

## Antiferromagnetism in the magnetoelectric effect single crystal $\text{LiMnPO}_4$

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Elastic and inelastic neutron-scattering studies reveal details of the antiferromagnetic transition and intriguing spin dynamics in the magnetoelectric effect single crystal  $\text{LiMnPO}_4$ . The elastic-scattering studies confirm that the system is antiferromagnetic below  $T_N=33.75$  K with local magnetic moments ( $\text{Mn}^{2+}$ ;  $S=5/2$ ) that are aligned along the crystallographic  $a$  axis. The spin-wave dispersion curves propagating along the three principal axes, determined by inelastic scattering, are adequately modeled in the linear spin-wave framework assuming a spin Hamiltonian that is parametrized by inter- and in-plane nearest- and next-nearest-neighbor interactions and by easy-plane anisotropy. The temperature dependence of the spin dynamics makes this an excellent model many-body spin system to address the question of the relationship between spin-wave excitations and the order parameter.

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### I. INTRODUCTION

The recent discoveries of colossal magnetoelectric (ME) effects in rare-earth manganites ( $\text{RMnO}_3$ ) (Refs. 1 and 2) and manganese oxides ( $\text{R}_2\text{MnO}_5$ ) (Ref. 3) triggered a revival interest in the so-called insulating multiferroic materials that exhibit ferroelectricity in coexistence with ferromagnetism or antiferromagnetism (FM or AFM).<sup>4,5</sup> Systematic studies of the coupling between the electric and magnetic fields in crystals date back to the early 1960s with the discovery of the first ME compound  $\text{Cr}_2\text{O}_3$ .<sup>6,7</sup> Early on, the isostructural transition-metal lithium orthophosphates  $\text{LiMPO}_4$  ( $M=\text{Mn, Fe, Co, Ni}$ ) were identified as ME systems<sup>8–10</sup> and have been the subjects of numerous studies.<sup>11–13</sup> Like other members of the lithium orthophosphates,  $\text{LiMnPO}_4$  is an antiferromagnetic insulator with  $Pnma$  symmetry group.<sup>14,15</sup> In this structure, each  $\text{Mn}^{2+}$  ion occupies the center of a slightly distorted  $\text{MnO}_6$  octahedron that shares oxygen anions with a tetrahedral  $\text{PO}_4$  forming a closely packed oxygen framework. The  $\text{Mn}^{2+}$  ions ( $S=5/2$ ) form buckled layers that are stacked along the  $[100]$  crystallographic axis, as shown in Fig. 1(a). The nearest neighbors (NNs) in the  $b$ - $c$  plane are coupled magnetically by a relatively strong exchange interaction  $J_1$  through an Mn-O-Mn oxygen bond, whereas the in-plane next NNs (NNNs) are coupled via Mn-O-O-Mn ( $J_2$ ) (Refs. 16 and 17) [see Fig. 1(b) for the definitions of the exchange couplings]. The interlayer magnetic coupling is mediated through phosphates by higher-order superexchange via Mn-O-P-O-Mn, which was found to be relatively large in similar frameworks.<sup>18</sup>

Neutron diffraction of polycrystalline samples<sup>19–21</sup> and single crystal NMR (Ref. 16) measurements showed that all  $\text{LiMPO}_4$  share the same collinear (up-down) AFM ground state with spin orientation along  $a$ ,  $b$ ,  $b$ , and  $c$  crystallographic directions for  $\text{LiMnPO}_4$ ,  $\text{LiFePO}_4$ ,  $\text{LiCoPO}_4$ , and  $\text{LiNiPO}_4$ , respectively. However, recent single crystal neutron-diffraction studies of  $\text{LiCoPO}_4$ ,  $\text{LiFePO}_4$ , and  $\text{LiNiPO}_4$  (Refs. 22–25) show that the moments in the ground state are slightly tilted away from principal crystallographic

directions, indicating that the magnetic symmetries for these systems are lower than those determined from polycrystalline measurements, giving rise to spontaneously induced weak ferromagnetism. Weak ferromagnetism (WFM) in magnetic susceptibility measurements has also been reported for  $\text{LiNiPO}_4$  (Ref. 26) and  $\text{LiMnPO}_4$  (Ref. 27) below  $T_N$ . Indeed, domain structures observed by second-harmonic-generation (SHG) experiments in  $\text{LiCoPO}_4$  were interpreted as ferrotoroidic domains<sup>28</sup> facilitated by the lower magnetic symmetry obtained in neutron-scattering experiments.<sup>22</sup> Based on the detailed spin configuration observed in  $\text{LiNiPO}_4$ , Jensen *et al.*<sup>25</sup> were able to model the temperature dependence of the ME coefficients of this system.

