MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2012PM0008 実験課題名 Title of experiment Studies on strongly correlated electron system by PDF analysis using iMATERIA data 実験責任者名 Name of principal investigator Katsuaki Kodama 所属 Affiliation Japan Atomic Energy Agency	装置責任者 Name of responsible person Toru Ishikagi 装置名 Name of Instrument/(BL No.) iMATERIA /(BL20) 実施日 Date of Experiment 2013/3/8/-9

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 sample of ^{7}Li-enriched $^{7}LiMn_2O_4$

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.

$LiMn_2O_4$ exhibits a structural phase transition from cubic structure with space group Fd3-m to orthorhombic structure with Fddd at around 260K with decreasing temperature. In the orthorhombic phase, the system is in the charge ordering state because inequivalent Mn sites with the valences of +3 and +4 arrange periodically [1]. However, even in the cubic phase, the electrical resistivity is insulating although all Mn atoms are equivalent and their valence is +3.5 [2]. These results suggest that the valence electron of Mn site is localized like a glass and the arrangement of Mn^{3+} and Mn^{4+} has short range periodicity in the cubic phase. Actually, atomic pair distribution function (PDF) of $^{7}LiMn_2O_4$ in cubic phase (above 300K) obtained at NOVA, can be reproduced by orthorhombic structure with Mn^{3+} and Mn^{4+}, supporting above suggestion [3].

In this beam time, we have performed powder neutron diffraction measurements on $^{7}LiMn_2O_4$ in order to check the following points. (1) In the cubic phase at 300K, the PDF obtained by using the powder diffraction data at iMATERIA can reproduce the PDF obtained at NOVA which includes orthorhombic local lattice distortion. (2) In the orthorhombic phase at 200K, the local structure which is similar to the cubic phase is also observed in PDF.

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

In Fig. 1, neutron powder diffraction patterns at 200K and 300K are shown by red crosses. The data were collected by 90 degree bank. The blue lines are results of Rietveld fittings. The space groups of Fd3-m and Fddd are used in the fittings on the data at 300K and 200K, respectively. In the fitting on the pattern at 200K, the structural parameters are fixed at the values obtained by PDF analysis as mentioned below. The R-factors are about 4.9% for both fittings, indicating that the diffraction patterns at 300K and 200K can be well fitted by the cubic Fd3-m and orthorhombic Fddd structures, respectively. In Fig. 2, the PDFs at 300K obtained by using the diffraction patterns at 90 degree banks of NOVA and iMATERIA are shown by blue and red lines, respectively. Although the vertical scales of both lines disagree half, the PDF obtained at iMATERIA almost reproduces the shape of the PDF at NOVA, indicating that PDF at iMATERIA includes the same orthorhombic local lattice distortion. In Fig. 3, the PDF obtained from the diffraction pattern at 200K where the compound has orthorhombic structure is shown by a green line. The PDF at 300K is also shown in Fig. 3 by the red line. The PDF at 200K almost correspond with the PDF at 300K, indicating that the local structure at 200K almost correspond with the local structure at 300K. Actually, the atomic distances between Mn and O determined by analyzing the PDF at 200K are almost consistent with the values of Mn-O distances obtained from the PDF at 300K. These results confirm the above two points.

[1] Rodriguez-Caravajal et al. Rhys. Rev. Lett. 81 (1998) 4660.
[2] for example, Sugiyama et al. J. Phys. : Condens. Matter 9 (1997) 1729.
[3] Kodama et al. preprint