MLF Experimental Report	提出日 Date of Report May 24, 2014.
課題番号 Project No. 2013B0047 実験課題名 Title of experiment Diffusive behavior in Na-based olivine-type compounds 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 April 02, 2014 – April 03, 2014

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.

Sodium iron phosphate $Na_{0.5}FePO_4$ and $Na_{0.9}FePO_4$.

A powder sample 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.

Currently, Li-ion batteries have become a main stream of the power supply for portable electronics and electric vehicles. However, due to the uneven distribution of lithium resources in the world and future demand for Li-ion batteries in hybrid and all-electric motor vehicles, Na-ion batteries would be one of the significant alternatives for the Li-ion batteries [1], since Na is more abundant than Li. We have, therefore, attempted to measure D_{Na} for $Na_{0.7}CoO_2$ with μ^+SR and found that Na-diffusion is also detected by μ^+SR [2]. Consequently, it was found that μ^+SR detects Na-diffusion in Na_xCoO_2, as well as Li-diffusion in Li_xCoO_2 [3].

Then, we have initiated a μ^+SR research on the Na-based olivine-type compound, i.e. Na_xFePO_4, because this compound has been investigated as a novel cathode material for future Na^+-ion batteries [4,5]. Moreover, Fe is more preferable for industrial applications than Co. Note that there is no study on D_{Na} for $NaFePO_4$ by NMR due to large Fe moments. Following upon the μ^+SR experiment on Na_xFePO_4 with x=0.7 in 2012 (#2012B0063) [6], we have attempted to measure two more samples with different Na contents, that is, $Na_{0.5}FePO_4$ and $Na_{0.9}FePO_4$ in order to study the variation of Na-diffusion with x. According to the magnetization measurements, the $Na_{0.5}FePO_4$ sample is very similar to $Na_{0.7}FePO_4$ [7], while the $Na_{0.9}FePO_4$ sample is likely a

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

a mixture of $Na_{0.7}FePO_4$ and $NaFePO_4$ [8] (Fig. 1). In fact, Rietvelt analyses of powder XRD patterns revealed that the $Na_{0.5}FePO_4$ sample consists of a $FePO_4$ phase with 20vol% and a $Na_{0.7}FePO_4$ phase with 80vol%, while the $Na_{0.9}FePO_4$ sample consists of a $Na_{0.7}FePO_4$ phase with 33vol% and a $NaFePO_4$ phase with 67vol%. Here, the previous $Na_{0.7}FePO_4$ sample is identified as an almost single phase of $Na_{0.7}FePO_4$ by XRD and ICP analyses [7].

For the present two samples, the ZF-spectra obtained above T_N were well fitted by a combination of an exponentially relaxing dynamic Kubo-Toyabe signal [9] and a time-independent offset signal from the Ti sample cell, as in the case for $Na_{0.7}FePO_4$ [6]. Figure 2 shows the T dependences of the field distribution width (Δ) and field fluctuation rate (ν). Here, we assumed that the T dependence of λ is similar to that of χ.

For the $Na_{0.5}FePO_4$ sample, the $\Delta(T)$ and $\nu(T)$ curves are very similar to those for $Na_{0.7}FePO_4$. The diffusive behavior is observed above 200 K. For the $Na_{0.9}FePO_4$ sample, on the other hand, the diffusive behavior is observed at T>250 K, probably due to the absence of Na vacancies in the major phase, i.e. $NaFePO_4$.

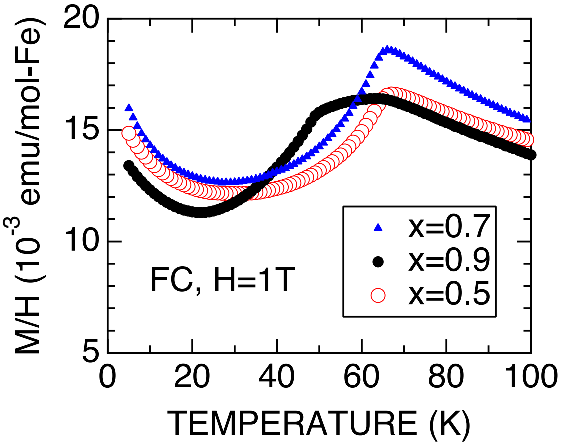

Fig. 1 T dependence of susceptibility (M/H) for the $Na_{0.7}FePO_4$, $Na_{0.5}FePO_4$ and $Na_{0.9}FePO_4$ samples. For $Na_{0.7}FePO_4$, T_N=61 K [7], and, for $NaFePO_4$, T_N=50 K [8].

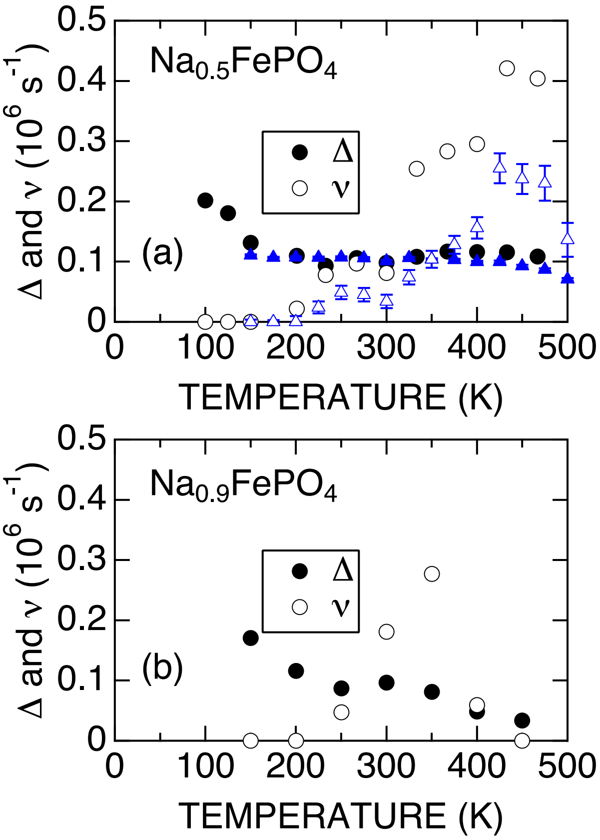

Fig. 2 T dependences of the field distribution width (Δ) and field fluctuation rate (ν) for (a) the $Na_{0.5}FePO_4$ sample and (b) the $Na_{0.9}FePO_4$ sample. In (a), the data for $Na_{0.7}FePO_4$ (blue triangles) [6] are also plotted for comparison.

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