



# ADVANCE PROGRAM



# INTERMAG

ASIA International Magnetics Conference

# TAIPEI 2011

Taipei, Taiwan April 25-29, 2011

# Mössbauer studies of spin-orbit coupling in $\text{LiCo}_{0.99}\text{Fe}_{0.01}\text{PO}_4$

C. Rhee, S. Kim, C. Kim

Department of Physics, Kookmin University, Seoul, Republic of Korea

## Introduction

Olivine  $\text{LiMPO}_4$  materials ( $M = \text{Fe, Co, Ni, Mn}$ ) have been studied for large magnetoelectric effect in the anti-ferromagnetic (AF) phase. These lithium orthophosphates showed an induced electric polarization, depending on a magnetic field at low temperature[1]. The M ion and six oxygen ions make up a distorted octahedral structure. The resulting strong crystalline field from the distorted  $\text{MO}_6$  structure affects the M ions and their magnetic properties[2, 3]. In this study, we investigated the microscopic interaction at Fe site in  $\text{LiCo}_{0.99}\text{Fe}_{0.01}\text{PO}_4$  compound with  $^{57}\text{Fe}$  external field Mössbauer spectroscopy, XRD (X-Ray Diffractometer), superconducting quantum interference device (SQUID) measurements.

## Experiment

The  $\text{LiCo}_{0.99}\text{Fe}_{0.01}\text{PO}_4$  sample was synthesized by solid-state reaction method. Starting materials were  $\text{Li}_2\text{CO}_3$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{CoO}$  and  $^{57}\text{Fe}$  metal with purities above 99.99 %. The mixture was calcined at 400 °C under Ar atmosphere and pelletized at 5000 N/cm<sup>2</sup>. The sample was heated up to 700 °C for 12 hours in an evacuated quartz tube. The crystal structure was analyzed by XRD with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Its magnetic properties were investigated by SQUID measurements. The Mössbauer spectra were recorded using transmission type with a  $^{57}\text{Co}$   $\gamma$ -ray source in a rhodium matrix.

## Results and discussions

The crystal structure of the  $\text{LiCo}_{0.99}\text{Fe}_{0.01}\text{PO}_4$  sample was determined to be orthorhombic with the space group of  $Pnma$  at room temperature. The lattice constants were  $a_0 = 10.200 \text{ \AA}$ ,  $b_0 = 5.919 \text{ \AA}$  and  $c_0 = 4.699 \text{ \AA}$  respectively. Figure 1 shows the temperature dependences of the zero-field-cooled (ZFC) and the field-cooled (FC) magnetizations of  $\text{LiCo}_{0.99}\text{Fe}_{0.01}\text{PO}_4$  under an applied field of 100 Oe. These curves showed AF transitions at  $T_N = 23 \text{ K}$ . While the magnetization decreases temperature below  $T_N$ , we have observed a rapid increase when reaches below 9 K.

Below  $T_N$ , the Mössbauer spectra of  $\text{LiCo}_{0.99}\text{Fe}_{0.01}\text{PO}_4$  showed one set of asymmetric 8 absorption lines due to the strong crystalline field in the distorted  $\text{FeO}_6$  ( $\text{CoO}_6$ ). The temperature dependence of magnetic hyperfine field ( $H_{\text{hf}}$ ) shows different rate of change and abrupt increase at 9 K as shown in figure 2. This is consistent with the magnetization curves from SQUID measurements. In addition, below 9 K the temperature dependent electric quadrupole splitting ( $\Delta E_Q$ ) decreases with decreasing temperature due to spin-orbit coupling. Above 9 K, the temperature dependent  $\Delta E_Q$  decreases with increasing temperature due to thermal contribution without any spin-orbit coupling, which is due to the fact that the orbital angular momentum is quenched by strong crystalline field. The external magnetic field dependence of the microscopic interaction was measured with Mössbauer spectroscopy under an applied magnetic field of 4.8 T below  $T_N$ . The  $H_{\text{hf}}$  showed a rapid increase and  $\Delta E_Q$  decreased rapidly below 9 K. The rates of change of  $H_{\text{hf}}$  and  $\Delta E_Q$  under external magnetic field are much larger than those without external magnetic field as shown in figure 2. From these results, we conclude that the orbital angular momentum contribution of  $\text{Fe}^{2+}$  ( $\text{Co}^{2+}$ ) ion enhances  $H_{\text{hf}}$  and magnetization due to spin-orbit coupling effect.

[1] D. Vaknin, J. L. Zarestky, J.-P. Rivera, and H. Schmid, Phys. Rev. Lett. 92, 207201 (2004).

[2] G. Liang, K. Park, J. Li, R. E. Benson, D. Vaknin, J. T. Markert, and M. C. Croft, Phys. Rev. B 77, 064414 (2008).

[3] W. Kim, C. H. Rhee, H. J. Kim, S. J. Moon, and C. S. Kim, Appl. Phys. Lett. 96, 242505 (2010).

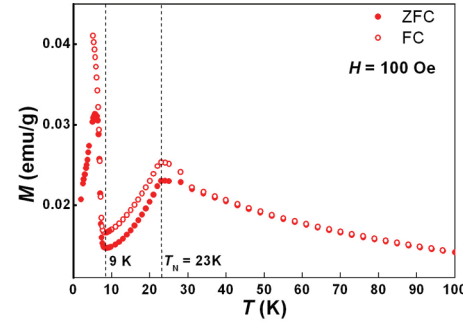


Fig. 1. Temperature dependences of the ZFC and the FC magnetizations of  $\text{LiCo}_{0.99}\text{Fe}_{0.01}\text{PO}_4$  at an applied field of 100 Oe.

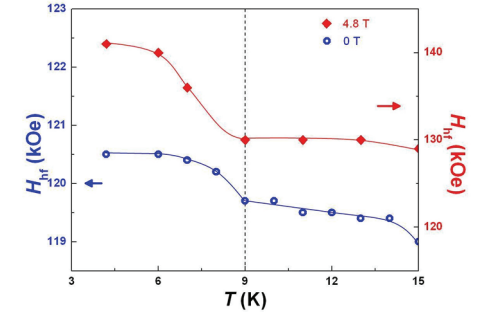


Fig. 2. Temperature dependence of the magnetic hyperfine field ( $H_{\text{hf}}$ ) of  $\text{LiCo}_{0.99}\text{Fe}_{0.01}\text{PO}_4$ .