

Magnetic Order and Spin Dynamics in Ferroelectric HoMnO₃

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Hexagonal HoMnO₃ is a frustrated antiferromagnet ($T_N = 72$ K) ferroelectric ($T_C = 875$ K) in which these two order parameters are coupled. Our neutron measurements of the spin-wave dispersion for the $S = 2$ Mn³⁺ on the layered triangular lattice are well described by a two-dimensional nearest-neighbor Heisenberg exchange $J = 2.44$ meV, and an anisotropy D that is 0.28 meV above the spin-reorientation transition at 40 K and 0.38 meV below. For $H \parallel c$ the magnetic structures and phase diagram have been determined, and reveal additional transitions below 8 K where the ferroelectrically displaced Ho³⁺ ions are ordered magnetically.

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Magnetic-ferroelectric materials are rare, and rarer still are systems where these two disparate order parameters exhibit significant coupling [1]. Such multiferroics have been of particular interest recently to understand the fundamental aspects of this coupling [2–6], as well as because of the intriguing possibility of using these coupled order parameters in novel device applications [7]. The hexagonal HoMnO₃ system of particular interest here is a prototype multiferroic where the Ho-O displacements give rise to a ferroelectric moment ($T_C = 875$ K) along the c axis, the Mn moments order at 72 K, and the order parameters are naturally coupled through the Ho-Mn exchange and anisotropy interactions. The magnetic system has the added interest that the Mn moments occupy a fully frustrated triangular lattice. Our inelastic neutron scattering measurements of the Mn spin dynamics reveal the planar nature of the spin system, and allow us to establish the basic model for the magnetic interactions in the system and to determine the interaction parameters. Field-dependent neutron diffraction measurements reveal the nature of the magnetic phase diagram, and, in particular, the Ho involvement in the hysteretic magnetic transitions at low temperatures. Our results also suggest that the Ho coupling may be responsible for the first-order spin-flop transition found at intermediate temperatures.

We have grown single crystals of HoMnO₃ using a traveling solvent optical floating zone furnace, and the diffraction and inelastic neutron measurements were performed at the NIST Center for Neutron Research on the BT2 and BT9 thermal triple-axis instruments. The magnetic structure of HoMnO₃ has been studied previously with neutron powder diffraction [8–10], optical second-harmonic generation (SHG) [11–14], and magnetic and dielectric susceptibility [2]. The Mn³⁺ ions are arranged in a two-dimensional (2D) triangular lattice, with successive layers offset from each other. Figure 1 shows the integrated intensities of the (1, 0, 0) and (1, 0, 1) (commensurate) magnetic Bragg peaks, where we see that below $T_N \approx 72$ K the spin-2 Mn³⁺ moments order antiferromag-

netically in a noncollinear 120° structure within each plane. At $T_{SR} \approx 40$ K a sharp spin-reorientation transition is observed associated with a change in the magnetic symmetry to the $P6'_3cm'$ structure, as indicated in Fig. 1. Below 8 K, half of the Ho³⁺ moments order [9,10], which results in a third zero-field spin-reorientation transition of the Mn spins. The three zero-field Mn spin structures are also shown in Fig. 1.

Measurements of the spin-wave dispersion were performed on a 1.8 g single crystal in both the $(H, K, 0)$ and $(H, 0, L)$ scattering planes. An example of a constant- Q scan at 20 K showing two distinct magnetic modes is shown in Fig. 2(a). Fits to individual scans were used to establish the peak positions. The dispersion relations at 20 K, in the intermediate-temperature phase, are plotted in Figs. 2(b) and 2(c) along two different directions in reciprocal space. Data for the spin-wave dispersion along the $(1, 0, L)$ direction [inset, Fig. 2(c)] show no discernible

