MLF Experimental Report	提出日 Date of Report June 26, 2010
課題番号 Project No. 2009B0005 実験課題名 Title of experiment Lithium diffusion in LiCrO2 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 June 9, 2010 – June 15, 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.

Lithium chromium dioxide, $LiCrO_2$, and lithium nickel dioxide, $LiNiO_2$. The powder sample was pressed in a disc with 27 mm diameter and 2 mm thickness, and then the disc was packed in an Au-sealed 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.

Based on the neutron scattering [1], susceptibility (χ) [2], NMR [2], and μSR [3] measurements, $LiCrO_2$ is known to exhibit a magnetic transition into a long-range AF ordered state at T_N=62 K. However, the same bulk χ data does not follow Curie-Weiss law below approximately 300 K. This could indicate that a possible short-range order sets in well above T_N and long-range order is finally achieved for $T \leq T_N$. Some support for this statement could be found in heat capacity measurements [2] that shows a contribution to magnetic entropy all the way up to $T=4T_N$. However, the ZF-spectrum exhibits a typical Kubo-Toyabe behavior just above T_N due to mainly the nuclear magnetic moments of Li [3]. This clearly excludes the existence of magnetic short-range order above T_N. It was also found that the field fluctuation rate (ν) -vs-T curve exhibits a step-like increase at around 115 K, although the field distribution width (Δ) is roughly T-independent. This suggests a change in Li position/motion around 115 K. In order to study the Li positon/motion and a diffusion coefficient of Li^+ ions (D_{Li}) above 115 K, we measured ZF- and LF-spectra in J-PARC up to 500 K.

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

Figure 1 shows the T dependences of Δ and ν for $LiCrO_2$. The $\nu(T)$ curve exhibits a sharp maximum at 150 K, but ν levels off to a constant value above 275 K. On the other hand, the $\Delta(T)$ curve shows broad minimum around 150 K, although Δ, in principle, decreases with T due to averaging caused by thermal vibration. The anomalies around 150 K both in the $\nu(T)$ and $\Delta(T)$ curve suggest an additional magnetic contribution to the Kubo-Toyabe parameters. In fact, the $\chi(T)$ curve obtained in FC mode deviates from the $\chi(T)$ curve obtained in ZFC mode below around 200 K (see Fig. 2), indicating the presence of a spin-glass like behavior far above T_N.

Figure 3 shows the $\nu(T)$ curve for $Li_{0.73}CoO_2$ [4], $Li_{0.97}Ni_{1.03}O_2$, and $LiCrO_2$. Besides $LiCrO_2$, the other two compounds are used as a positive electrode material of lithium-ion batteries. Indeed, their $\nu(T)$ curves show a drastic increase above around 200 K, while ν for $LiCrO_2$ is almost T-independent above 275 K. The μSR result on $LiMO_2$ is, therefore, found to be very consistent with their electrochemical properties. In other words, it is confirmed that the increase in ν above 200 K is caused not by muon diffusion but by Li diffusion, as proposed for $LiCoO_2$ [4].

[1] H. Kadowaki et al., J. Phys.: Condens. Matter **7**, 6869 (1995).
[2] L. K. Alexander et al., Phys. Rev. B **76**, 064429 (2007).
[3] J. Sugiyama et al., Phys. Rev. B **79**, 184411 (2009).
[4] J. Sugiyama et al., Phys. Rev. Lett. **103**, 147601 (2009).

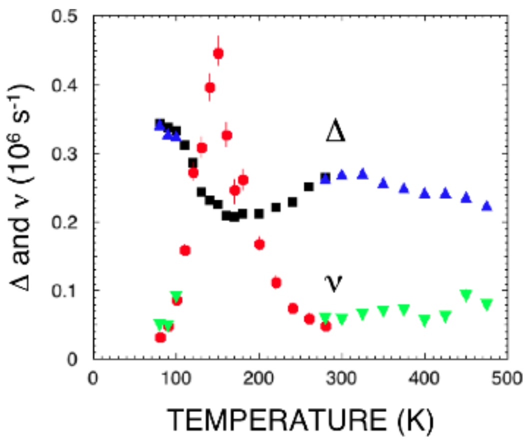

Fig.1 T dependences of Δ and ν for $LiCrO_2$.

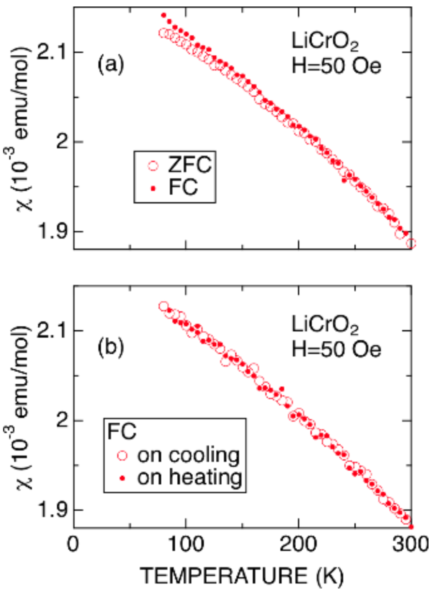

Fig.2 T dependences of χ for $LiCrO_2$; (a) χ obtained ZFC and FC mode and (b) χ observed FC mode on heating and on cooling.

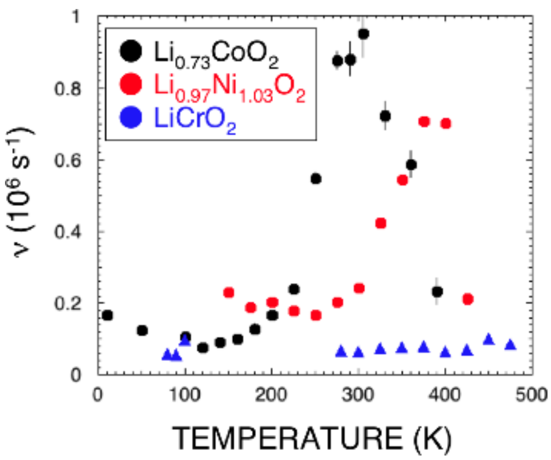

Fig.2 T dependences of ν for $Li_{0.73}CoO_2$, $Li_{0.97}Ni_{1.03}O_2$ and $LiCrO_2$.