

Magnetic orders and spin-flop transitions in the cobalt doped multiferroic $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$

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We present a comprehensive single crystal neutron diffraction investigation of the $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ with $0.02 \leq x \leq 0.30$. At lower concentration $x \leq 0.05$, the system is quickly driven into the multiferroic phase with spin structure forming an elliptical spiral order similar to the parent compound. The reduction of electric polarization is ascribed to the tilting of the spiral plane. For $x \sim 0.075$, the magnetic structure undergoes a spin flop transition that is characterized by a sudden rotation of the spin helix envelope into the ac plane. This spin structure persists for concentration up to $x = 0.15$, where additional competing magnetic orders appear at low temperature. For $0.17 \leq x \leq 0.30$, the system experiences another spin flop transition and recovers the low- x spiral spin configuration. A simple commensurate spin structure with $\vec{q} = (0.5, 0, 0)$ is found to coexist with the incommensurate spiral order. The complex evolution of magnetic structure in Co doped MnWO_4 contrasts sharply with other transition metal ion doped $\text{Mn}_{1-x}\text{A}_x\text{WO}_4$ ($\text{A}=\text{Zn}, \text{Mg}, \text{Fe}$) where the chemical substitutions stabilize only one type of magnetic structure. The rich phase diagram of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ results from the interplay between magnetic frustration and spin anisotropy of the Co ions.

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I. INTRODUCTION

The observation of spontaneous electric polarization and magnetic control of ferroelectricity in perovskite manganite TbMnO_3 ¹ has inspired much theoretical and experimental efforts searching for new magnetoelectric multiferroic materials due to their great technological and fundamental importance.²⁻⁴ New of magnetic multiferroics among transition metal oxides have since been discovered that include rare-earth manganite derivative RMnO_3 and RMn_2O_5 ($\text{R}: \text{Y}, \text{Gd}, \text{Dy}$),⁵⁻⁸ geometrically-frustrated triangular lattice CuTmO_2 ($\text{Tm}: \text{Fe}, \text{Cr}$),^{9,10} Kagome lattice antiferromagnet $\text{Ni}_3\text{V}_2\text{O}_8$.¹¹ In the conventional (type-I) ferroelectric materials, the electric polar state arises either from the covalent bonding between filled-shell oxygen atom and empty d -shell non-magnetic transition metal ion (*e.g.* BaTiO_3),¹² or the inversion symmetry breaking caused by the $6s^2$ orbital (lone pair) that moves away from the centrosymmetric position (*e.g.* BiMnO_3).¹³ Even if magnetic ions might be present in these materials, the spins order at much lower temperature than the electric dipoles and the effect of magnetic transition on the dielectric constant is weak. In contrast, the new family of magnetoelectric multiferroics (type-II) exhibits an exceptionally strong sensitivity to an applied magnetic field that causes reversal and sudden flops of the electric polarization.^{1,6,8} Such level of control indicates the electric polarization is induced by the magnetic order, which typically has an incommensurate noncollinear spiral configuration. The onset of ferroelectricity correlates with the transition to

the spiral spin order. The intimate link between these two order parameters marks the prominent and intriguing feature of the new class of multiferroics.