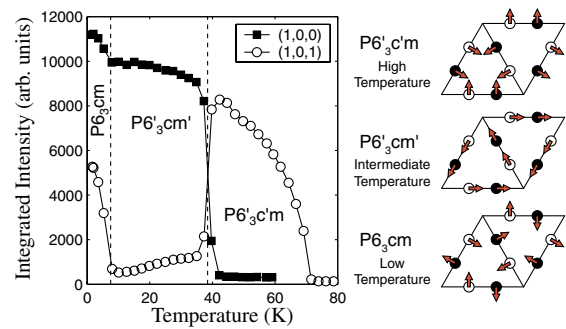


FIG. 1 (color online). Neutron diffraction measurements of the (1, 0, 0) and (1, 0, 1) magnetic Bragg reflection integrated intensity. Two spin-reorientation transitions (indicated by dashed lines) lead to changes in the intensities of both peaks. The Mn³⁺ spin configurations for these phases are shown in the schematics to the right, where open circles indicate the position of Mn ions at $z = 0$, filled circles indicate Mn ions at $z = c/2$, and arrows indicate the direction of the local magnetic moment. Ho³⁺ moments (not shown) order in the low-temperature phase.

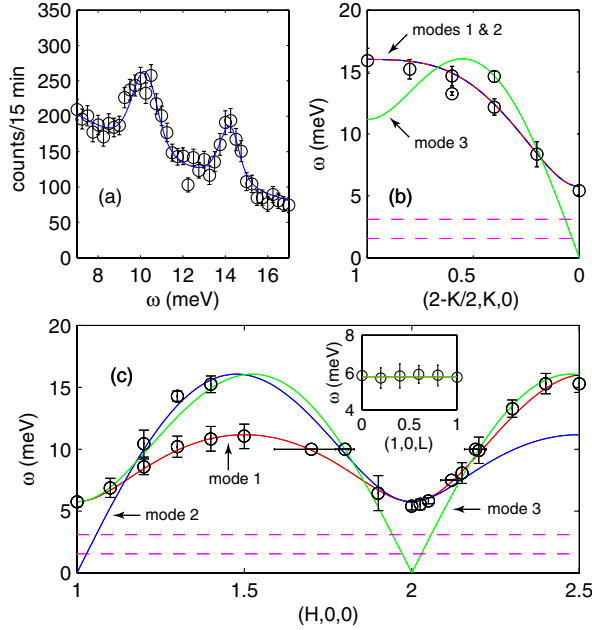


FIG. 2 (color online). Spin-wave dispersion at 20 K. (a) Measurements of the spin waves at $Q = (1.3, 0, 0)$. Data were taken on BT2 with horizontal collimations of $60'-40'-40'-80'$ and a fixed final energy of 14.7 meV. The line shows a fit to the data using two modes convoluted with the resolution function. Peak positions from both constant-energy and constant- Q scans are plotted for two in-plane directions in reciprocal space in (b) and (c), along with the three modes of the dispersion curve (solid lines) given by Eq. (4) [$J = 2.44(7)$ meV and $D = 0.38(7)$ meV]. Dashed lines indicate two (dispersionless) crystal field levels of Ho at 1.5(1) and 3.1(1) meV. Inset: L dependence of the spin-wave spectrum, showing no discernible dispersion.

dispersion in the out-of-plane direction, indicating primarily 2D spin dynamics. Data were also taken at 50 K, in the high-temperature phase, and a comparison of two constant- Q scans at the magnetic zone center are shown in Fig. 3(a). The zone-center gap decreases significantly, as shown in the comparison of the 20 and 50 K dispersion data in Fig. 3(b).