Here, we report on elastic and inelastic neutron-scattering studies of a single crystal  $\text{LiMnPO}_4$  to determine the nature of the AFM transition and the spin dynamics in this system. Recent susceptibility measurements indicated WFM in this system<sup>27</sup> implying spin canting that may be detected in neutron-diffraction measurements. There is also some inconsistency in the literature with regard to the transition tem-

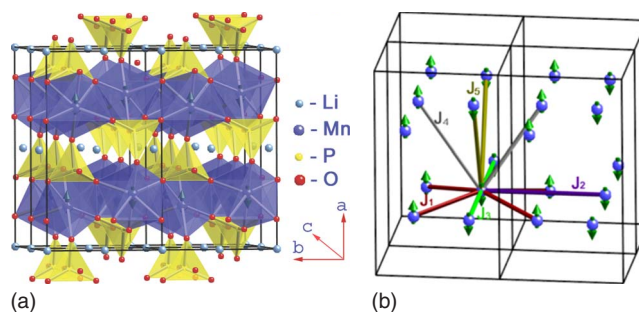


FIG. 1. (Color online) (a) Atomic structure of  $\text{LiMnPO}_4$ . The  $\text{Mn}^{2+}$  ions form buckled layers stacked perpendicular to the  $[100]$  crystallographic direction. The ground state of  $\text{LiMnPO}_4$  is collinear antiferromagnetic with average moments along the  $a$  axis. (b) Spin arrangement of the two  $\text{Mn}^{2+}$  layers. The in-plane nearest- and next-nearest-neighbor interactions  $J_1$ ,  $J_2$ , and  $J_3$  and interplane nearest- and next-nearest-neighbor interactions  $J_4$  and  $J_5$  are labeled.

perature;  $T_N=34.85$  (Refs. 19 and 20) and 42 K were reported<sup>27</sup> for polycrystalline samples. The spin dynamics of the  $\text{LiFePO}_4$ ,  $\text{LiCoPO}_4$ , and  $\text{LiNiPO}_4$  were measured and modeled in the linear spin-wave framework only recently<sup>23,24,29</sup> to successfully yield the exchange couplings and the single ion anisotropy parameters in these systems. Determining and analyzing the spin dynamics of  $\text{LiMnPO}_4$  is an important step toward developing a universal understanding of the magnetic properties of this isostructural group of compounds.

## II. EXPERIMENTAL DETAILS

A  $\text{LiMnPO}_4$  single crystal (0.41 g, pink in color) was grown by the standard flux growth technique (LiCl was used as the flux) from a stoichiometric mixture of high-purity  $\text{MnCl}_2$  (99.999% Aldrich) and  $\text{Li}_3\text{PO}_4$  (99.999% Aldrich).<sup>30</sup> Powder, for the x-ray powder diffraction (XRD), was prepared by crushing typical isolated single crystals. The composition and structure were confirmed by carrying out Rietveld analysis of XRD data using the GSAS software package.<sup>31</sup> No extra peaks from impurities were detected in the XRD pattern. The lattice parameters yielded from the refinement at room temperature ( $a=10.524$  Å,  $b=6.095$  Å, and  $c=4.75$  Å) are in good agreement with the values reported in the literatures.<sup>20,32,33</sup>

Neutron-scattering measurements were carried out on the BT7 and BT9 thermal triple axis spectrometer at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR). A monochromatic neutron beam of wavelength  $\lambda=2.36$  Å (14.7 meV and  $k_o=2\pi/\lambda=2.66$  Å<sup>-1</sup>) was selected by a vertical focusing monochromator system using the (002) Bragg reflection of highly oriented pyrolytic graphite (HOPG) crystals. HOPG crystals were also used as analyzer for both the elastic and the inelastic studies. The high-resolution inelastic-scattering measurements were conducted on the cold neutron Spin Polarized Inelastic Neutron Spectrometer (SPINS) at the NCNR.

