3 K, this phase transition was thought to be discontinuous, as had been reported [7]. For the $\text{LiMn}_2\text{O}_{3.9}$ sample, the magnitude of T_C and ΔT_C were determined to be 288 ± 2 and 14 ± 2 K.

On the basis of the area of the DSC peak, the latent heat of the phase transition at T_C (ΔH) was estimated to be 0.30 ± 0.05 kJ/mol for LiMn_2O_4 and 1.03 ± 0.08 kJ/mol for $\text{LiMn}_2\text{O}_{3.9}$. These values of ΔH were considerably smaller than those for the spinels, which have Mn^{3+} ions at the octahedral sites and a structural phase transition occurs from the cubic phase to the tetragonal phase, i.e. $\Delta H = \sim 21$ kJ/mol for Mn_3O_4 and ~ 14.7 kJ/mol for MgMn_2O_4 [7]. This is probably due to a small distortion of the tetragonal phase (c/a) of LiMn_2O_4 compared with those of Mn_3O_4 and MgMn_2O_4 ; that is, the value of c/a of LiMn_2O_4 was 1.011 [1] near T_C , while those were 1.13 and 1.16 for Mn_3O_4 and MgMn_2O_4 [7], respectively.

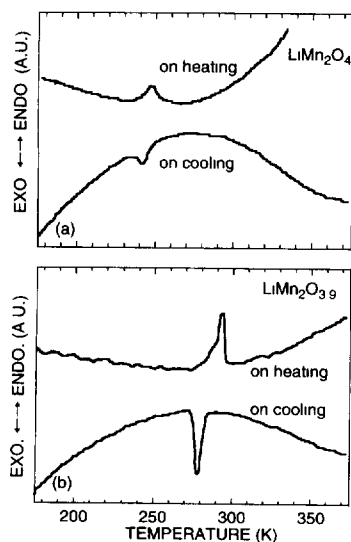


Fig. 1. DSC curves for: (a) LiMn_2O_4 , and (b) $\text{LiMn}_2\text{O}_{3.9}$. The data were obtained with the rate of 5 K/min.

3.2. $^7\text{Li-NMR}$

The $^7\text{Li-NMR}$ lines at temperatures between 160 and 400 K are shown in Fig. 2 for the LiMn_2O_4 sample; the frequency employed for the measurement was 117 MHz. For each of the resonance lines obtained at temperatures above 260 K, the line shape looks symmetrical, showing no indications of peak splitting; furthermore, the shape of the $^7\text{Li-NMR}$ line was fitted using a Gaussian curve at each temperature. At temperatures below 260 K, the line seems asymmetrical having a shoulder in a low-magnetic field side, i.e. on the high-shift side.

Fig. 3(a) and (b) shows the temperature dependence of the full width at half-maximum (FWHM) of the $^7\text{Li-NMR}$ line for the LiMn_2O_4 and $\text{LiMn}_2\text{O}_{3.9}$ samples. It was found that FWHM increases monotonically as temperature is lowered from 400 to 270 K and then increases rapidly with further lowering the temperature. Assuming that the change in the FWHM slope is responsible to the structural phase transition, the magnitude of T_C was estimated to be ~ 265 K for LiMn_2O_4 . For the $\text{LiMn}_2\text{O}_{3.9}$ sample, it is seen that the FWHM versus T curve was similar to that of LiMn_2O_4 , though a sudden change in the slope of FWHM was observed at ~ 285 K on cooling and ~ 305 K on heating; thus, the magnitudes of T_C and ΔT_C were estimated to be 295 ± 10 K and 20 ± 10 K. It should be noted that the magnitudes of T_C estimated from the present NMR results were 7–18 K higher than those determined by the DSC curves, though the same sample was used for both measurements. This discrepancy, especially for the LiMn_2O_4 sample, is probably due to a difference in temperature between the sample and the N_2 gas flow around the sample probe in the NMR apparatus.

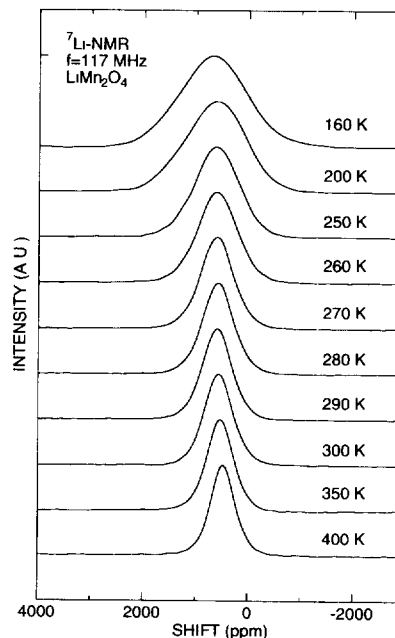


Fig. 2. Temperature dependence of $^7\text{Li-NMR}$ spectra of LiMn_2O_4 under magnetic field $H = \sim 7$ T.

