Long-range magnetic interactions in the multiferroic antiferromagnet MnWO₄

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(Rceived 1 December 2010; revised manuscript received 9 March 2011; published 12 April 2011)

The spin-wave excitations of the multiferroic MnWO₄ have been measured in its low-temperature collinear commensurate phase using high-resolution inelastic neutron scattering. These excitations can be well described by a Heisenberg model with competing long-range exchange interactions and a single-ion anisotropy term. The magnetic interactions are strongly frustrated within the zigzag spin chain along the c axis and between chains along the a axis, while the coupling between spin along the b axis is much weaker. The balance of these interactions results in the noncollinear incommensurate spin structure associated with the magnetoelectric effect, and the perturbation of the magnetic interactions leads to the observed rich phase diagrams of the chemically doped materials. This delicate balance can also be tuned by the application of external electric or magnetic fields to achieve magnetoelectric control of this type of materials.

DOI: 10.1103/PhysRevB.83.140401

Magnetoelectric multiferroic materials, which exhibit the coexistence of ferroelectric (FE) and magnetic orders, have attracted great attention in recent years.¹–⁴ Several classes of multiferroics among transition metal oxides have been discovered, including geometrically frustrated CuMO₂ (M is Fe or Cr)⁵–⁷, RbFe(MoO₄)₂,⁷ Ni₃V₂O₆,⁸ or rare-earth (R) manganites RMnO₃ and RMn₂O₅.⁹–¹¹ The ability to simultaneously control the electric (E) and magnetic (M) properties makes these multiferroics promising candidates for technological applications.⁹,¹² A characteristic feature in those magnetically induced multiferroics is the presence of long-range magnetic structures with noncollinear spiral spin configurations. Such magnetic order is a consequence of magnetic frustration either due to geometric constraints or competing exchange interactions resulting in a close competition of different magnetic structures that are nearly degenerate in energy.

The mineral Hübnerite MnWO₄ appears to be a unique material that not only exhibits intriguing multiferroic phenomena but also shows rich magnetic phases via chemical substitutions.¹³–²¹ It has been considered one of the prototypical multiferroics capable of magnetoelectric (ME) control.¹⁶,²² Unlike RMnO₃, where the spiral magnetic structure often involves ordering of the rare-earth moments, MnWO₄ is a frustrated antiferromagnet (AF) with only one type of magnetic ion. The Mn⁺⁺⁺ spins (S = 5/2) undergo successive transitions in zero field.²³ The low-temperature (T) magnetic structure has a collinear spin configuration [Fig. 1(a)]. For T between 7.8 K (TN₁) and 12 K (TN₂), the magnetic structure evolves into an incommensurate (ICM) elliptical spiral configuration accompanied by a spontaneous electric polarization P along the crystalline b axis. When T is further raised between TN₂ and TN₃ (∼13.5 K), MnWO₄ becomes a collinear ICM and paraelectric.

In MnWO₄, the electric polarization that is correlated with the spiral magnetic structure can be well understood by the microscopic picture regarded as inverse Dzyaloshinskii-Moriya interaction.²⁴–²⁶ On the other hand, characterizing the magnetic interactions that cause the formation of the complex spin structures and understanding how the modification of exchange couplings affects the evolution between different phases remains an unresolved issue despite intensive experimental and theoretical studies.²⁷–²⁹ Early inelastic neutron scattering (INS) work suggested that the stabilization of the collinear configuration requires higher-order magnetic interactions.²⁷ Although the magnetic exchange parameters obtained by Ehrenberg et al. fit the experimental data, the longest bond distance was associated with the strongest coupling constant. Later, density functional calculation and classical spin analysis were performed to investigate the magnetic structure and FE polarization in MnWO₄.²⁸ Tian et al. concluded that the spin-exchange interactions are frustrated along both the a and c axes. However, a quantitative experimental characterization of the magnetic interactions is still lacking. Here we report high-resolution INS measurements that show that the low-T magnetic ground state of pure MnWO₄ indeed results from the competition of long-range interactions that are highly frustrated and sensitive to small perturbations. The comprehensive mapping of the of the magnetic excitations along several symmetry directions allowed an unambiguous determination of the dispersion relations and the exchange interactions. Most importantly, such microscopic characterization of the spin coupling constants provides a fundamental step toward the construction of the ground-state Hamiltonian from which the FE phase can be derived.