The mineral Hübnerite MnWO_4 is one of few multiferroics that is ideal for studying the complex spin orders caused by magnetic frustrations and the interplay between magnetism and ferroelectricity.¹⁴⁻¹⁶ Without chemical doping, the parent compound undergoes sequential magnetic transitions in zero magnetic field.^{17,18} The system first enters a collinear spin structure (AF3) around 13.5 K with sinusoidal modulation of the magnetic moment, the corresponding incommensurate (ICM) wavevector appears at $\vec{q}_3 = (0.214, 0.5, -0.457)$ and the moment of the Mn ions are confined in the ac plane at a angle of 35° towards the a axis. At 12.6 K, an ICM elliptical spiral spin order (AF2) sets in, accompanied by the spontaneous electric polarization along the crystallographic b axis. The magnetic order at AF2 phase has the same magnetic wavevector $\vec{q}_2 = \vec{q}_3$ while the helix spin structure is characterized by the moment tilting out of the ac plane towards the b axis. As the system is further cooled down below 7 K, the ICM magnetic order is replaced by a commensurate (CM) magnetic order (AF1) that also suppresses the electric polarization. The close proximity of three different magnetic phases and the metamagnetic transitions proves the existence of significant magnetic frustration in the system, as revealed by the inelastic neutron scattering measurements.^{19,20} Consistent with the theoretical studies,^{21,22} investigation of spin wave excitations in the low- T $\uparrow\uparrow\downarrow\downarrow$ spin order indicates that the collinear spin state results from the bal-

ance of long range magnetic interactions between Mn^{2+} ions up to 11th neighbors.²⁰ There are higher order magnetic exchange interactions with strength comparable to the nearest neighbor exchange coupling along the zigzag spin chain in the c axis and between the zigzag chains in the a axis direction. However, the magnetic interactions between the chains in the b axis are much weaker. This finding suggests that different magnetic structures are close in energy and compete for the magnetic ground state. Like other multiferroic materials, the magnetic and ferroelectric phases in this system are expected to be tuned with small perturbations in the form of magnetic field,^{7,8,14,23} pressure^{24–27}, and even chemical substitution with various transition metal ions. MnWO_4 is known to form stable compounds when Mn is replaced by Fe,^{28,29} Co, Ni, Cu³⁰ or Zn.³¹ It was reported that the chemical doping with magnetic Fe ions stabilize the low- T collinear and CM spin order.^{32–34} Both neutron diffraction and electric polarization measurements show that the low- T magnetic ground state is completely converted into the collinear spin order (AF1 phase) with 5% of Fe substitution, which is largely due to the increased Fe single ion anisotropy.³⁵ In contrast, substitution with nonmagnetic ions (Zn or Mg) has shown to alter the magnetic ground state differently from the Fe ions. Replacement of only a few percent of above mentioned nonmagnetic ions seems to be sufficient to suppress the commensurate AF1 phase and stabilize the spiral spin order.^{36,37} A similar effect was also observed in the Co-substituted compound $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ by neutron diffraction and bulk magnetic measurements on polycrystalline samples. Song *et al.*³⁸ found that the CM collinear state is replaced by the ICM spiral phase with 5% Co concentration; a spin flop transition occurs with increasing Co doping with the corresponding spiral plane tilting away from the b axis. The modification of the magnetic structure is expected to switch the electric polarization direction from the b to a axis as it was later confirmed in a single crystal of $\text{Mn}_{0.9}\text{Co}_{0.1}\text{WO}_4$.^{39,40} However, it was discovered that with further increasing of Co doping ($\sim 15\%$), the only measurable polarization was along the b axis.⁴¹ This result indicates that new type of spin structure responsible for the a axis polarization is bound to a narrow range of Co substitution and the actual x – T phase diagram of the $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ is more complex than the one reported from powder diffraction studies.³⁸

In order to elucidate the nature of the magnetic ground state upon Co doping, we performed a comprehensive neutron single-crystal diffraction study of the doped $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$. We observed a systematic evolution of the magnetic structure with increasing Co doping. The spin configurations at different phases are depicted in Figure 1. For lower concentration ($x \leq 0.05$), the system exhibits a spiral spin configuration similar to the undoped MnWO_4 , but with decreased angle between the normal axis of the spiral plane and the c axis. At $x \approx 0.075$, the system undergoes a magnetic transition to a phase in which the spin helix flops into the ac plane. The ac