## III. RESULTS AND DISCUSSION

### A. Elastic neutron scattering

The  $\text{LiMnPO}_4$  crystal was oriented with its  $a$ - $b$  plane (and subsequently rotated with its  $b$ - $c$  plane) to coincide with the scattering plane of the spectrometer. The elastic measurements, with the strongest magnetic reflection (010) peak, confirmed that the magnetic structure of  $\text{LiMnPO}_4$  is AFM with spin orientation along the  $a$  axis.

The temperature dependence of the magnetic (010) reflection was used to extract the behavior of the order parameter in the temperature range from 5 to 50 K. Figure 2 shows the square root of the integrated intensity, representing the staggered magnetization, (i.e., order parameter) as a function of temperature for the (010) peak. The order parameter was fit to a power-law function near the transition temperature

$$\sqrt{I} \propto M^\dagger = M_0^\dagger t^\beta, \quad (1)$$

where  $M_0^\dagger$  is the sublattice magnetization at  $T=0$  K,  $t=(1-T/T_N)$  is the reduced temperature, and  $\beta$  is the critical ex-

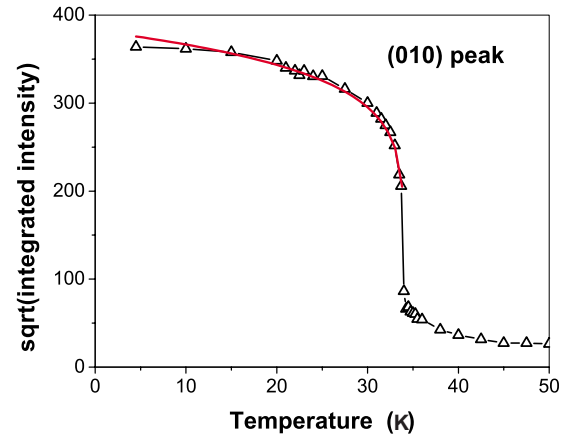


FIG. 2. (Color online) Temperature dependence of the square root of the integrated intensity of the (010) magnetic peak. The transition temperature obtained from a power-law fit is  $T_N=33.85 \pm 0.1$  K and the critical exponent is  $\beta=0.126 \pm 0.017$ .

ponent. The obtained transition temperature for the fit is  $T_N=33.85 \pm 0.1$  K and the critical exponent for the temperature-dependent magnetization  $\beta$  is  $0.126 \pm 0.017$ . This is very close to the theoretical value of the critical exponent of the two-dimensional (2D) Ising system  $\beta=0.125$ ,<sup>34</sup> consistent with the layered nature of the magnetic system, as also demonstrated by the weak interlayer coupling obtained from the analysis of the spin waves discussed below. The transition temperature is found to be very close to the value of  $34.85 \pm 0.1$  K measured by Mays<sup>16</sup> using nuclear magnetic resonances performed on a single crystal of  $\text{LiMnPO}_4$ , whereas susceptibility measurements of powder samples yielded  $T_N=42$  K.<sup>27</sup>