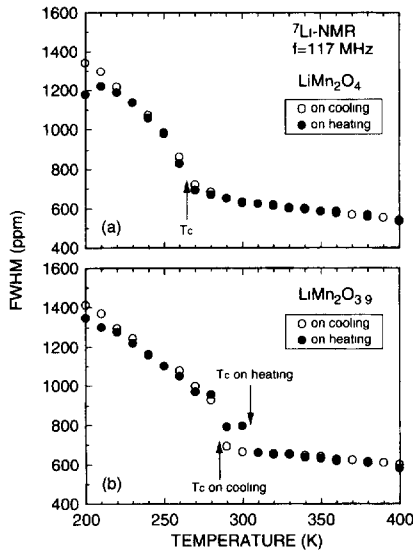


Fig. 3 Temperature dependence of the full width at half-maximum (FWHM) of the ⁷Li-NMR line for: (a) LiMn₂O₄, and (b) LiMn₂O_{3.9}. *T_C* represents the transition temperature estimated from the change in the FWHM slope of the ⁷Li-NMR line.

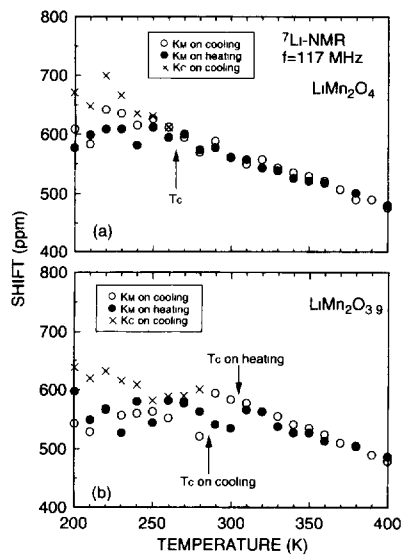


Fig. 4. Temperature dependence of the shift (*K*) of the ⁷Li-NMR line for: (a) LiMn₂O₄, and (b) LiMn₂O_{3.9}; both open and solid circles represent *K* at the maximum intensity (*K_M*) and crosses *K* at the center of the area of ⁷Li-NMR peak (*K_C*). *T_C* represents the transition temperature estimated from the change in the FWHM slope of the ⁷Li-NMR line.

Fig. 4(a) and (b) shows the shift at the maximum intensity (*K_M*) of the ⁷Li-NMR line for LiMn₂O₄ and LiMn₂O_{3.9} as a function of temperature. For both samples, as temperature is lowered from 400 K, *K_M* increases with temperature down to *T_C*, and then seems to level off at temperatures below *T_C*. In order to understand the asymmetrical shape of the ⁷Li-NMR line, we introduce the shift at the center of the area of ⁷Li-NMR peak (*K_C*); that is, *K_C* is expressed as

$$K_C = \frac{\int I(K)K dK}{\int I(K) dK} \quad (1)$$

where *I(K)* means the intensity of the ⁷Li-NMR signal at the shift *K*. As seen in Fig. 4(a) and (b), at temperatures below *T_C*, the magnitude of *K_C* estimated using the data obtained on cooling is larger than that of *K_M* for both samples. This indicates that the ⁷Li-NMR peak has a shoulder in a low-magnetic field side at temperatures below *T_C*; the reason of the appearance of the shoulder will be discussed later.

4. Discussion

Since the ⁷Li-NMR lines of both samples are symmetrical and can be fitted using a Gaussian curve at temperatures above *T_C*, all Li⁺ ions are considered to be located on one equivalent site. On the other hand, the asymmetrical shape of the ⁷Li-NMR line at temperatures below *T_C* suggests that there is at least one more possible site for Li⁺ ions in the sample at temperatures below *T_C*. This is in a good agreement with the result of the X-ray diffraction analysis [1], e.g. both the tetragonal and the cubic phases co-exist in LiMn₂O₄ at temperatures below *T_C*, whereas LiMn₂O₄ is a single-phase cubic *Fd3m* system above *T_C*. Indeed, the ⁷Li-NMR lines at 160 K for both samples can be decomposed into two Gaussian peaks, as seen in Fig. 5(a) and (b). Since the spin of the ⁷Li nucleus is 3/2, both the shift and FWHM are affected by the quadrupole effects in the tetragonal phase. Hence, the distribution of the local magnetic field at the lithium site in the tetragonal