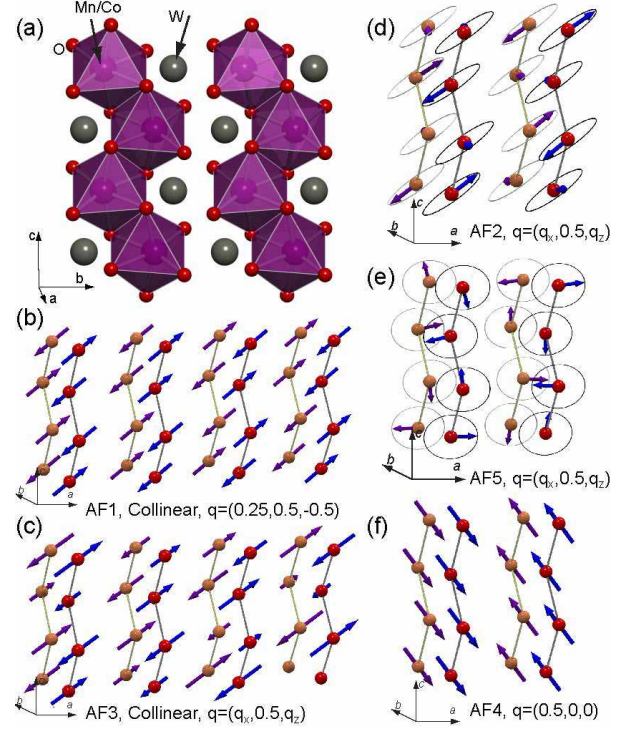


FIG. 1. (Color online) (a) The crystal structure of the $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$. The spin structures of (b) the collinear, commensurate (CM) AF1 phase, spin moments are in the ac plane with a angle of $\sim 35^\circ$ to the a axis, (c) the collinear, incommensurate (ICM) AF3 phase, magnetic moments have the same direction as AF1 but with modulated amplitude, (d) the noncollinear, ICM AF2 phase, one axis of the spiral ellipse lies in the ac plane, the other along the b axis. (e) the noncollinear ICM AF5 phase, the envelope of the spin helix lies in the ac plane, (f) the collinear, CM AF4 phase, spin moments are in the ac plane with a angle of -50° to the a axis. Per rotation convention for the right-handed coordinates, the positive rotation angle with respect to the a axis is associated with the counterclockwise rotation when viewing the system along the negative direction of the axis of rotation.

spiral spin structure and the associated polarization P_a and P_c survive in the range of $0.075 \leq x \leq 0.15$. For higher Co concentration, the system experiences a second spin flop transition such that the spin order switches back to low- x spiral structure coexisting with a collinear CM magnetic structure as observed in pure CoWO_4 .⁴² The complete phase diagram shown in Figure 2 of Co-substituted MnWO_4 is obtained based on the neutron diffraction and bulk property measurements. The chemical substitution of magnetic Co ion provides an unique method to fine tune the magnetic property that is capable of achieving magnetoelectric control with multiple value states.

Single crystals of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ with thirteen different compositions ($0.02 \leq x \leq 0.3$) have been grown in a floating zone optical furnace. We use powder X-ray diffraction to check the phase purity of the polycrystalline feed rod before the crystal growth. No impurity