Unlike  $\text{LiCoPO}_4$  and  $\text{LiFePO}_4$ , strong critical scattering above the AFM transition is observed in  $\text{LiMnPO}_4$  and persists to almost twice  $T_N$  (traced to temperatures as high as 70 K) before the spins become uncorrelated. These correlations were already evident in Fig. 2. Figure 3 shows longitudinal and transversal scans at the (010) magnetic peak above the transition with energy transfer  $\Delta E=0$ . The peaks are much broader than the spectrometer's resolution indicating some type of short-range correlations. This is reminiscent of the behavior in  $\text{LiNiPO}_4$  where this critical scattering<sup>21</sup> was later found to be associated with an incommensurate (IC) short- and long-range magnetic orders above  $T_N$ .<sup>35</sup> Below  $\sim 33$  K all peaks are practically resolution-limited Gaussian-shaped. Above  $T_N$ , the peaks were fitted to a Lorentzian line shape  $1/(q^2+\kappa^2)$ , where  $q=h$  or  $k$  and  $\kappa$  is inversely proportional to the coherence length  $\xi=2\pi/\kappa$ , convoluted with an instrumental Gaussian-shaped resolution function. The calculated coherence lengths along the  $a$  and  $b$  axis, as a function of temperature are shown in Fig. 3(c). Below the transition temperature, the in-plane coherence lengths (along the  $b$  axis) are significantly longer than that between the planes (along the  $a$  axis), consistent with the quasi-2D nature of  $\text{LiMnPO}_4$ . The correlation lengths were remeasured on BT9 using the integrated energy (two-axis mode) method and yielded similar results. Attempts to correlate the in-plane coherence length in the critical regime with the 2D Ising model failed, but the Kosterlitz-Thouless (KT) 2D XY model,  $\xi(T)$

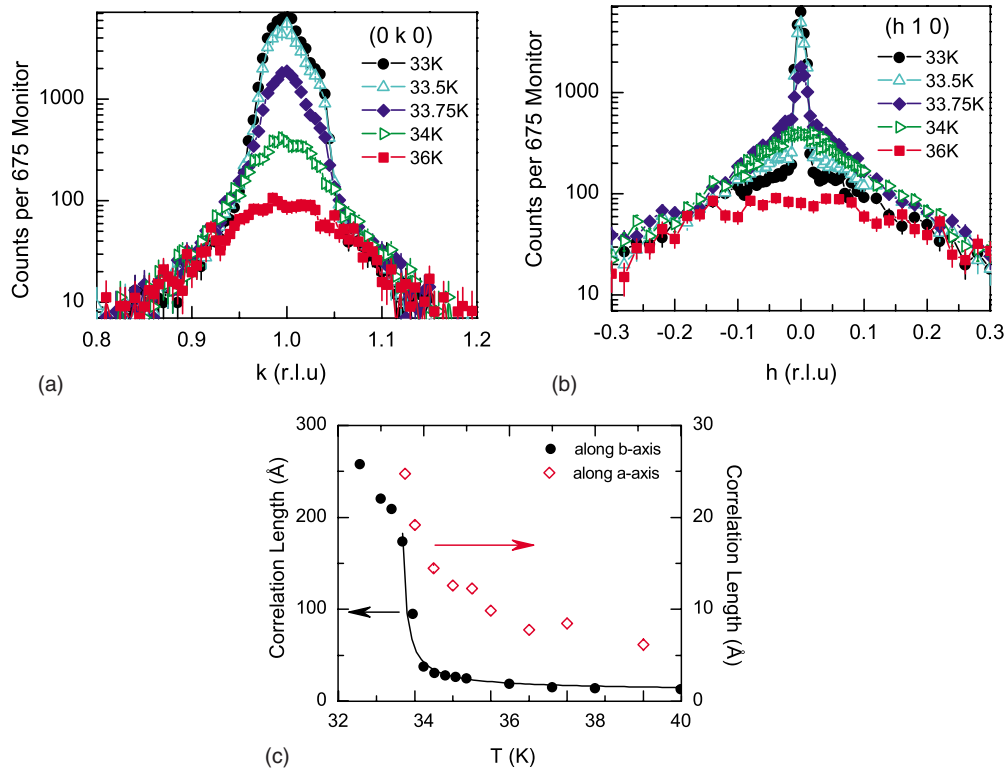


FIG. 3. (Color online) (a) Longitudinal and (b) transversal, (i.e., interplane) critical magnetic scattering scans at the (010) magnetic reflection above  $T_N$ . (c) Correlation lengths obtained after deconvoluting the spectrometer's resolution function (in-plane and interplane as indicated) versus temperature. Solid line is calculated assuming Kosterlitz-Thouless theory. The error bars in this paper are statistical in origin and represent one standard deviation. (r.l.u. stands for reciprocal lattice units.)

