MLF Experimental Report	提出日 Date of Report December 20, 2010
課題番号 Project No. 2010A0041 実験課題名 Title of experiment Lithium diffusion in $LiFePO_4$ and related materials 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 December 16, 2010 – December 18, 2010

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.

A powder sample of lithium nickel phosphate, $LiNiPO_4$, was synthesized at Tokyo Institute of Technology 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.

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.

The phospho-olivines have numerous advantages over the layered rock salt oxides (e.g. $LiCoO_2$ and $LiNiO_2$) that are currently used in commercial batteries. Besides its high capacity (ca. 170 mAh/g), Li$M$$PO_4$ cathode material shows high stability during lithium extraction/insertion and does not deteriorate when used at moderately high temperatures [1]. According to μSR measurements at low temperatures in TRIUMF to elucidate the magnetic nature of Li$M$$PO_4$ with M=Mn, Fe, Co, Ni, all the four olivines were found to enter into a static AF ordered state below around 50 K. Furthermore, even in the paramagnetic state, the ZF-spectrum for the M=Mn, Fe, and Co olivens exhibits a fast relaxing behavior due to fluctuating magnetic moments of the M ions, although the ZF-spectrum for $LiNiPO_4$ shows a Kubo-Toyabe behavior due to nuclear magnetic fields.

We have, therefore, measured wTF-, ZF- and LF-spectra for $LiNiPO_4$ in the temperature range between 50 and 500 K in order to know a diffusive behavior at high temperatures. The obtained spectrum was fitted using a combination of a dynamic Gaussian Kubo-Toyabe signal and an offset background signal; $A_0P(t)=A_{KT}G_{KT}(\Delta, \nu, t, H_{LF}) + A_{BG}$. Here, we used a global fitting technique to fit all the spectra using common parameters, i.e., two asymmetries, A_{KT} and A_{BG}. Such fit provided A_{KT} =0.1629±0.0007 and A_{BG}= 0.0331±0.0007.

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

Figure 1 shows the T variation of ZF- and LF-spectra for $LiNiPO_4$ at 100 K, 275 K, and 450 K. The applied LF was 5 Oe. At 100 K, the ZF spectrum shows a minimum around 9 μs, indicating the presence of a small random nuclear field (H_{int}^{n}). Moreover, the applied LF clearly decouples the effect of H_{int}^{n}. Since the whole signal from the sample is well fitted by a dynamic Kubo-Toyabe function, the origin of the muon-spin depolarization is assigned as a nuclear magnetic field caused by Li and P.

The ZF-spectrum at 275 K, on the other hand, relaxes monotonically until at least 18 μs. Additionally, the effect of LF is very small. This suggests the increase in fluctuation of H_{int}^{n}. However, at 450 K, the ZF-spectrum exhibits a minimum again around 17 μs and the LF-spectrum shows a decoupling behavior, meaning a static nature of H_{int}^{n}.

Figure 2 shows the T dependences of Δ and ν for $LiNiPO_4$. As T increases from 50 K, Δ is almost T-independent up to 200 K, and decreases linearly until 300 K, and then increases slowly with T. The ν(T) curve shows a sharp maximum around 290 K. ν is most likely to increase with T above 350 K. This behavior is unlikely explained by Li diffusion, which would start to occur above 200 K. In order to clarify the change in muon sites with T, it is preferable to investigate a small structural variation below 300 K, although $LiNiPO_4$ is reported to keep its orthorhombic symmetry down to the lowest T measured [2].

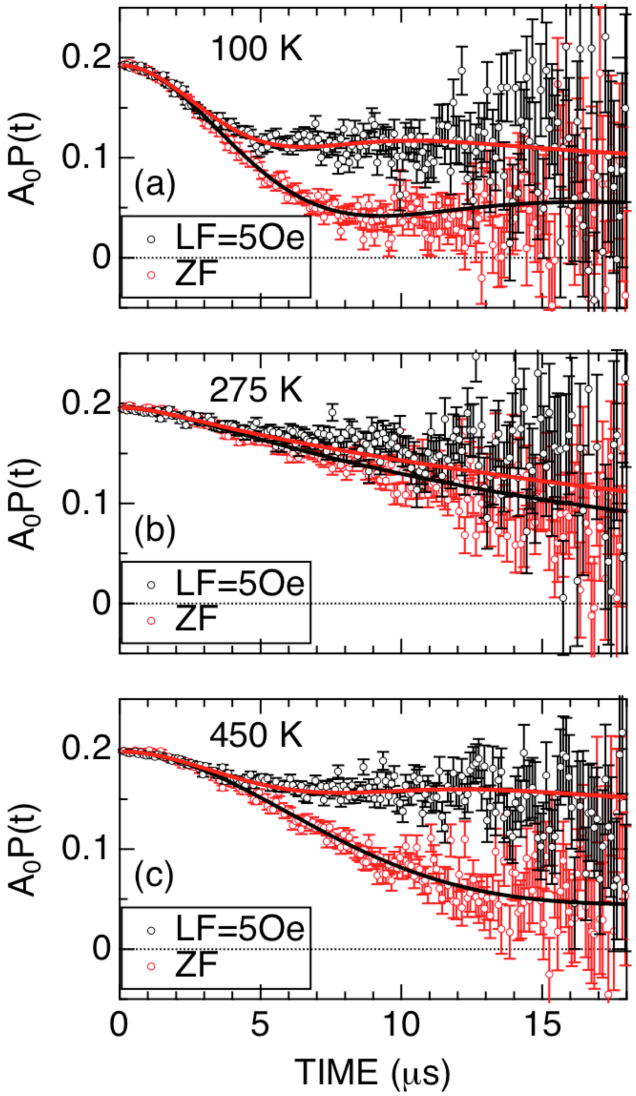

Fig. 1 T variation of the ZF- and LF-spectra for $LiNiPO_4$ at (a) 100 K, (b) 275 K, and (c) 450 K.

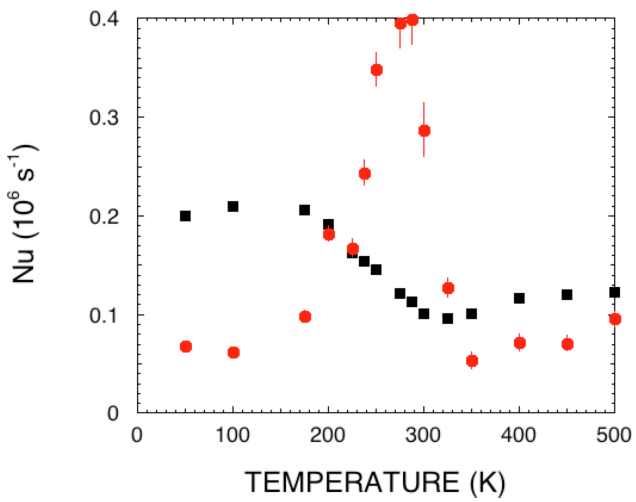

Fig. 2 T dependences of Δ (black square) and ν (red circle) for $LiNiPO_4$.

[1] C. M. Julien et al., Ionics **12**, 21 (2006), and references cited therein.

[2] T. B. S. Jensen et al., Phys. Rev. B **79**, 092412 (2009).