A 5-g single crystal of MnWO₄ was grown by the floating-zone technique. Neutron diffraction was performed on a small piece of this crystal (0.2 g) to verify the spin structure using the four-circle single-crystal diffractometer HB3A at the High Flux Isotope Reactor at the Oak Ridge National Laboratory (ORNL). The inelastic neutron scattering measurements were performed using the Cold Neutron Chopper Spectrometer (CNCS) at the Spallation Neutron Source at ORNL. The
FIG. 1. (Color online) (a) The magnetic structure of MnWO$_4$ in the collinear, commensurate phase at low temperature. The magnetic spins lie in the $ac$ plane with the moment canted to the $a$ axis about 35$^\circ$. The magnetic spins form zigzag $\uparrow\uparrow\uparrow\uparrow\downarrow\downarrow$ chains along the $c$ axis and are coupled antiferromagnetically along the $b$ axis. (b) The magnetic interactions along and between spin chains in the $bc$ plane. (c) Higher-order magnetic interactions along the $a$ axis direction. The magnetic couplings are labeled with increasing bonding distance. Note the monoclinic crystal structure ($\beta = 91.14^\circ$) makes $J_6/J_7$, $J_8/J_9$, $J_{10}/J_{11}$ pairs different.

momentum transfer wave vectors $q = (q_x, q_y, q_z)$ are in units of $\text{Å}^{-1}$ at positions $(H, K, L) = (q_x/2\pi, q_y/2\pi, q_z/2\pi)$ in reciprocal lattice units (rlu), where $a = 4.83$ Å, $b = 5.75$ Å, $c = 4.99$ Å. We aligned the crystal in several scattering planes such that the spin-wave (SW) dispersion along the [1,0,−2], [1,0,2] and [0,1,0] symmetric directions that pass across the magnetic Bragg peaks can be readily measured. The incident neutrons with wavelength of $\lambda = 4.4$ Å were chosen to ensure the needed energy resolution to separate various magnetic excitation branches.

MnWO$_4$ orders in the collinear phase with two inequivalent commensurate wave vectors $q_M = (1/4, 1/2, \pm 1/2)$. Figures 2(a) and 2(b) present the spin excitation spectra along the [1,0,2] direction with $K = 0.5$ and 1.0. This scanning direction goes through the magnetic Bragg peak (1/4,1/2,1/2). The data clearly show four distinct branches that disperse out from the magnetic zone center (ZC) to the zone boundary. The spectra reveal a spin gap of 0.5 meV and boundary energy around 2.2 meV. The excitation bandwidth is consistent with the energy scale of the ordering temperature of 13.5 K. The intensity of the excitation spectra is highly asymmetric with respect to the magnetic Bragg point. For example, the spectral weight of lowest branch in Fig. 2(a) is completely missing as $H$ approaches zero, while it shows the highest intensity as it moves toward $H = 0.5$. This highlights the importance of a complete survey in reciprocal space to fully map out the magnetic dynamics.

Figures 3(a) and 3(b) display the magnetic scattering spectra along the [1,0,−2] direction that crosses the other magnetic wave vector (1/4,1/2,−1/2), while Figs. 4(a) and 4(b) illustrate the spectra along the [0,1,0] direction. The scattering intensity map shows similar asymmetric features.
This work located at position (1 Mn of meV for comparison.

The SW dispersion curves can be modeled by a general effective Heisenberg Hamiltonian:

\[
H = - \sum_{i,j} J_{ij} S_i \cdot S_j - D \sum_i S_i^z,
\]

where \( \sum_{i,j} \) indicates summation over pairs of spins, \( D \) is the single-ion anisotropy, and \( S_i^z \) denote the spin components along the easy axis. To calculate the corresponding spectral weight, the low-\( T \) spin structure has been verified by collecting a complete set of magnetic reflections that covers the entire reciprocal space. The spin configuration obtained by Rietveld refinement with group theory analysis is in good agreement with a previous report. This configuration is then used to evaluate the magnetic scattering cross section:

\[
\frac{d^2\sigma}{dQdE} \propto f^2(Q)e^{-2W} \sum_{\alpha\beta} (\hat{Q}_\alpha \hat{\rho}_\beta - \hat{Q}_\beta \hat{\rho}_\alpha)S^{\alpha\beta}(Q,\omega)\]