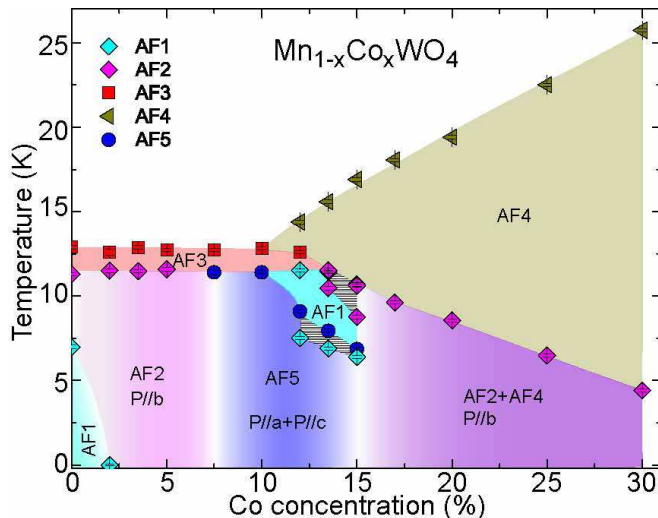


FIG. 2. (Color online) The phase diagram of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ as function of temperature and Co concentration x . Due to the strong hysteresis of the magnetic order, transitions between different phases are identified with warming protocol. Labels of various magnetic phases correspond to the spin structures displayed in Figure 1.

phase could be detected within the resolution of the spectra. The chemical composition and the Co content of the single crystals were verified by energy-dispersive X-ray (EDX) measurements testing up to 15 different spots of a single crystal. As further confirmed by neutron diffraction measurement, the Co content of all samples was close to the nominal composition. In the following sections, we will use the nominal composition to distinguish between different substitution levels. Single crystal neutron diffraction experiments were carried out at the High Flux Isotope Reactor of the Oak Ridge National Laboratory. We used the HB1A, HB1, and HB3 triple axis spectrometers to study the doping and temperature evolution of the magnetic diffraction pattern. We chose an incident neutron beam with wavelength of 2.366 Å and pyrolytic graphite (PG) crystals as monochromator and analyzer. The crystals were aligned in several scattering planes in order to probe different magnetic reflections. For nuclear and spin structure determination, we used the HB3A four-circle single crystal diffractometer to collect both the nuclear and magnetic reflections with neutrons of wavelength 1.536 Å at selected temperatures. The crystal and magnetic structure refinement were performed using the FULLPROF SUITE package.⁴³ Magnetic representation analysis is performed to choose appropriate basis vectors to describe the various spin structures. The sample temperature was regulated either using close cycle refrigerator (CCR) or liquid Helium cryostat. All samples under study belong to the monoclinic P2/C (No. 13) space group. With increasing Co concentration x , the lattice parameters of a, b, c , and the angle of β systematically decrease over the range studied, as determined by the X-ray powder diffraction measurement shown in Figure 3.

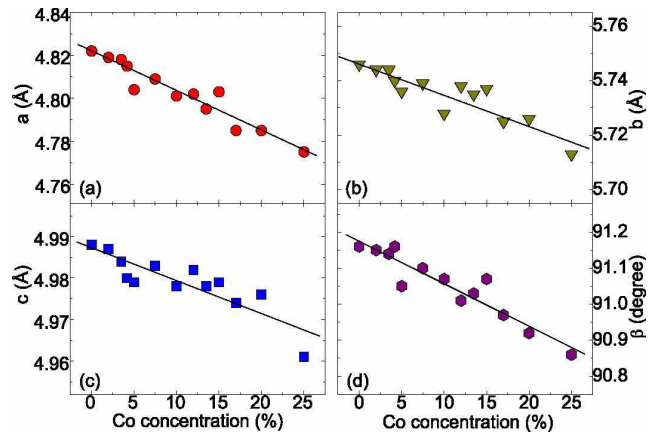


FIG. 3. (Color online) Doping dependence of the lattice parameter a, b, c and the angle β of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ at room temperature characterized by X-ray powder diffraction. The crystal structure of all samples are refined with the monoclinic P2/C space group. Solid lines are guides to the eye.