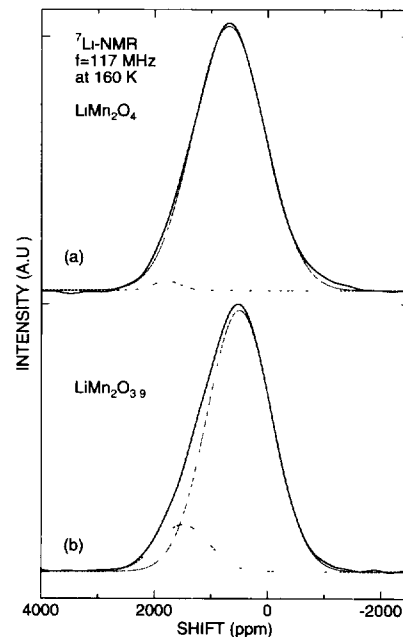


Fig. 5. ⁷Li-NMR spectrum at 160 K for: (a) LiMn₂O₄, and (b) LiMn₂O_{3.9}. It should be noted that both spectra can be decomposed into two Gaussian peaks.

phase would be different from that in the cubic phase. As a result, the FWHM versus T and shift versus T curves exhibit changes in the slope at T_C .

The magnitude of T_C of $\text{LiMn}_2\text{O}_{3.9}$ is found to be higher by ~ 30 K than that of LiMn_2O_4 . In order to balance the charge in the sample, $[\text{Mn}^{3+}] > [\text{Mn}^{4+}]$ in $\text{LiMn}_2\text{O}_{3.9}$, though $[\text{Mn}^{3+}] = [\text{Mn}^{4+}]$ in LiMn_2O_4 , where $[\text{Mn}^{3+}]$ and $[\text{Mn}^{4+}]$ mean the amount of Mn^{3+} and Mn^{4+} ions. Therefore, the magnitude of T_C is considered to rise with increasing $[\text{Mn}^{3+}]$ due to a co-operative Jahn–Teller distortion of Mn^{3+} ions at the octahedral site, as had been reported for $\text{Zn}_{1-x}\text{Co}^{2+}\text{Mn}_{2+x}\text{O}_4$ spinel [8].

5. Summary

According to differential scanning calorimetry (DSC) analyses and ^7Li nuclear magnetic resonance (^7Li -NMR) measurements, it was found that LiMn_2O_4 undergoes a structural phase transition at ~ 250 K and $\text{LiMn}_2\text{O}_{3.9}$ at ~ 290 K, respectively. Thus, the magnitude of the transition temperature (T_C) of $\text{LiMn}_2\text{O}_{4-\delta}$ depended on the oxygen deficiency (δ). In addition, at temperatures below T_C , the NMR line seemed to decompose into two Gaussian peaks, though it was a symmetrical singlet at temperatures above T_C . This suggested that there are two possible sites for the lithium ions in the sample at temperatures below T_C , and one equivalent site

above T_C . Therefore, this result can be explained by the co-existence of both the tetragonal and the cubic phases at temperatures below T_C , and a single-phase cubic above T_C .

Acknowledgements

We would like to thank Mr T. Atsumi of Akita University and Professor N. Kamegashira of Toyohashi University of Technology for their help in preparation of the samples.

References

- [1] A. Yamada and M. Tanaka, *Mater. Res. Bull.*, **30** (1995) 715–721.
- [2] J. Sugiyama, T. Tamura and H. Yamauchi, *J. Phys. Condens. Matter*, **7** (1995) 9755–9764.
- [3] J.M. Tarascon, W.R. McKinnon, F. Coowar, G. Amatucci and D. Guyomard, *J. Electrochem. Soc.*, **141** (1994) 1421–1431.
- [4] A. Yamada, K. Miura, K. Hinokuma and M. Tanaka, *J. Electrochem. Soc.*, **142** (1995) 2149–2156.
- [5] J. Sugiyama, T. Atsumi, T. Hioki, S. Noda and N. Kamegashira, *J. Alloys Comp.*, **235** (1996) 163–169.
- [6] J. Sugiyama, T. Atsumi, A. Koiwai, T. Sasaki, T. Hioki, S. Noda and N. Kamegashira, *J. Phys. Condens. Matter*, **9** (1997) 1729–1741.
- [7] R. Englman and B. Halperin, *Phys. Rev. B*, **2** (1996) 75–94, and Refs. therein.
- [8] D.G. Wickham and W.J. Croft, *J. Phys. Chem. Solids*, **7** (1958) 351–360.