$=Ae^{B/(T-T_c)^{\nu}}$ , seems to fit our data well<sup>36</sup> (solid line, Fig. 3) with  $T_c=33.6 \pm 0.008$  and  $\nu=0.51 \pm 0.1$ . This strong critical scattering above the transition with KT characteristics may therefore indicate spin-dimensionality crossover from the 2D Heisenberg to the 2D XY model.

### B. Inelastic and quasielastic neutron scatterings

Spin waves along the three principal reciprocal lattice directions  $(q, 1, 0)$ ,  $(0, 1+q, 0)$ , and  $(0, 1, q)$  were measured in energy loss mode at  $T=5$  K. Examples of the excitations measured on BT7 at  $q=0.2$  are shown in Fig. 4. A single excitation was observed at each  $q$  along the three directions on BT7 which has an energy resolution of  $\sim 1$  meV. At  $T \approx 50$  K, no similar peaks are observed confirming the magnetic origin of the excitations. The inelastic signals at various constant wave vectors  $q$  were fit to Gaussian-shaped functions (solid line in Fig. 4), and the set of energies at maximum intensity was used to construct the spin-wave dispersion curves shown in Fig. 6. It is shown that the spin waves propagating in the plane along the (001) and (010) directions have higher energy than the spin waves propagating along (100) at the same  $q$  values. Qualitatively, this behavior reflects the anisotropy in the strength of the exchange couplings in the system; as expected, the in-plane exchange couplings are much stronger than those between planes. Using the cold neutron triple axis SPINS spectrometer, an energy gap  $E_G=0.48$  meV was observed around the (010) zone cen-

ter, which is much smaller than 2,<sup>29</sup> 5.86,<sup>23</sup> and 4.7 meV (Ref. 24) observed in  $\text{LiNiPO}_4$ ,  $\text{LiFePO}_4$ , and  $\text{LiCoPO}_4$ , respectively. With the high energy resolution of SPINS (approximately 0.1 meV, using 3.7 meV final energy), two energy excitation peaks were identified at the zone center, as shown in Fig. 5.

To model the spin-wave dispersions, we use a spin Hamiltonian based on the ground-state spin structure of  $\text{LiMnPO}_4$  as shown in Fig. 1, as follows:

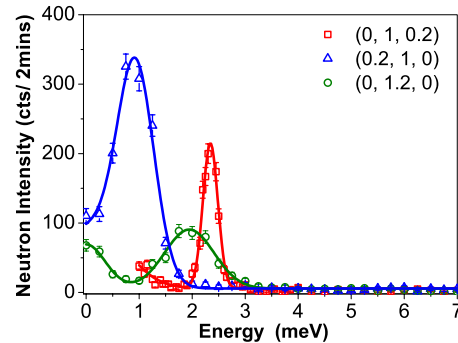


FIG. 4. (Color online) Examples of constant- $Q$  energy scans measured on BT7 at 5 K at wave vectors  $q=0.2$  along  $(q, 1, 0)$ ,  $(0, 1+q, 0)$ , and  $(0, 1, q)$  reciprocal directions. A single energy excitation is present in every direction with the typical energy resolution of BT7 around 1 meV.

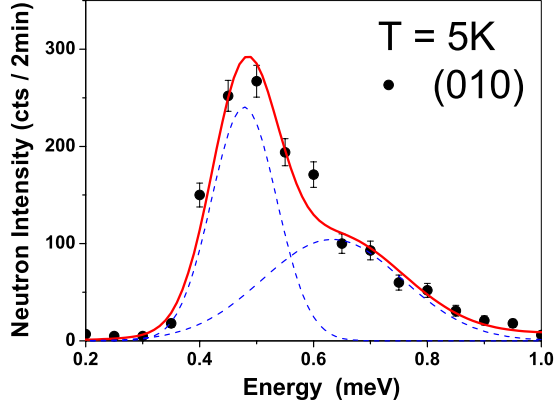


FIG. 5. (Color online) The energy excitation at the zone center measured on SPINS with an energy resolution of  $\sim 0.1$  meV. Two excitations are clearly identified at the zone center.

