Submillimetre and millimetre wave ESR study of manganese spinel compound $LiMn_2O_4$

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Abstract

Submillimetre and millimetre wave electron spin resonance (ESR) measurements of LiMn$_2$O$_4$ powder samples have been performed using a pulsed magnetic field up to 16 T in the temperature region from 4.2 to 265 K. Although competition between spin and charge orderings of Mn ions on the octahedral B sites of lithium manganese spinel is expected, geometrical frustration is also expected in LiMn$_2$O$_4$ because the octahedral B sites form the pyrochlore lattice. LiMn$_2$O$_4$ calcined at 600 °C was employed in this study because it turned out to be stoichiometric and have fewer impurities. The detailed temperature dependence of the submillimetre and millimetre wave ESR of this sample will be given and its spin dynamics will be discussed.

1. Introduction

Lithium manganese spinel LiMn$_2$O$_4$ has attracted much attention because it provides very rich physical properties in connection with charge and spin degrees of freedom, and the competition between them. LiMn$_2$O$_4$ has a spinel structure where Li ions occupy the tetrahedral A sites and Mn ions occupy the octahedral B sites. As the octahedral B sites form the pyrochlore lattice,

the existence of geometrical frustration is expected. From the charge neutrality requirement, the mixed valence state of Mn ions with the equivalent concentration of Mn^{3+} ($3d^4$, $S = 2$) and Mn^{4+} ($3d^3$, $S = 3/2$) ions is also expected. A first-order structural phase transition is known to occur at around room temperature [1, 2]. It is suggested that this structural phase transition arises from the partial charge ordering combined with the Jahn–Teller effect at Mn^{3+} ion sites in the crystal [3]. However, the experimental results reported among authors are rather controversial. The spin–glass behaviour at low temperature is reported by magnetic susceptibility measurements [4], and no long-range magnetic order was found down to 8 K by neutron measurements [5]. On the other hand, a ^{7}Li-NMR (nuclear magnetic resonance) measurement suggests an antiferromagnetic transition at $T_N = 40$ K [6], while antiferromagnetic ordering below $T_N = 65$ K is reported by neutron measurements [7]. Moreover, the coexistence of the magnetic Bragg peaks and the magnetic diffuse peaks between 1.5 and 65 K is suggested by Greedan *et al* [8]. These discrepancies probably come from the differences in the chemical composition of the samples, because it is well known that the chemical composition of lithium manganese spinel $LiMn_2O_4$ strongly depends on the synthesis conditions [9] and, as a result of thermal decomposition, coexistence of the impurity phase is reported [10]. Therefore, in order to understand the interesting magnetic properties of the system, systematic characterization of $LiMn_2O_4$ powder samples is required. Such characterization is also interesting from the application point of view, because $LiMn_2O_4$ is promising as a cathode material in lithium rechargeable batteries [11].

This systematic characterization by x-ray diffraction (XRD), thermal gravimetry analysis-mass spectrometry (TGA-MS), differential scanning calorimetry (DSC), Raman spectroscopy, magnetization and highfrequency ESR measurements was performed in our previous papers [12–15]. $LiMn_2O_4$ is usually obtained by high-temperature (above $700\,°C$) solid-state reaction. However, $LiMn_2O_4$ samples QHX ($X = 600$–900) used in our study are prepared by the sol–gel method [15], which yields fine crystalline materials with a uniform distribution of cations, and by additional calcinations of samples at high temperature $X\,°C$ in air for 24 h and subsequent quenching. The additional calcinations induce the growth of crystal. XRD result shows that $X = 600$ and 700 samples show the cubic $Fd3m$ spinel phase with no impurities, but others show the possible existence of impurities. Our high-field ESR measurements at low temperature showed clear differences between the $LiMn_2O_4$ samples QHX [12, 13]. As a result, the existence of the impurity phase Li_2MnO_3, which undergoes antiferromagnetic ordering below 36.5 K, is suggested from the observation of the antiferromagnetic resonance (AFMR) of Li_2MnO_3 below 40 K [12, 13]. This impurity phase may be the origin of the antiferromagnetic transition observed at $T_N = 40$ K in previous studies. On the other hand, although the expected exchange interaction from the Weiss temperature $\theta = -254$ K for QH600 is strong, the magnetic susceptibility does not show magnetic order down to 10 K [12]. This result indicates the effect of geometrical frustration, which was also suggested by Oohara *et al* [5]. In this paper, we focus on the $LiMn_2O_4$ sample QH600, which seems to be stoichiometric and with fewer impurities. In order to get information about the spin frustration effect, detailed temperature-dependence measurements of submillimetre and millimetre wave ESR measurements for QH600 have been performed in the temperature regime from 4.2 to 265 K. The spin dynamics of $LiMn_2O_4$ will be discussed in connection with the temperature dependences of the g-value and linewidth.

