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

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Introduction
Since the magnetoelectric (ME) effect was observed in Lithium-orthophosphates, 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 as a high potential cathode material by using in secondary Li-ion rechargeable battery [4]. Recently, the observation of ferrotoroidic (FTO) domains in LiCoPO$_4$ was reported by Bas. Van Aken et al [5]. They claimed that the ferrotoroidic system has asymmetric structure by migration of Co$^{2+}$ ions in antiferromagnetic (AFM) structure with rotation of the spins. The studies of neutron scattering demonstrated the magnetic properties of 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 mmmm to mmmm', and weak ferromagnetism along y axis reduces the symmetry from mmmm' to 2'mm', therefore, finally, it has two AFM and two FTO domains in LiCoPO$_4$ [5].

From these complex magnetic structures, LiCoPO$_4$ show the various anomaly effects. Therefore, it is essential to determine the unusual magnetic properties of LiCoPO$_4$ in low temperatures for properly understand the mechanism. We present crystallographic and magnetic properties of LiCo$_{0.99}$Fe$_{0.01}$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 ($^{57}$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- Kα radiation ($λ=1.5406$ Å) and was analyzed by using a Rietveld refinement. The Mössbauer spectra were recorded using a conventional spectrometer of the electromechanically type with a $^{57}$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 10.241Å, 5.924Å, 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 ($H_{hf}$) and the quadrupole splitting ($ΔE_Q$) at 4.2 K were fitted and yielded the following results: $H_{hf}=127$ kOe, $θ=16^°$, $ϕ=0^°$, $η=0.95$, $ΔE_Q=(1/2)e^2q[1+(1/3)η^2]^{-1/2}=0.36$ mm/s, and $R=3.0$. Here, $η$ 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 $H_{hf}$ has a maximum value at 0 K and decreases with increasing temperature. In Fig. 2, we observe that the $H_{hf}$ has a maximum at 9 K. The unusual reduction of $H_{hf}$ 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 $H_{hf}$. The magnitude quadrupole shift at below $T_N$ was caused by large crystal field due to the asymmetric struc-