The dispersion of the excitations in HoMnO_3 was calculated using a linear spin-wave analysis. We start from the Hamiltonian

$$H = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + D \sum_i S_i^z S_i^z, \quad (1)$$

where $\langle i, j \rangle$ indicates the sum is over nearest-neighbor in-plane pairs, J is the primary antiferromagnetic exchange, and D is the anisotropy. Introducing three different flavors of bosons and using a Holstein-Primakoff transformation, we derive a linearized Hamiltonian which we diagonalize by mapping to the Hamiltonian of the quadratic quantum mechanical oscillator, similar to Ref. [15]. We define the lattice Fourier sum as

$$z = \frac{1}{12} \{ e^{-2\pi i(H/3-K/3)} + e^{2\pi i(2H/3+K/3)} + e^{-2\pi i(H/3+2K/3)} \}. \quad (2)$$

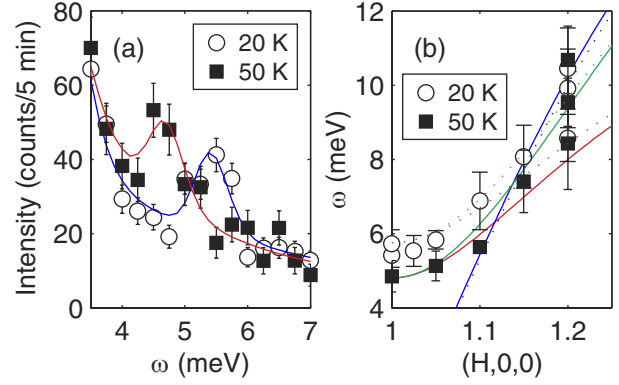


FIG. 3 (color online). (a) Inelastic neutron measurements at $Q = (2, 0, 0)$ at 20 and 50 K. Data were taken on BT9 with horizontal collimations of $40'-40'-40'-40'$ and fixed incident energy of 13.7 meV. Lines show fits to the data. The increase in intensity at lower energies is primarily due to a crystal field excitation at 3.1 meV. (b) Comparison of 20 and 50 K dispersion data near the zone center. Data have been reduced to the first Brillouin zone. Dotted lines show spin-wave dispersion curves for 20 K data, as in Fig. 2. Solid lines show fits of Eq. (4) to 50 K data [$J = 2.44$ meV is fixed and $D = 0.28(3)$ meV].

For simplicity, we now define

$$\begin{aligned} z_1 &= z + z^*, & z_2 &= -(z + z^*)/2 + i(\sqrt{3}/2)(z - z^*), \\ z_3 &= -(z + z^*)/2 - i(\sqrt{3}/2)(z - z^*). \end{aligned} \quad (3)$$

We obtain three modes whose dispersion is given by

$$\omega_i = 3SJ\sqrt{(1 + 4z_i + 2D/3J)(1 - 2z_i)}, \quad (4)$$

where $i = 1, 2, \text{ or } 3$, and $S = 2$ is the spin at the Mn^{3+} ion. Equation (4) was used to fit our data, with the results shown by the curves in Figs. 2(b), 2(c), and 3(b). This simple model provides a remarkably good description of the spin dynamics. Quantitatively, we obtain $J = 2.44(7)$ meV and $D = 0.38(7)$ meV at 20 K. Data taken away from the zone center showed little temperature dependence, while at the zone center there was a significant difference between the 20 and 50 K data, indicating that the temperature dependence of the spin-wave spectrum comes largely from changes in the anisotropy. For the 50 K data, J was therefore kept fixed at 2.44 meV, yielding $D = 0.28(3)$ meV. The increase in the anisotropy D at lower temperatures is significant, and suggests that this anisotropy, likely originating from the holmium, drives the spin-reorientation transition.

In the presence of a magnetic field T_{SR} shifts to lower T and broadens, and HoMnO_3 develops a reentrant $P6_3c/m$ phase. A sharp anomaly in the dielectric susceptibility at T_{SR} indicates a coupling between the magnetic and ferroelectric order [5]. Second-harmonic generation (SHG) measurements as a function of magnetic field also show the change in magnetic symmetry and the reentrant phase as a function of magnetic field suggested by dielectric susceptibility [13]. More recent measurements show a

marked decrease in the strength of the SHG signal (which is due to the magnetic ordering of the Mn^{3+} ions) when an electric field is applied [6].