2. Experimental details

Submillimetre and millimetre wave ESR measurements of powder samples of $LiMn_2O_4$ were performed under the pulsed magnetic field up to 16 T using the ESR system at Kobe
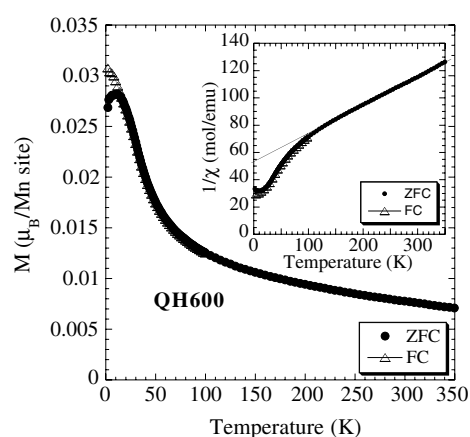
Figure 1. Temperature dependence of the magnetization measured in QH600. The field cooled (FC) measurement at 1 T is performed after zero-field cooling (ZFC). The inset shows the inverse susceptibility.

University and in the temperature region from 4.2 to 265 K. The detailed experimental setups of our submillimetre and millimetre wave ESR system can be found in [16, 17]. LiMn$_2$O$_4$ powder sample QH600 studied in this paper was obtained using the sol–gel method described in [10, 14]. Sample SH300 was obtained by calcinations at 300 °C after chemical treatment, and sample QH600 was obtained by calcinations of SH300 at 600 °C in air for 24 h and subsequent quenching. From the x-ray diffraction (XRD) measurements, the XRD patterns characteristic of the spinel structure was observed for QH600, and it turned out to be in a single phase [14]. The magnetization measurement was performed using the physical property measurement system (PPMS), made by Quantum Design, at Kyushu University.

3. Results and discussion

Figure 1 shows the field cooled (FC) and zero field cooled (ZFC) magnetization results of QH600. By comparing the FC and ZFC results, the spin–glass transition is visible at around 10 K but no anomalies are observed at around room temperature, 65 K or 40 K.

The temperature dependences of the ESR spectra observed in QH600 at 160 and 315 GHz are shown in figures 2 and 3, respectively. The observed ESR spectra show a broad signal at low temperature, which is difficult to observe via conventional X-band ESR. Therefore, our submillimetre and millimetre wave ESR measurements are essential. At 265 K, an isotropic broad ESR signal is observed near the resonance field with $g = 2.0$, which is indicated by the sharp field marker DPPH, for both frequencies. The resonance field is almost constant in the high-temperature region, while a gradual shift towards lower magnetic fields and a broadening of the ESR signal with decreasing temperature are observed below around 90 K at both frequencies, as shown in figures 2 and 3. The temperature dependence of the linewidth is shown in figure 4. A change in gradient was observed at around 80 and 60 K for 160 and 315 GHz, respectively. However, the magnitude of the linewidth is almost the same for both frequencies in the low-temperature region. Estimating the linewidth becomes difficult for 160 GHz below 20 K because the ratio of the linewidth to the resonance field is larger for 160 GHz than that for 315 GHz. The kink observed at around 20 K for 315 GHz may be related to the spin–glass temperature at 10 K, which is observed via the temperature dependence
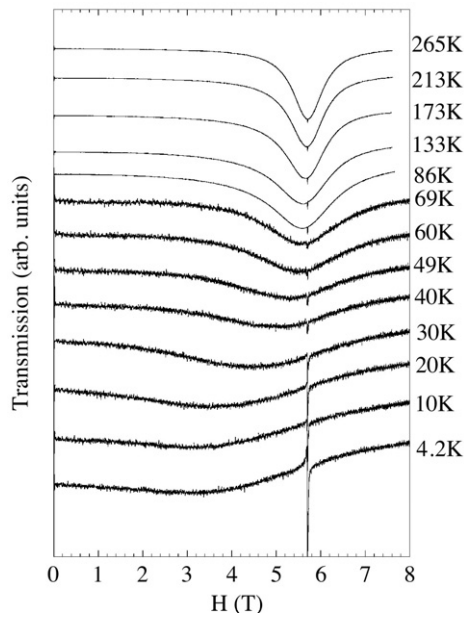
Figure 2. Temperature dependence of the ESR spectra observed at 160 GHz in QH600.
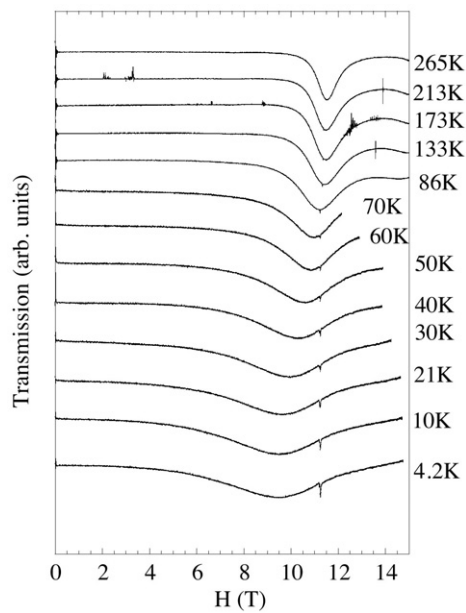

Figure 3. Temperature dependence of the ESR spectra observed at 315 GHz in QH600.

magnetization measurement in figure 1. As the observed absorption line is isotropic and an isotropic *g*-value is expected, as discussed later, the observed linewidth will reflect the intrinsic linewidth of the system. Therefore, as no divergence in the linewidth is observed down to 4.2 K, we can say that there is no long-range magnetic order down to 4.2 K for QH600.