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

$J_1$ – $J_5$  are the spin coupling constants (see Fig. 1) and  $D_{\xi}$  are the single ion anisotropies. Since the excitation spectrum is insensitive to an overall shift of the ground-state energy, we can define  $D_z = 0$  for simplicity. The  $x$ ,  $y$ , and  $z$  coordinates are defined along the  $c$ ,  $b$ , and  $a$  axes, respectively, to align the spin direction in the ground state with the quantum  $z$  axis in Eq. (2). The magnon dispersion curves derived from Eq. (2) by linear spin-wave theory<sup>37</sup> are given in Ref. 29. In the model, the calculated spin waves have two nondegenerate branches [denoted by the  $\pm$  sign in Eq. (3)] as a result of the different anisotropies along the  $x$  and  $y$  directions,

$$\hbar\omega = \sqrt{A^2 - (B \pm C)^2}, \quad (3)$$

where

$$A \equiv 4S(J_1 + J_5) - 2S\{J_3[1 - \cos(\mathbf{q} \cdot \mathbf{r}_5)] + J_2[1 - \cos(\mathbf{q} \cdot \mathbf{r}_6)] + J_4[2 - \cos(\mathbf{q} \cdot \mathbf{r}_7) - \cos(\mathbf{q} \cdot \mathbf{r}_8)]\} + (S - 1/2)(D_x + D_y),$$

$$B \equiv (S - 1/2)(D_x - D_y),$$

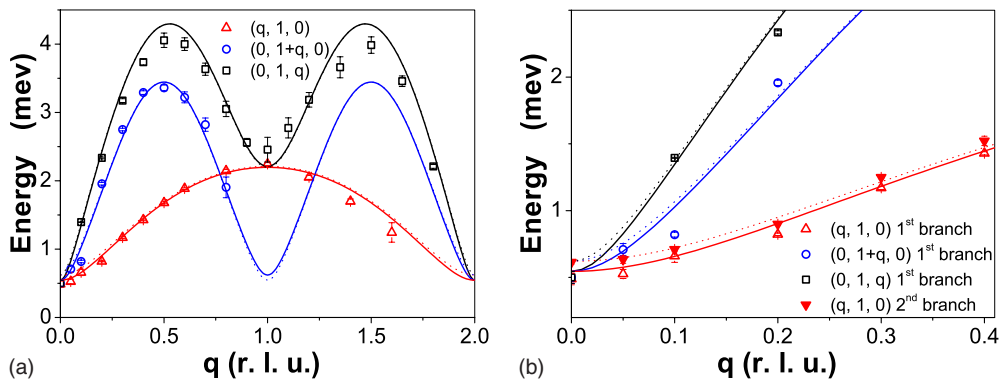


FIG. 6. (Color online) (a) Spin-wave dispersion curves along the  $a^*$ ,  $b^*$ , and  $c^*$  reciprocal space directions measured at 5 K. Solid lines are best-fit calculations obtained from linear spin-wave theory using Eq. (3). (b) Zoomed plot of (a) near the zone center. The predicted second spin-wave dispersion branches are shown as dashed lines.

$$C \equiv 2J_1S[\cos(\mathbf{q} \cdot \mathbf{r}_1) + \cos(\mathbf{q} \cdot \mathbf{r}_2)] + 2J_5S[\cos(\mathbf{q} \cdot \mathbf{r}_3) + \cos(\mathbf{q} \cdot \mathbf{r}_4)],$$

