Neutron Scattering Studies of LiCoPO$_4$ & LiMnPO$_4$

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Abstract. LiCoPO$_4$ ($T_N \approx 21.8$ K) & LiMnPO$_4$ ($T_N \approx 34$ K) are antiferromagnetic insulators exhibiting large magnetoelectric effects. We performed inelastic neutron scattering (INS) experiments to investigate the spin dynamics of these systems and analyzed the measured magnetic spectra by linear spin-wave theory, taking into account intra- and inter-plane nearest, next nearest neighbor magnetic exchange interactions and single ion anisotropy. The INS results indicate that the single ion anisotropy in LiCoPO$_4$ is comparable to the nearest-neighbor magnetic exchange interaction rendering Ising-type behavior of LiCoPO$_4$. Neutron diffraction studies of LiMnPO$_4$ in applied magnetic fields reveal a spin-flop transition at $\sim 3.5$ Tesla with characteristics of a second order phase transition.

1. Introduction

LiCoPO$_4$ and LiMnPO$_4$ are antiferromagnetic (AFM) insulators belonging to the olivine family of lithium orthophosphates LiMPO$_4$ ($M = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$) [1, 2]. These materials are known for their exceptionally large magnetoelectric (ME) effect [3, 4] and continue to attract much attention. The recent observations of weak ferromagnetism [5], ME “butterfly loop” anomaly [6], and in particularly the ferrotoroidic domain structure in LiCoPO$_4$ [7] have ignited renewed interest in these materials [8, 9, 10, 11, 12].

Figure 1. (Color online) Schematic crystal structure of LiMPO$_4$ ($M = \text{Co, Mn}$). The P and $M^{2+}$ magnetic ions are shown, and only one layer of the MO$_6$ octahedrons and PO$_4$ tetrahedrons is illustrated for clarity. The in-plane nearest-neighbor ($J_1$), next-nearest-neighbor ($J_2$, $J_3$), and inter-plane nearest, next-nearest-neighbor ($J_4$, $J_5$) magnetic exchange interactions included in the spin wave theory are labeled.

LiCoPO$_4$ and LiMnPO$_4$ crystallize in the orthorhombic crystal structure, space group $Pnma$ (no. 62) at room temperature. As illustrated in Fig. 1 where only the P and $M^{2+}$ ($M = \text{Co, Mn}$) ions are shown for clarity, the magnetic $M^{2+}$ ($S = 3/2$ for Co$^{2+}$ and $S = 5/2$ for Mn$^{2+}$) ions are at the center of a slightly distorted MO$_6$ octahedron that share an oxygen anion.
with the PO$_4$ tetrahedra forming buckled M-O layers stacked along the $a$-axis. LiCoPO$_4$ ($T_N \approx 21.8$ K) and LiMnPO$_4$ ($T_N \approx 34$ K) undergo long range AFM transitions with a collinear AFM ground state. They adopt the same magnetic structure ($Pmn'a$) differing only in spin orientation. The spins are oriented along the $b$-axis for LiCoPO$_4$ and along the $a$-axis for LiMnPO$_4$ [2, 8]. As depicted in Fig. 1, the magnetic coupling in the layer is through the M-O-M super-exchange interactions, and the coupling between adjacent layers is mediated through the PO$_4$ phosphate group, rendering the magnetic system quasi-two-dimensional. We have recently reported inelastic neutron scattering (INS) studies and determined the microscopic magnetic interactions in these two systems (the detailed results have been published in Ref.13 and Ref.14). In this manuscript, we briefly present the main INS results of LiCoPO$_4$ and preliminary neutron diffraction measurements under applied magnetic field ($H \parallel a$-axis) of LiMnPO$_4$ that reveal a spin-flop transition at $\sim 3.5$ Tesla.