Figure 5 shows the temperature dependence of the *g*-value. The frequency-dependent *g*-shift below around 70 K, which corresponds to the temperature where the linewidth changes in gradient, is observed, as shown in figure 4. The obtained *g*-values in the high-temperature
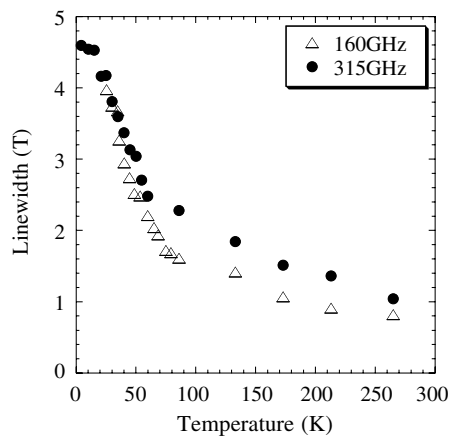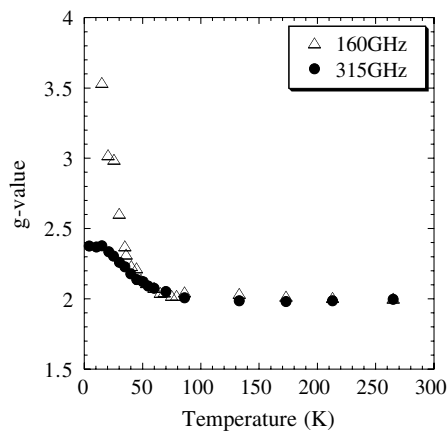
Figure 4. Temperature dependence of linewidth.

Figure 5. Temperature dependence of *g*-value.

region are $g = 2.03 \pm 0.02$ for 160 GHz and $g = 1.99 \pm 0.01$ for 315 GHz, which are obtained by averaging in the temperature region from 86 to 265 K because there is almost no temperature dependence of the *g*-values in this temperature region. In this high-temperature region, we can discuss the electron paramagnetic resonance (EPR) of Mn ions. There are fair amounts of EPR data on Mn^{4+} ions, and *g* is found to be about 1.98 with a very small anisotropy with the initial splitting parameter *D* of order 0.1 cm^{-1} [18]. On the other hand, there is no EPR data on Mn^{3+} ion, and the only known data for the $3d^4$ ion is Cr^{2+} in $CrSO_4 5H_2O$, which has a value of *g* very close to 2 and *D* of order 2 cm^{-1} [18]. As we can distinguish the initial splitting of order 2 cm^{-1} (about 2 T) in figures 2 and 3 if we are observing Mn^{3+} ions, it is more likely that EPR from Mn^{4+} ions is observed in our measurements.

As the Jahn–Teller structural transition is not observed by differential scanning calorimetric (DSC) [14] and magnetization measurements (figure 1) in the case of QH600, the cubic spinel structure seems to be preserved at low temperature. This means that charge ordering will not take place. Thus Mn^{3+} and Mn^{4+} ions are distributed randomly over the octahedral B sites in the spinel structure even at low temperature. Then it can be considered that the magnetic interaction between Mn ions will have a degree of randomness. Such randomness, which is combined with the geometrical frustration inherent in the spinel structure, will cause the spin–glass-like magnetic ground state. The behaviour of ESR spectra in QH600 at 4.2 K [12], which is related to the *g*-shift below 70 K, resembles that observed in copper

containing Mn impurity, which is a typical system exhibiting spin–glass behaviour [19]. Moreover, the gradual shift towards lower magnetic fields and a broadening of the ESR signal with decreasing temperature were also observed in $SrCr_xGa_{12-x}O_{19}$, which is the strongly frustrated *Kagome* lattice antiferromagnet and shows spin–glass behaviour at low temperature [20]. Whether the geometrical frustration or the randomness plays a dominant role in the dynamical properties of QH600 remains as a future problem.

In summary, submillimetre and millimetre wave ESR measurements on powder samples of $LiMn_2O_4$ synthesized using the sol–gel method have been performed using pulsed magnetic fields up to 16 T in the temperature region from 4.2 to 265 K. From the results of the temperature dependence of the ESR spectra, the sample obtained by calcination at 600 °C (QH600) appears to show no long-range magnetic ordering down to 4.2 K. The comparison of the observed EPR with available EPR data for Mn^{3+} and Mn^{4+} ions suggests that Mn^{4+} seems to be responsible for the behaviour of high-field ESR spectra. The observed *g*-shift and the line broadening at low temperatures are discussed in connection with the charge randomness and the geometrical frustration.

Acknowledgments

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