To investigate the magnetic field-dependent phase diagram, a 0.5 g sample was mounted in the $(H, K, 0)$ scattering plane inside a vertical-field 7 T superconducting magnet with a helium-3 insert. A magnetic field of up to 5 T was applied along the c axis, and the (commensurate) $(1, 0, 0)$ and $(2, 1, 0)$ magnetic peaks were used to track the evolution of the magnetic phases with magnetic field and temperature. In the intermediate-temperature phase, a sufficiently strong applied magnetic field along the c axis pushes HoMnO_3 into the high-temperature phase [5,13]. The boundary between the intermediate- and high-temperature phases (shown in Fig. 5 below as a function of temperature and magnetic field) is in agreement with the phase diagram established from dielectric susceptibility measurements [5,16].

At lower temperatures the transition becomes considerably more complicated. Figure 4(a) shows the peak intensity of the $(1, 0, 0)$ Bragg scattering as a function of magnetic field at several temperatures. At higher temperatures, the intensity decreases approximately linearly with increasing field over a well-defined transition region. At 0.4 K, however, there are two distinct, steplike transitions, with considerable hysteresis in the lower-field transition,

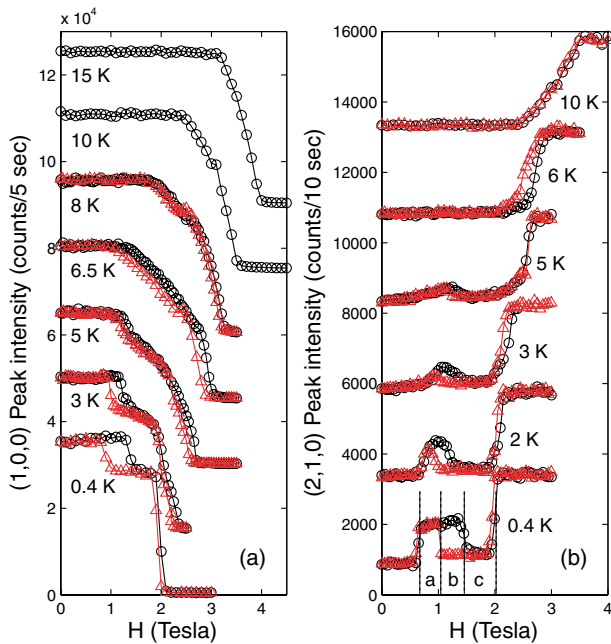


FIG. 4 (color online). (a) $(1, 0, 0)$ magnetic Bragg peak intensity versus magnetic field for different temperatures (offset by 15000 counts for clarity). (b) $(2, 1, 0)$ magnetic Bragg peak intensity versus magnetic field for different temperatures. Circles are data taken with increasing field, while triangles are data taken with decreasing field. Dashed lines show 0.4 K transitions, with two intermediate phases a and c and hysteretic overlap in region b .

indicating the existence of a well-defined intermediate phase between the low- and high-field phases. As the temperature increases, these transitions become broader and the hysteresis decreases, merging together into the single transition (without appreciable hysteresis) observable at higher temperatures.

Figure 4(b) shows equivalent measurements of the $(2, 1, 0)$ Bragg peak intensity. Again, at high temperatures, an approximately linear change in scattering intensity over a well-defined transition region is observable. At low temperatures, as for the $(1, 0, 0)$ reflection, the situation becomes more complicated. Instead of two, we find three transitions, with an additional lower-field transition not observable in the $(1, 0, 0)$ data. Unlike the $(1, 0, 0)$ reflection, the scattering intensity of the $(2, 1, 0)$ reflection does not change monotonically.

Figure 5 shows a phase diagram extracted from the $(1, 0, 0)$ and $(2, 1, 0)$ diffraction data. Below 4 K there are two distinct intermediate phases (labeled a and b) between the zero-field and high-field phases, with significant hysteretic overlap between them. These data are not sensitive to the low-temperature spin reorientation observable in the $(2, 1, 0)$ diffraction data (Fig. 1), indicated roughly by the dashed line in Fig. 5. It is interesting to note, however, that the intermediate phases are observable only below the low-temperature spin-reorientation transition where Ho^{3+} ordering becomes significant.