2. Experimental Techniques, Results and Discussions
Neutron scattering experiments were carried out using single crystal samples grown by the standard LiCl flux method similar to that reported in Ref.11,15. The crystals were characterized by X-ray diffraction measurements and no impurity phases were detected. Inelastic neutron scattering measurements of LiCoPO$_4$ were performed on the HB1A triple-axis spectrometer (TAS) at HFIR, and the BT7, BT9 and SPINS TAS spectrometers at NIST. The neutron diffraction measurements of LiMnPO$_4$ in applied magnetic fields were performed on the BT7 TAS employing a 11 Tesla vertical magnet with the crystal oriented in the $(0 K L)$ scattering plane and the magnetic field applied along the $a$-axis, $H \parallel a$. All data have been normalized to beam monitor counts.

![Figure 2.](image-url)

Figure 2. (Color online) (a) Constant wave-vector scans of LiCoPO$_4$ measured at $(0 1 0)$ ($T = 8$ K and $35$ K) and at $(0 1 1.5)(T = 8$ K). (b) LiCoPO$_4$ spin-wave dispersion curves along three reciprocal lattice directions. Data points are obtained based upon a Gaussian peak approximation. The solid and dashed lines are calculations based upon a global fit to the linear spin wave approximation theory as described in the text.

Figure 2 (a) depicts representative constant wave-vector scans of LiCoPO$_4$ (error bars in this paper are statistical in origin and represent one standard deviation). It shows that a single excitation of $\hbar \omega \approx 4.7$ meV is detected at $(0 1 0)$ at $T = 8$ K ($T < T_N$). At $T = 35$ K ($T > T_N$) the peak intensity is significantly reduced demonstrating the excitation is magnetic in origin. Comparing $T = 8$ K constant wave-vector scans measured at $(0 1 0)$ and $(0 1 1.5)$, which typically correspond to the minimum and maximum spin wave excitations along the $L$ direction, the $\sim 4.7$ meV excitation at $(0 1 0)$ shifts to higher energy transfer, $\sim 5.3$ meV at $(0 1 1.5)$ indicating weak dispersion along the $L$ direction. Measurements along the $(H 1 0)$ and $(0 K 0)$ directions indicate the $\sim 4.7$ meV excitation propagating weakly along both the
H and K directions as well. The spin wave dispersion curves of LiCoPO$_4$ determined from a series of constant wave-vector energy-scans below $T_N$ are shown in Fig. 2 (b). Weak dispersion was observed in LiCoPO$_4$ with a bandwidth less than 1 meV exhibiting Ising-type behavior. The large uncertainties in the LiCoPO$_4$ experimental data are associated with instrumental energy resolution which for the TAS used is $\Delta E \sim 1$ meV at the elastic position. The large experimental uncertainty has a significant effect on the theoretical modeling of LiCoPO$_4$.

The measured spin wave dispersion curves are analyzed in the linear spin wave theory framework. The proposed spin Hamiltonian [16] taking into account different magnetic exchange interactions ($J_1$ to $J_5$ in Fig. 1) can be written by the following equation:

$$\mathcal{H} = \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{i,\alpha} D_{\alpha} (S_i^\alpha)^2$$

(1)

where $D_{\alpha}$ ($\alpha = x, y, z$) represents the single-ion anisotropy along the $x$, $y$, and $z$-directions. Within the linear spin wave approximation, the derived spin wave dispersion from Eq. (1) is given by:

$$h\omega = \sqrt{A^2 - (B \pm C)^2}.$$  

(2)

The definition of parameters $A$, $B$ and $C$ in Eq. (2) is described in Ref.13. The $(B \pm C)$ in Eq. (2) indicates that there are two non-degenerate spin wave branches due to the different values of $D_x$ and $D_y$.