II. MAGNETIC ORDER AT LOW CONCENTRATION ($0.02 \leq x \leq 0.05$)

We start with the neutron diffraction results of the lower Co concentration. The samples were aligned in a horizontal scattering plane defined by two orthogonal vectors of $[1,0,-2]$ and $[0,1,0]$. Although the magnetic propagation wavevectors in the pure MnWO_4 is determined to be $\vec{q} = (0.214, 0.5, -0.457)$ that deviates slightly from the scattering plane used in the measurement, the coarse vertical resolution of the triple axis spectrometer is sufficient to capture the magnetic Bragg reflections and track their temperature and doping evolution. In the rest of the paper, we will use the wavevector $(q, 0.5, -2q)$, which is the projected value in the horizontal scattering plane, to denote the ICM magnetic Bragg peak unless specified otherwise. Figure 4 summarizes the thermal evolution of the ICM magnetic order at lower cobalt concentration with $x = 0.02, 0.035, 0.042$, and 0.05. The integrated intensities of magnetic scattering for these samples grow monotonically below 13 K without any sign of anomaly at lower temperatures. Such feature contrasts with the undoped MnWO_4 where the multiferroic AF2 phase is sandwiched between the high- T AF3 and the low- T AF1 phases, resulting in an abrupt suppression of the ICM magnetic scattering. Like the nonmagnetic Zn and Mg doping,^{36,37} the multiferroic state associated with the noncollinear ICM phase is stabilized with Co substitution and becomes the ground state. It is noted that the T -dependence of the integrated intensities does not separate the phase boundary between the high- T AF3 and the multiferroic AF2 phases [Fig. 4(a)]. However, there are clear changes of the peak center across the phase transition that label the phase boundary between the collinear and noncollinear phases. In addition, the peak position is independent of the temperature in the AF2 phase, but changes continuously in the AF3 phase,

as demonstrated in Figs. 4(b)-(c) for the $x = 0.035$ and 0.05 samples.

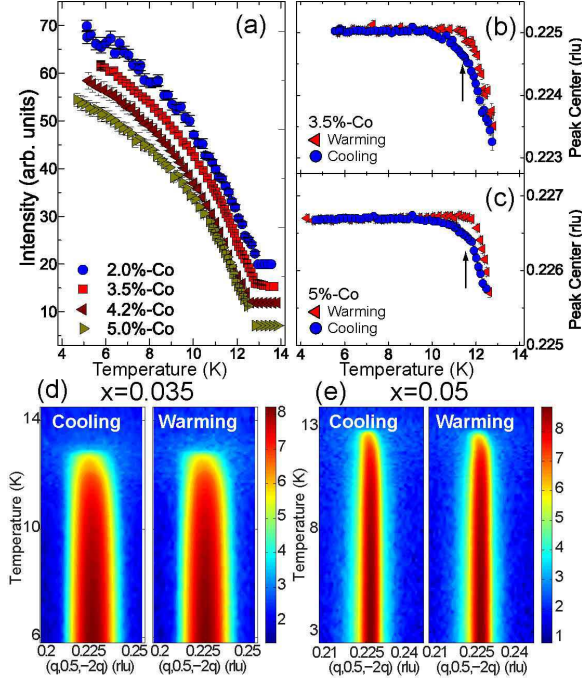


FIG. 4. (Color online) (a) The T -dependence of ICM magnetic order parameters for $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ with $x = 0.02, 0.035, 0.042$, and 0.05 . The order parameter data are shifted vertically for clarity. (b) and (c) display the T -dependence of the ICM peak centers upon cooling and warming for the $x = 0.035$ and $x = 0.05$ samples, respectively. Arrows indicate the transition between the high- T collinear and the low- T noncollinear phases. Contour plot of wavevector scans as function of temperature for (d) $x = 0.035$ and (e) $x = 0.05$ upon cooling and warming.