At higher temperatures, our phase diagram agrees well with previous dielectric measurements [5]. These SHG measurements did not observe any intermediate phase at low temperatures [13], while more recent magnetic sus-

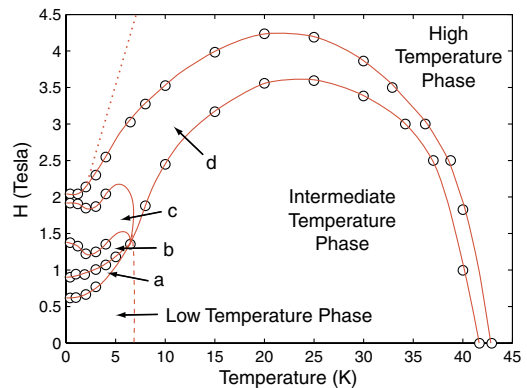


FIG. 5 (color online). Temperature and magnetic field phase diagram for HoMnO_3 obtained from diffraction measurements of the $(1, 0, 0)$ and $(2, 1, 0)$ Bragg reflections. Lines are guides to the eye. Regions a and c are intermediate phases, with hysteretic overlap in region b , as in Fig. 4. Region d is an intermediate phase where peak intensities change continuously. The dashed line is the approximate location of the low-temperature Ho^{3+} ordering transition, and the dotted line is the approximate transition observed by SHG and magnetic susceptibility measurements [13,16]. These transitions were not observable from the $(1, 0, 0)$ and $(2, 1, 0)$ diffraction data.

ceptibility and heat capacity measurements have identified one intermediate phase [16]. While we observe two unambiguous, distinct intermediate phases at low temperatures, the combined intermediate phases we observe agree qualitatively with the intermediate phase recently observed [16]. Further measurements of out-of-plane magnetic peaks will be necessary in order to determine the exact magnetic structure of these intermediate phases. Recent SHG measurements suggest that Ho^{3+} magnetic moments can even be ordered ferromagnetically with the application of an electric field [6]. Neutron scattering reveals considerable complexity in the magnetic field phase diagram for HoMnO_3 , and extending these neutron measurements to the electric field phase diagram may also prove similarly revealing.

The out-of-plane magnetic interactions in HoMnO_3 , both between successive Mn^{3+} layers and between Mn^{3+} and Ho^{3+} , are almost completely frustrated. It is therefore not surprising that the spin dynamics in the intermediate- and high-temperature phases are two dimensional in nature, and we find that the spin-wave spectrum is well described by Eq. (1). Ferroelectric lattice distortions relieve the interplane frustrations in HoMnO_3 [6], and may be the driving force behind the spin-reorientation transitions of the Mn^{3+} magnetic lattice. The role of Ho in these reorientation transitions may be very similar to the role of Nd in Nd_2CuO_4 , another layered transition-metal oxide in which frustrated interplanar interactions enable weak, higher-order interactions to dictate the magnetic structure. Nd_2CuO_4 has a noncollinear structure [17] with Cu spin-reorientation transitions [18,19] that are controlled by the rare earth single-ion anisotropy [20,21]. We suggest that it is a similar interaction in HoMnO_3 that controls the spin-flop transition, and is the origin of the magnetic-ferroelectric coupling.

There has been considerable experimental progress in recent years on mapping out the magnetic phase diagram of HoMnO_3 and discovering signatures of the interplay of magnetic and ferroelectric order in various physical properties. However, a theoretical understanding of these interactions is still lacking. Although a complete theoretical description of HoMnO_3 will necessarily require significantly more complexity than Eq. (1), having experimentally determined the dispersion relations and values for the primary magnetic exchange constants is an important step toward being able to model the interaction between ferroelectric and magnetic order in HoMnO_3 .

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