and  $\mathbf{r}_i$  denotes a vector to a NN and NNN,

$$\mathbf{r}_1 = (c/2, b/2, 0), \quad \mathbf{r}_2 = (-c/2, b/2, 0),$$

$$\mathbf{r}_3 = (0, b/2, a/2), \quad \mathbf{r}_4 = (0, -b/2, a/2),$$

$$\mathbf{r}_5 = (0, b, 0), \quad \mathbf{r}_6 = (c, 0, 0),$$

$$\mathbf{r}_7 = (c/2, 0, a/2), \quad \mathbf{r}_8 = (-c/2, 0, a/2).$$

The spin-wave dispersion curves along the three directions in Fig. 6 were simultaneously fit to Eq. (3), using the “ $-$ ” sign, yielding the following values:  $J_1 = 0.48 \pm 0.05$  meV,  $J_2 = 0.2 \pm 0.038$  meV,  $J_3 = 0.076 \pm 0.004$  meV,  $J_4 = 0.036 \pm 0.002$  meV,  $J_5 = 0.062 \pm 0.003$  meV,  $D_x = 0.0069 \pm 0.001$  meV, and  $D_y = 0.0089 \pm 0.001$  meV. In the equation,  $S = 5/2$  for  $\text{Mn}^{2+}$ . As expected, the in-plane NN exchange coupling  $J_1$  is the strongest compared to the in-plane NNNs  $J_2$  and  $J_3$ . The sign of both  $J_2$  and  $J_3$  indicates that the NNN interactions compete with the simple AFM ordering dictated by  $J_1$ . For weakly coupled layers, it has been predicted theoretically that an IC magnetic structure should be realized when  $J_2/J_1 > 0.5$ .<sup>38</sup> Thus, unlike in  $\text{LiNiPO}_4$  where  $J_2/J_1 \approx 0.6$  and an IC has been observed, the ratio for  $\text{LiMnPO}_4$  ( $\sim 0.4$ ) seems to be too small to induce any IC phase transition.<sup>29</sup> The spin couplings between the interplane nearest neighbors ( $J_4$  and  $J_5$ ) are relatively weak at about 12% of  $J_1$  consistent with the quasi-2D behavior of this system. The values of the single ion anisotropies  $D_x = 0.0055$  and  $D_y = 0.0071$  are much smaller than those of  $\text{LiNiPO}_4$ ,<sup>29</sup>  $\text{LiFePO}_4$ ,<sup>23</sup> and  $\text{LiCoPO}_4$  (Ref. 24) indicating that the ground state with magnetic moments along the  $a$  axis is not very stable, and the moments are prone to a spin-flop transition in relatively weak magnetic fields.<sup>39,40</sup>

The second spin wave dispersion branches, given by “ $+$ ” sign in Eq. (3), are calculated using the  $J$ 's and  $D$ 's obtained from the fits listed above. The two branches almost overlap one another for the dispersions along all the three principal

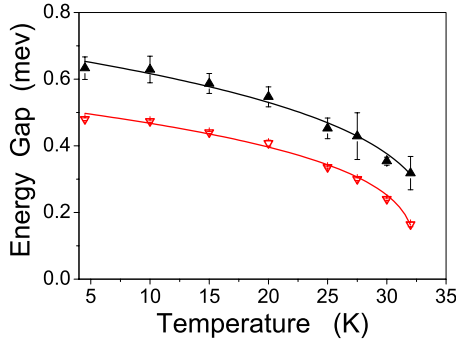


FIG. 7. (Color online) The energy gap as a function of temperature measured on the SPINS cold neutron triple axis.

reciprocal directions and are only separated by  $\sim 0.1$  meV at the zone center. The spin-wave dispersion along the  $(q, 1, 0)$  direction, where the model predicts the largest separation between the two branches, was remeasured with the high-energy resolution on SPINS. Figure 6(b) shows an enlargement graph of Fig. 6(a), with fairly good agreement with the model calculations.

The energy gaps at the zone center for the two branches are

$$\Delta E = 2S\sqrt{4D_x(J_1 + J_5) + D_xD_y} \quad (4)$$

for  $(B-C)$  in Eq. (3) and

$$\Delta E = 2S\sqrt{4D_y(J_1 + J_5) + D_xD_y} \quad (5)$$

for  $(B+C)$ .  $J_5$  represents the interplane NN coupling. From the equations, we notice that the energy gap not only depends on the single ion anisotropy terms, but also on the two nearest-neighbor antiparallel exchange interactions.

