	提出日 Date of Report
MLF Experimental Report J-PARC	June 13, 2012

課題番号 Project No.	装置責任者 Name of responsible person
2011B0040	Yasuhiro Miyake
実験課題名 Title of experiment	装置名 Name of Instrument/(BL No.)
Diffusive behavior in Li-deficient olivine-type compounds	D1
実験責任者名 Name of principal investigator	実施日 Date of Experiment
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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.

Lithium iron phosphate, Li_xFePO_4 with x=0.9.

A 2g powder sample was pressed in a disc with 27 mm diameter and 1 mm thickness, and then the disc was packed in a gold O-ring 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.

Following upon the μ^+SR studies of the stoichiometric phospho-olivines, $LiFePO_4$ and related compounds [1,2], we have initiated a study to investigate the diffusive nature of the charged state compounds, Li_xFePO_4 with $x \leq 1$, in order to know a diffusion coefficient of Li^+ (D_{Li}) caused by a Li^+ jump between the regular occupied site and regular vacant site. Although the approved 6-days-beamtime was arranged in the middle of March in 2012, we made an experiment eventually only for 2.5 days, due to a weak power, i.e. 100 kW operation for the first two days, difficulty to control sample temperature caused by contamination of liquid He, and the failure of Klystron power source in LINAC. As a result, we measured only one sample.

Based on electrochemical measurements [3,4], the Li_xFePO_4 compounds with x<0.9 are found to consist of two phases; namely, Li_xFePO_4 and $FePO_4$ phase. On the contrary, it should be noted that the past calculations of D_{Li} for $Li_{7/8}FePO_4$ are performed under assumption that $Li_{7/8}FePO_4$ is a single phase [5]. Hence, at first, we measured μ^+SR spectra for $Li_{0.9}FePO_4$, which was assigned as a single phase by XRD. However, the field fluctuation rate (ν) was strongly suppressed compared with that for $LiFePO_4$ (see Fig. 1), although the field distribution width (Δ) versus T curve clearly exhibits a motional narrowing

behavior in the T range between 150 and 250 K, as in the case for LiFePO$_4$.

If we assume that the Li$_{0.9}$FePO$_4$ sample also microscopically separates into two phases, such as, LiFePO$_4$ and FePO$_4$, the Li$^+$ ions are likely to diffuse mainly across the boundary between two phases [4]. As a result, a diffusive behavior, particularly the increase in ν, would be suppressed in the Li$_{0.9}$FePO$_4$ sample. Note that electrostatic potential calculations support that not positive muons but Li$^+$ ions are diffusing even in the Li$_x$FePO$_4$ lattice with $x \rightarrow 0$ (see Fig. 2).

In order to further elucidate the diffusive nature of Li$_x$FePO$_4$, we need a systematic μ^+SR experiment on Li$_x$FePO$_4$ with x=0.75, 0.5, 0.25, and 0. Such experiment provides crucial information on Li-diffusion across the phase boundary, since the volume fraction of the FePO$_4$ phase systematically increases with decreasing x.

REFERENCES

[1] J. Sugiyama *et al.*, PRB **84**, 054430 (2011).
[2] J. Sugiyama *et al.*, PRB **85**, 054111 (2012).
[3] A. K. Padhi *et al.*, J. Electrochem. Soc. **144**, 1188 (1997).
[4] W.-J. Zhang *et al.*, J. Power Sources **196**, 2962 (2011).
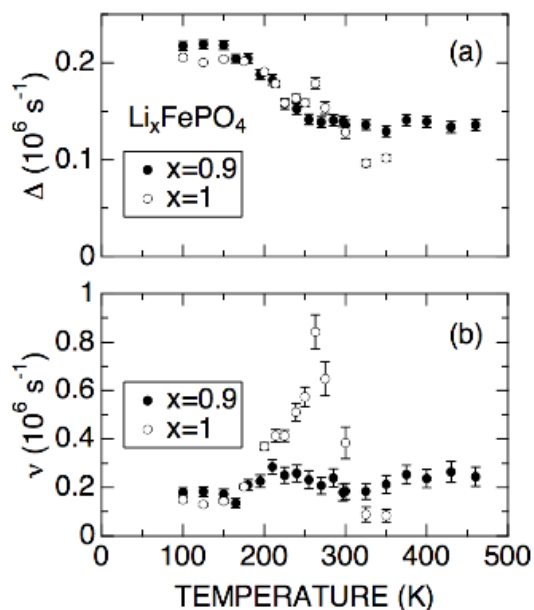[5] D. Morgan *et al.*, Electrochem. Solid-State Lett. **7**, A30 (2004).

Fig. 1: The T dependences of (a) the field distribution width (Δ) and (b) field fluctuation rate (ν) for LiFePO$_4$ and Li$_{0.9}$FePO$_4$.
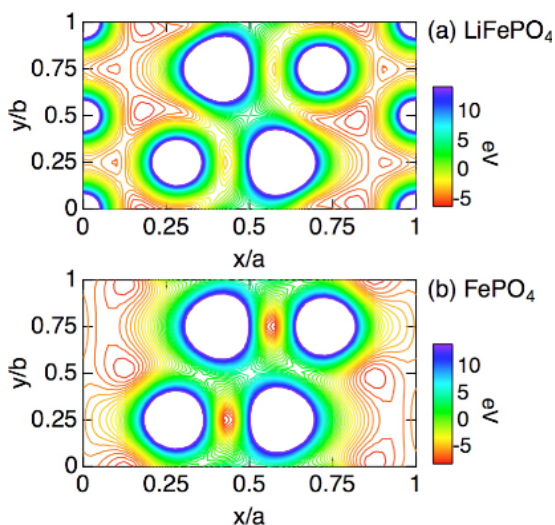

Fig. 2: Electrostatic potential (E) distribution in the (x, y, 0) plane for (a) LiFePO$_4$ and (b) FePO$_4$. Here, E for the μ^+, which locates at the vicinity of O^{2-} ions but 1Å away, ranges between -9 and -11 eV for LiFePO$_4$ and between -11 and -12 eV for FePO$_4$. This indicates that μ^+ locates not at the vacant Li site but at the vicinity of the O^{2-} ions even in FePO$_4$.