The magnetic spectra of LiCoPO$_4$ can be adequately described by the proposed spin-wave model. The non-linear least squares fit of the obtained LiCoPO$_4$ magnetic spectra using Eq. (2) (“B-C” branch) yields: $J_1 = 0.771 \pm 0.144$ meV, $J_2 = 0.129 \pm 0.113$ meV, $J_3 = 0.208 \pm 0.102$ meV, $J_4 = -0.167 \pm 0.067$ meV, $J_5 = -0.193 \pm 0.102$ meV, $D_x = 0.73 \pm 0.15$ meV, $D_y = 0.808 \pm 0.159$ meV. The solid and dashed lines in Fig. 2 (b) are the calculations of the two spin wave branches using the obtained parameters. It is remarkable that large single-ion anisotropy was obtained that is comparable to the strongest nearest-neighbor magnetic interaction $J_1$, $D_x \sim D_y \sim J_1$. Such relatively strong anisotropy may split the $S = 3/2$ quartet of the Co$^{2+}$ ion into two doublets effectively resulting in the suggested Ising-type character of LiCoPO$_4$ [9]. Our studies indicate that single ion anisotropy plays an important role in the spin dynamics of LiCoPO$_4$. As shown in Fig. 2 (b), the calculated spin wave dispersion predicts a maximum separation of $\sim 0.3$ meV at $(0 \ 1 \ 0)$. Both thermal neutron TAS data (with a resolution of $\sim 1$ meV) and cold neutron SPINS high resolution data (with a resolution of $\sim 0.28$ meV) show only one excitation around $\sim 4.7$ meV. In our measurements, we could not resolve the two branches. It is possible that the second excitation is very weak in intensity since the model does not predict intensities. Another possibility is that the intrinsic linewidth of the observed excitations are broader than the resolution ($\sim 1$ meV) suggesting contributions from both branches overlap and cause the broadening. Detailed studies together with the observation of an anomalous low energy magnetic excitation are reported in Ref.13.

Neutron diffraction measurements of LiMnPO$_4$ in magnetic field reveal a spin-flop transition at $\sim 3.5$ Tesla. Fig. 3 shows typical scans monitoring the $(0 \ 1 \ 0)$ and $(0 \ 0 \ 1)$ strong magnetic reflections as a function of applied magnetic field. The magnetic field was applied along the moment direction, $H \parallel a$-axis. The data of $(0 \ 0 \ 1)$ (Fig. 3 (a)) at 2 K shows that the peak intensity of $(0 \ 0 \ 1)$ disappears above $H_c \sim 3.5$ Tesla indicating a spin-flop transition, we refer to $H_c$ as the critical field associated with the spin-flop transition. On the other hand, as shown in Fig. 3 (b), the peak intensity of $(0 \ 1 \ 0)$ remains nearly the same at fields both above and below $H_c$. For magnetic scattering, only those spin components which are perpendicular to the scattering vector have a non-vanishing cross-section. Hence the disappearance of the $(0 \ 0 \ 1)$ peak, and the nearly unchanged $(0 \ 1 \ 0)$ peak indicate that the flopped spins are aligned nearly along the $c$-axis above $H_c$. As depicted in the inset in Fig. 3 (a), no hysteresis is observed upon
Figure 3. (Color online) Magnetic field induced spin-flop transition in LiMnPO$_4$, the magnetic field was applied along the $a$-axis, $H \parallel a$. (a) $(0 0 1)$ peak intensity vs. $H$ at 2 K. Inset: $(0 0 1)$ peak intensity measured with increasing and decreasing $H$ at 29 K. (b) $(0 1 0)$ peak intensity vs. $H$ at 2 K.

increasing and decreasing the applied magnetic field through the transition, indicating this may be a second order phase transition. An anomalous dip is observed in the $(0 1 0)$ field scan (Fig. 3 (b)) suggesting the existence of an intermediate phase with the critical field $H_c$ extending over a range of $\sim$ 1.6 Tesla at 2 K. We derived the magnetic field versus temperature phase diagram based on field and temperature dependent neutron diffraction and magnetization measurements. The phase diagram and detailed data analysis of this spin-flop transition will be reported elsewhere [17]. Our preliminary results of the characteristics of the spin-flop transition suggest the existence of anisotropic magnetic exchange that competes with the single ion anisotropy.

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