TABLE I. Magnetic exchange coupling parameters derived from spin-wave model calculation according to the Eq. (1). The Mn\(^{2+} \) ions located at position (1/2, 0.685, 1/4) interact with neighboring spins through one or two oxygens. The bonding distance (in units of Å) between Mn\(_{\text{Mn}}\) are also listed. The magnetic interaction constants from previous experimental and theoretical studies have been normalized in units of meV for comparison.

<table>
<thead>
<tr>
<th></th>
<th>( J_1 )</th>
<th>( J_2 )</th>
<th>( J_3 )</th>
<th>( J_4 )</th>
<th>( J_5 )</th>
<th>( J_6 )</th>
<th>( J_7 )</th>
<th>( J_8 )</th>
<th>( J_9 )</th>
<th>( J_{10} )</th>
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<td>-0.47(1)</td>
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<td>0.09(1)</td>
<td>-0.49(1)</td>
<td>-0.12(1)</td>
<td>0.05(1)</td>
<td>-0.23(1)</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
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<td>-0.32(1)</td>
<td>-0.26(1)</td>
<td>0.05(1)</td>
<td>-0.43(1)</td>
<td>-0.12(1)</td>
<td>0.02(1)</td>
<td>-0.26(1)</td>
<td>-0.15(1)</td>
<td>0.02(1)</td>
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<td>0.009</td>
<td>-0.219</td>
<td>0.010</td>
<td>0.212</td>
<td>-0.980</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
<td>0.061</td>
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<td>-0.153</td>
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<td>-0.185</td>
<td>-0.031</td>
<td>-0.115</td>
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strong long-range magnetic interactions comparable to NN interaction ($J_1$) along the $c$ axis ($|J_{1c}/J_1| > 1/2$) and $a$ axis ($|J_{1a}/J_1| > 1/2$, $|J_{2a}/J_1| \approx 1$, and $|J_{1b}/J_1| > 1/4$) are observed. This reflects the magnetic frustration in those two directions and is consistent with the ICM components present in the $a$ and $c$ directions but not in the $b$ direction, when the system enters the spiral phase. The exchange coupling remains sizable ($J_{10}$) even at a rather long distance. Such an unusual extended interaction could also be viewed as a much-reduced NN exchange coupling because of a nearly 90◦ Mn-O-Mn bonding angle.24 Thus, the unique crystalline structure makes MnWO$_4$ a promising material to achieve novel physical properties when the magnetic interactions are modified. It was reported that doping a few percent magnetic or nonmagnetic impurities can drastically affect the spin order.17–20 For instance, while replacing Mn$^{2+}$ with Fe$^{3+}$ ions that have a larger local magnetic anisotropy seems to enhance the collinear structure,17 the introduction of nonmagnetic Zn$^{2+}$ ions that weaken the overall magnetic interactions switches the ground state from collinear to spiral order.18,20 Those results demonstrate that chemical substitutions are a viable tool to tune the multiferroic properties in the extremely sensitive MnWO$_4$.

In summary, high-resolution INS is used to study the SWs in the collinear phase of MnWO$_4$. The collinear spin order is stabilized by the delicate balance of competing long-range magnetic interactions. We provide an effective Hamiltonian to describe the highly frustrated magnetic order within the zigzag spin chains along the $c$ axis and between spin chains along the $a$ axis. Rich and complex magnetic phases are expected in chemically doped MnWO$_4$ due to the fine-tuning of the magnetic interactions. The delicate balance of exchange interactions in MnWO$_4$ can also be used to achieve magnetoelectric control using external electric or magnetic fields.

This work was partially supported by the Division of Scientific User Facilities of the Office of Basic Energy Sciences, U.S. Department of Energy. Work at Houston is supported in part by the T. L. L. Temple Foundation, the J. J. and R. Moores Endowment, and the state of Texas through TCSUH and at LBNL through the US DOE, Contract No. DE-AC03-76SF00098.