TABLE I. Refined parameters of the magnetic structure for the $x = 0.02, 0.035, 0.042$, and 0.05 samples in the non-collinear AF2 phase. m_b and $m_{\perp b}$ denote the projected moments along the two principle axes of the spin ellipse along and perpendicular to the b axis. θ is the angle between $m_{\perp b}$ and the a axis, or the angle between the normal vector \vec{n} of the spiral plane and the c axis. The eccentricity of the spin helix is defined as $\epsilon = (1 - m_b^2/m_{\perp b}^2)^{1/2}$ to describe the deviation from a circular envelope. Notice the $x = 0.075$ sample undergoes rotation transition of the spiral plane on cooling and locks into the AF2 phase. R_{F2} is the R-factor calculated by $R_{F2} = 100 \sum_n (|G_{obs}^2 - G_{calc}^2|) / \sum_n G_{obs}^2$, where G^2 is the square of the structure factor for n observed reflections.

nominal x	$m_b(\mu_B)$	$m_{\perp b}(\mu_B)$	ϵ	θ	R_{F2}
0.02	3.86(5)	4.44(6)	0.49(2)	28.4(9)	4.22
0.035	3.91(5)	4.42(6)	0.47(2)	19.2(12)	5.83
0.042	3.86(6)	4.52(9)	0.52(2)	20.1(13)	5.71
0.05	3.82(5)	4.33(6)	0.47(2)	15.3(12)	4.90
0.075	3.47(5)	4.62(6)	0.66(2)	5.5(12)	7.56

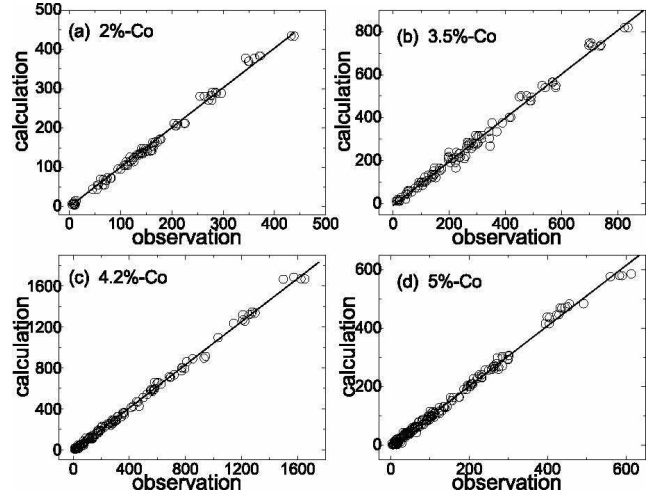


FIG. 5. Agreement plot of the magnetic structure refinement at (a) $x = 0.02$, (b) $x = 0.035$, (c) $x = 0.042$, and (d) $x = 0.05$. The calculated structural factor F_{calc}^2 are plotted against the experimental observation F_{obs}^2 . The corresponding spin structures are shown in Fig. 1(d) and the inset of Figure 6.

The magnetic configurations of the AF2 phase for $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ at low- x can be determined using single crystal magnetic diffraction experiments. As summarized in Tab. I, the refinement parameters indicate the spin structure is well described by the elliptical spiral as in the pure MnWO_4 and the doped $\text{Mn}_{1-x}\text{Zn}_x\text{WO}_4$.^{17,37} Figure 5 shows the agreement plot between model calculation and experimental observations for all samples. Contrary to the Zn substitution, where the angle θ between the normal vector \vec{n} of the spiral plane and the crystallographic c axis remains constant for Zn concentration up to $x = 0.40$, the value of θ shows a gradual decrease with increasing Co concentration [Fig. 6(a)]. The refinements also indicate that there is considerable deviation of the ellipse from a perfect circular envelope as quantified in the Tab. I. To correlate the spin structure and the ferroelectric properties, Fig. 6(b) displays the T -dependence of electric polarization \vec{P} at different x . Clearly, a smooth decrease of the saturated polarization along the b axis is observed, a trend similar to the doping dependence of the angle θ . Within the microscopic picture of spin current or inverse Dzyaloshinskii-Moriya (DM) model,^{44–46} the expected electric polarization can be expressed as

$$\vec{P} = A \vec{e}_{ij} \times (\vec{S}_i \times \vec{S}_j), \quad (1)$$

where \vec{e}_{ij} is the unit vector connecting the neighboring spins \vec{S}_i and \vec{S}_j . The inset of Fig. 6 describes a general spin helix configuration; the normal vector \vec{n} of the spiral plane has angle θ with respect to the c axis and its projection in the ab plane has angle ϕ towards the a axis. Using spherical coordinates, we can express $\vec{n} = \sin \theta \cos \phi \vec{e}_x + \sin \theta \sin \phi \vec{e}_y + \cos \theta \vec{e}_z$, where \vec{e}_i are the unit vectors along the i^{th} cartesian coordinates

