

 <b>MLF Experimental Report</b>	提出日 Date of Report June 16, 2011
課題番号 Project No. 2010B0069  実験課題名 Title of experiment Short-range magnetic order/correlation of LiFeO <sub>2</sub> and NaFeO <sub>2</sub> 実験責任者名 Name of principal investigator Jun Sugiyama 所属 Affiliation Toyota Central Research and Development Laboratories, Inc.	装置責任者 Name of responsible person Yasuhiro Miyake 装置名 Name of Instrument/(BL No.) D1 実施日 Date of Experiment February 2, 2011 – February 4, 2011

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)  
 Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Powder samples of lithium iron oxide, LiFeO<sub>2</sub>, and sodium iron oxide, NaFeO<sub>2</sub>, were synthesized at ISSP of Univ. of Tokyo by a solid state reaction technique. The powder was, then, pressed into a disc with 27 mm diameter and 1 mm thickness, and finally the disc was packed in an Au-sealed titanium cell. Since the window of the cell is made of Kapton, the highest temperature measured is limited at 500 K.

2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。)

Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

In order to study Li/Na diffusive behavior in T-LiFeO<sub>2</sub> and  $\alpha$ -NaFeO<sub>2</sub> by muon-spin spectroscopy, we have measured their wTF-, ZF- and LF-spectra in the temperature range between 100 and 500 K. Here, in the T-LiFeO<sub>2</sub> lattice, both Li and Fe ions are coordinated by four O<sup>2-</sup> ions so as to form LiO<sub>4</sub> and FeO<sub>4</sub> tetrahedra. The obtained spectrum was fitted using a combination of an exponentially relaxation signal and an offset background signal;  $A_0P(t)=A_{\text{exp}}\exp(-\lambda t)+A_{\text{BG}}$ . Here, we used a global fitting technique to fit all the spectra using common parameters, i.e., two asymmetries,  $A_{\text{exp}}$  and  $A_{\text{BG}}$ . Such fit provided  $A_{\text{exp}}=0.1454\pm 0.0007$  and  $A_{\text{BG}}=0.0345\pm 0.0001$ .

For T-LiFeO<sub>2</sub>, the ZF-spectrum was found to consist of a tail of a fast relaxing signal and a time independent BG signal even at 300 K [see Fig. 1(a)]. This means that the T-LiFeO<sub>2</sub> sample enters into a magnetic-ordered phase above ambient temperature. Since there are no oscillations in an early time domain from 0.1  $\mu$ s, we need to use a dc muon beam for clarifying the magnetic nature of T-LiFeO<sub>2</sub>. Also, due to the absence of a Kubo-Toyabe behavior, it is unfortunately impossible to estimate the hopping behavior caused by Li diffusion by  $\mu$ SR for T-LiFeO<sub>2</sub>.

2. 実験方法及び結果(つづき) Experimental method and results (continued)

Then, we moved to  $\alpha$ -NaFeO<sub>2</sub>. Figure 1(b) shows the temperature variation of the ZF-spectrum for  $\alpha$ -NaFeO<sub>2</sub> at 100 K, 300 K, and 500 K. All the spectra show an exponentially relaxing behavior in the whole temperature range measured, suggesting the presence of a fluctuating magnetic field due to Fe<sup>3+</sup> ( $S=5/2$ ) ions. In fact, the relaxation rate ( $\lambda$ ) shows a Curie-Weiss behavior [Fig. 1(c)]. Furthermore, even at 500 K, a decoupling behavior was not observed by longitudinal field (LF) measurements with  $H_{LF}=5$  and 10 Oe. In order to observe the Na diffusive behavior, it is, thus, highly likely to measure the  $\mu$ SR spectrum above 500 K. For such purpose, we are preparing a Ti-foil window for the powder cell.

