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## Mössbauer studies of $^{57}\text{Fe}$ -doped in $\text{LiCoPO}_4$ at low temperatures.

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### Introduction

Since the magnetoelectric (ME) effect was observed in Lithium-orthosphates,  $\text{LiMPO}_4$  (M=Transition metal) have been extensively investigated for information storage and electronic, magnetic and optical switches [1-3]. Also, the high lithium-ionic conductivity has been studied already as a high potential cathode material by using in secondary Li-ion rechargeable battery [4]. Recently, the observation of ferrotoroidic (FTO) domains in  $\text{LiCoPO}_4$  was reported by Bas. Van Aken et al [5]. They claimed that the ferrotoroidic system has asymmetric structure by migration of  $\text{Co}^{2+}$  ions in antiferromagnetic (AFM) structure with rotation of the spins. The studies of neutron scattering demonstrated the magnetic properties of  $\text{LiCoPO}_4$  which was related between 2D and 3D magnetic systems [2, 5]. These structures exhibit a strong linear magnetoelectric (ME) effect. AFM ordering reduces the symmetry from  $mmm$  to  $mmm'$ , and weak ferromagnetism along y axis reduces the symmetry from  $mmm'$  to  $2'mm'$ , therefore, finally, it has two AFM and two FTO domains in  $\text{LiCoPO}_4$  [5].

From these complex magnetic structures,  $\text{LiCoPO}_4$  show the various anomaly effects. Therefore, it is essential to determine the unusual magnetic properties of  $\text{LiCoPO}_4$  in low temperatures for properly understand the mechanism. We present crystallographic and magnetic properties of  $\text{LiCo}_{0.99}\text{Fe}_{0.01}\text{PO}_4$  (LCFPO) using the Mössbauer spectroscopy and the x-ray diffraction (XRD) Experiments

The polycrystalline sample of (LCFPO) was made by using a direct reaction. Lithium carbonate, ammonium dihydrogen phosphate, cobalt oxide, and iron metal ( $^{57}\text{Fe}$ ) were mixed in stoichiometric ratios and sealed in evacuated quartz tubes. The temperature was slowly raised up to 700 °C over a period of 1 day. The crystal structure of the sample was examined by using an X-ray diffractometer with Cu- $K\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ) and was analyzed by using a Rietveld refinement. The Mössbauer spectra were recorded using a conventional spectrometer of the electromechanically type with a  $^{57}\text{Co}$  source in a rhodium matrix.

### Results and discussion

X-ray diffraction pattern for LCFPO showed a pure olivine single phase. The crystals structure was determined to be an orthorhombic with space group  $Pnma$ . The determined lattice constants  $a_0$ ,  $b_0$ , and  $c_0$  are 10.241 Å, 5.924 Å, and 4.698 Å, respectively.

The Mössbauer spectra of LCFPO at various temperatures ranging from 4.2 to 300 K are shown in Fig. 1. We have analyzed the Mössbauer spectra by using the full Hamiltonian. The Mössbauer spectrum shows a large asymmetric and distorted line broadening at 4.2 K. The magnetic hyperfine field ( $H_{\text{hf}}$ ) and the quadrupole splitting ( $\Delta E_Q$ ) at 4.2 K were fitted and yielded the following results:  $H_{\text{hf}} = 127 \text{ kOe}$ ,  $\theta = 16^\circ$ ,  $\phi = 0^\circ$ ,  $\eta = 0.95$ ,  $\Delta E_Q = (1/2)e^2qQ[1+(1/3)\eta^2]^{1/2} = 0.36 \text{ mm/s}$ , and  $R = 3.0$ . Here,  $\eta$  is the asymmetric parameter, and  $R$  is the ratio of the electric quadrupole interaction to the magnetic dipole interaction. It is noticeable that the magnitude of  $R$  is greater than 1 below  $T_N$ . This result indicates that the electric quadrupole interaction is larger than the magnetic dipole interaction in the below  $T_N$  region. Generally, the  $H_{\text{hf}}$  has a maximum value at 0 K and decreases with increasing temperature. In Fig. 2, we observe that the  $H_{\text{hf}}$  has a maximum at 9 K. The unusual reduction of  $H_{\text{hf}}$  below 9 K can be explained in terms of the temperature dependence of the cancellation effect between the orbital current field term and the Fermi contact term in  $H_{\text{hf}}$ . The magnitude quadrupole shift at below  $T_N$  was caused by large crystal field due to the asymmetric struc-

ture through the rotation of the spins. From the analysis of Mössbauer spectra, we suggest that the asymmetric structure of  $\text{LiCoPO}_4$  is closely related to the elevation of ME effect.

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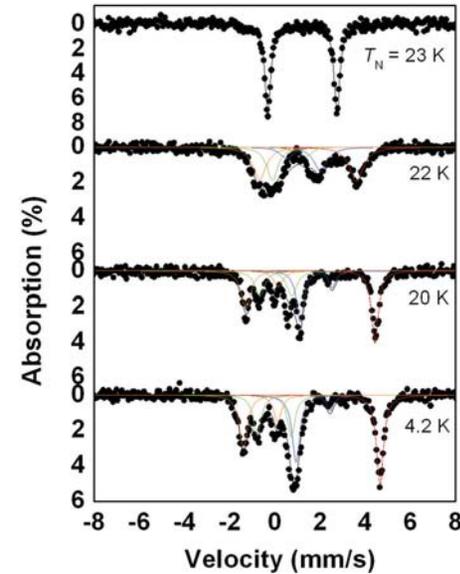


Fig. 1. Mössbauer spectra of  $\text{LiCo}_{0.99}\text{Fe}_{0.01}\text{PO}_4$  at various temperatures.

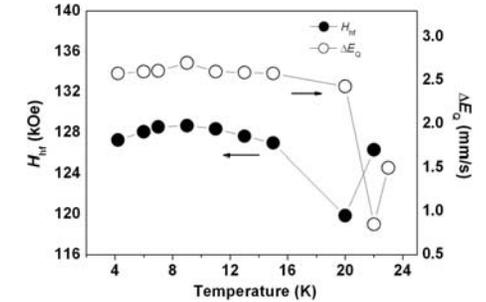


Fig. 2. The Temperature dependence of magnetic hyperfine field ( $H_{\text{hf}}$ ) and the electric quadrupole shift ( $\Delta E_Q$ ) at below  $T_N$  for  $\text{LiCo}_{0.99}\text{Fe}_{0.01}\text{PO}_4$  ( $T_N$  (23 K)).