($i = x, y, z$). Since the angle between the crystallographic a and c axes is close to 90° , we will consider $\vec{e}_x \parallel \vec{a}$, $\vec{e}_y \parallel \vec{b}$, and $\vec{e}_z \parallel \vec{c}$ for the sake of simplicity. The magnetic moments of two spins in the chemical unit cell for the helical state can be expressed as

$$m(\vec{R}_i, \alpha) = m_{\parallel} \cos(2\pi\vec{q}\vec{R}_i + \Phi_\alpha) + m_{\perp} \sin(2\pi\vec{q}\vec{R}_i + \Phi_\alpha), \quad (2)$$

where $\vec{R}_{i,\alpha}$ is the position vector of the Mn site $\alpha (= 1, 2)$ in the unit cell i , \vec{q} is the magnetic propagation wavevector of the spiral structure, $\Phi_2 = \Phi_1 + \pi(q_z + 1)$, and m_{\parallel} and m_{\perp} are the long and short half axis of the magnetic ellipse, respectively. If we consider the dominant magnetic exchange coupling is along the c axis zigzag chain, the electric polarization can be quantitatively written as

$$\vec{P}_1 = C_1 m_{\parallel} m_{\perp} \sin \pi q_z (-\sin \theta \sin \phi \vec{e}_x + \sin \theta \cos \phi \vec{e}_y). \quad (3)$$

If, however, there is additional non-negligible exchange interactions between the chains along the a axis, the extra contribution to the polarization is

$$\vec{P}_2 = C_2 m_{\parallel} m_{\perp} \sin 2\pi q_x (-\cos \theta \vec{e}_y + \sin \theta \sin \phi \vec{e}_z), \quad (4)$$

where C_1 and C_2 are constants independent on θ and ϕ , and q_x, q_z are components of the ICM magnetic wavevector. The spin structure refinement in the AF2 phase reveals $\phi = 0$; this leads to a simplified form of $\vec{P}_1 = C_1 m_{\parallel} m_{\perp} \sin \pi q_z \sin \theta \vec{e}_y$ and $\vec{P}_2 = -C_2 m_{\parallel} m_{\perp} \sin 2\pi q_x \cos \theta \vec{e}_y$, both contributing to the b axis polarization. It becomes evident that the magnitude of \vec{P} is proportional to the angle θ between spiral normal \vec{n} and the c axis, given there is no significant deviation of the ellipticity and the moment size. With both \vec{P}_1 and \vec{P}_2 taken into account, the total electric polarization becomes $P_b \sim C_1 m_{\parallel} m_{\perp} \sin \theta (1 - C_2/C_1 \cot \theta)$. It can be further simplified as $P_b \sim C_1 m_{\parallel} m_{\perp} \sin \theta$ assuming $|C_2| < |C_1|$ due to a shorter exchange path along the zigzag chain direction (3.29 Å along the c axis versus 4.83 Å along the a direction). One can then estimate that the saturated polarization $P_b(x = 0.05)$ decrease to $\sin 15^\circ / \sin 35^\circ \sim 0.45 P_b(x = 0)$ due to the rotation of the spiral plane, which is very close to the measured value. The close correlation between the rotation of the spin helix plane and the decreasing ferroelectric polarization emphasizes that the doped MnWO_4 is indeed a prototypical multiferroic material with inverse DM interaction being the origin of the spontaneous electric polarization.