Finally, we have measured ZF- and LF-spectra of an olivine-type compound, LiCoPO<sub>4</sub>, for which we submitted a proposal (2010A0041). Figure 2 shows the temperature dependences of the field distribution width ( $\Delta$ ) and field fluctuation rate ( $\nu$ ) for LiCoPO<sub>4</sub>, together with those for LiFePO<sub>4</sub> and LiNiPO<sub>4</sub>. For LiCoPO<sub>4</sub>, as  $T$  increases from 100 K,  $\Delta$  gradually decreases up to 350 K, and then levels off to a constant value above 350 K. On the other hand,  $\nu$  starts to increase above 175 K ( $=T_{\text{start}}$ ) and shows a clear maximum around 325 K ( $=T_{\text{max}}$ ), and finally levels off to a small value ( $0.1 \times 10^{-6} \text{ s}^{-1}$ ) above 440 K. This behavior is very similar to those for LiFePO<sub>4</sub> and LiNiPO<sub>4</sub>, although both  $T_{\text{start}}$  and  $T_{\text{max}}$  depend on the transition metal element. Since the static behavior is observed even at 500 K, the implanted muons are considered to be stable in the lattice until 500 K. Therefore, the origin of the increase in  $\nu$  is assigned as Li diffusion. However, due to an increase in  $\nu$ ,  $\nu/\Delta$  becomes out of range of a dynamic Kubo-Toyabe relation, leading to the difficulty to determine  $\nu$ . This is the reason for the clear maximum in the  $\nu(T)$  curve. At high- $T$ ,  $\mu$ SR, therefore, sees a static nuclear field of a MPO<sub>4</sub> skeleton.

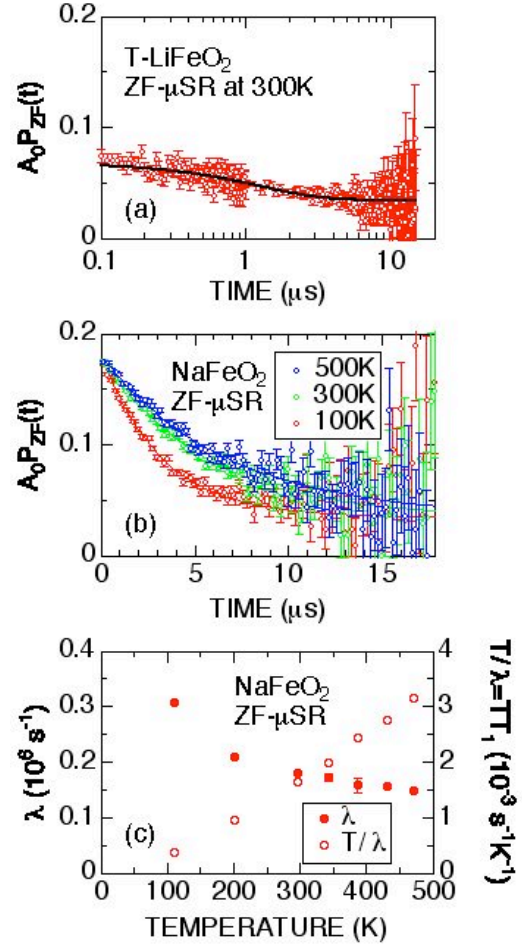


Fig.1 ZF-spectrum for (a) T-LiFeO<sub>2</sub> at 300 K and (b) for  $\alpha$ -NaFeO<sub>2</sub> at 100, 300, and 500 K and (c) the temperature dependences of  $\lambda$  and  $T/\lambda$  for  $\alpha$ -NaFeO<sub>2</sub>.

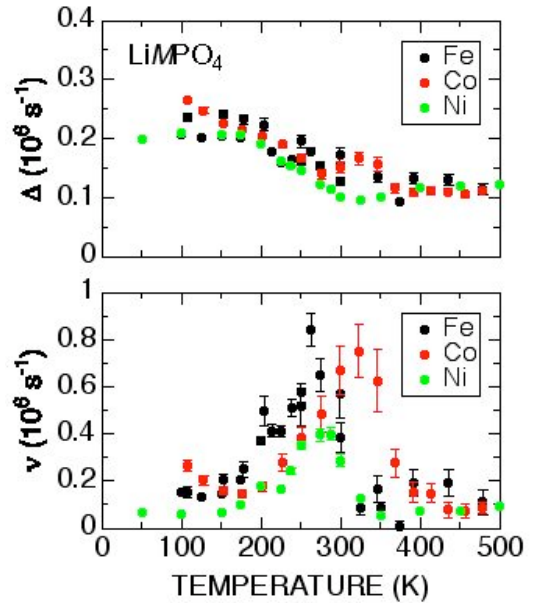


Fig.2 The temperature dependences of  $\Delta$  and  $\nu$  for LiMPO<sub>4</sub> with  $M=\text{Fe, Co, and Ni}$ .