The temperature-dependent energy gap up to the transition temperature was measured at the cold neutron triple axis spectrometer SPINS, and the results are shown in Fig. 7 (energy gaps at various temperatures were determined from Gaussian fits to constant- $Q$  energy scans such as the one

shown in Fig. 5 at  $T=5$  K). The energy gap monotonically decreases with increasing temperature and approaches zero at the transition temperature. The temperature dependence of the gap to a first approximation is proportional to the staggered magnetization which is temperature dependent.<sup>41</sup> However, it may deviate in the critical regime due to the different temperature dependencies of the coupling constants and the single ion anisotropy. In antiferromagnets, the exchange constants  $J_s$  usually decrease much faster than the single ion anisotropy near the transition temperature.<sup>41,42</sup>

Quasielastic scattering (QENS) around (010) at different temperatures was measured on BT9 using the integrated energy (two-axis) mode, and the results are shown in Fig. 8. At temperatures right below the transition, the (010) peak consists of a resolution-limited Gaussian-shaped magnetic Bragg peak superimposed on a broad Lorentzian shaped diffuse peak. Whereas the diffuse scattering becomes stronger with the increase in temperature (up to the transition), the elastic magnetic Bragg peak becomes weaker. The QENS intensity at each temperature was integrated over the  $K$  range shown in Fig. 8(a) excluding the region from 0.98 to 1.02 reciprocal lattice units (r.l.u.) which is dominated by elastic scattering. Figure 8(b) shows the QENS as a function of temperature, which exhibits a sharp peak at the transition ( $T_N=33.75$  K) with a tail that extends to about  $1.5T_N$ . This indicates that the short-range correlations observed in the elastic scattering are primarily due to (dynamics) spin fluctuations.

In summary, we determined the critical behavior near the AFM magnetic phase transition of  $\text{LiMnPO}_4$  ( $T_N=33.85$  K). The strong critical scattering around the (010) magnetic peak and the in-plane and interplane coherence lengths indicate that the system is a quasi-2D system with very weak easy-axis single ion anisotropy. Analysis of the spin-wave dispersions along the three principal axis directions shows that the in-plane couplings are dominant compared to the interplane couplings. These in-plane competing interactions between in-plane NN and NNN spins in  $\text{LiMnPO}_4$  seem to be too weak to lead to more complicated incommensurate magnetic structures. This is in contrast to the observation of incommensurate magnetic phases in  $\text{LiNiPO}_4$ .<sup>35</sup>

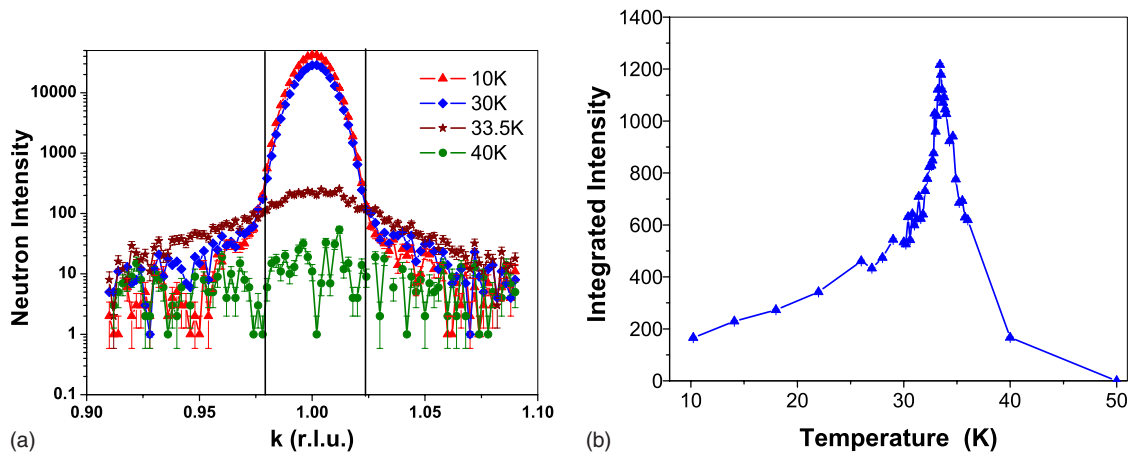


FIG. 8. (Color online) (a) Examples of the quasielastic-scattering scans around (010) magnetic peak at temperatures below and above the transition temperature  $T_N$ , which were measured on BT9 using the integrated energy method. (b) The temperature-dependent integrated intensity from the quasielastic scattering excluding  $K=0.98-1.02$  as indicated by the box in (a).

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