III. MAGNETIC ORDER AT INTERMEDIATE CONCENTRATION ($0.075 \leq x \leq 0.15$)

As the Co concentration increases to $x = 0.075$, ferroelectric polarization measurement does not detect any significant b axis component within the resolution of the experiment.⁴⁷ However, a large polarization was found along the a axis accompanied by a small component

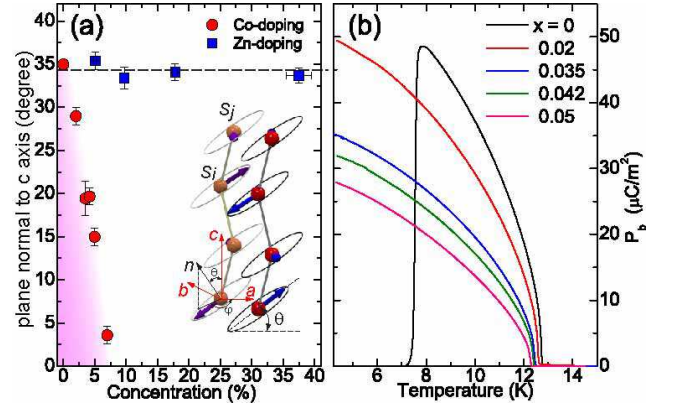


FIG. 6. (Color online) (a) The doping dependence of the angle θ between spiral plane normal and the c axis for the Co doped MnWO_4 . For comparison, the results of the Zn-doped samples are also shown. Inset shows the schematics of the elliptical spiral spin configuration in the AF2 phase. The normal vector \vec{n} of the spiral plane has a angle of θ with respect to the c axis, the projection of \vec{n} on the ab plane has a angle of ϕ to the a axis. (b) The T -dependence of electric polarization \vec{P}_b for $x = 0, 0.02, 0.035, 0.042$ and 0.05 .⁴⁷

along c , which implies that the system undergoes major change in spin structure that causes the reorientation of the polarization. To correlate the polarization result, we studied the T -dependence of the wavevector scans upon cooling and warming as displayed in Figs. 7(a)-(b). One can clearly observe a strong hysteresis in the magnetic scattering during thermal cycling. Upon cooling, the peak center shifts from $\vec{q}_1 \approx (0.234, 0.5, -0.468)$ that is associated with the high- T collinear AF3 phase and moves into a plateau with another ICM wavevector $\vec{q}_2 \approx (0.232, 0.5, -0.464)$ for $7 \text{ K} < T < 11 \text{ K}$ [Figs. 7(a) and 7(d)]. As the sample is further cooled to lower temperature, the magnetic peak resumes shifting and finally locks into the low- T ICM phase with $\vec{q}_3 = (0.229, 0.5, -0.458)$. On warming, the same low- T magnetic order remains at the wavevector \vec{q}_3 till $T \sim 10 \text{ K}$ and suddenly is converted to the high- T collinear AF3 phase.

To understand the complex evolution of the magnetic order, the same sample was placed on the four-circle single crystal diffractometer to investigate the spin structure. We chose the cooling protocol and collected data at two characteristic temperatures $T = 9 \text{ K}$ and 4.5 K . Figs. 8(a)-(b) display the refined spin configurations. At $T = 9 \text{ K}$, the magnetic spins form an ac spiral structure (termed as AF5 phase) with two principle axes of the ellipse lying along the crystallographic a and c directions. The normal vector \vec{n} of the new spiral plane is characterized by $\theta = 90^\circ$ and $\phi = 90^\circ$. According to Eqn. 1, such magnetic structure will cause the rotation of P_b into other directions. If we only consider that the dominant magnetic interactions are along the spin chain direction (c axis), the cross product of \vec{n} and \vec{e}_{ij} would only induce the a axis electric polarization in a form of $P_a = -C_1 m_a m_c \sin \pi q_z \vec{e}_x$, where m_a and m_c are the pro-

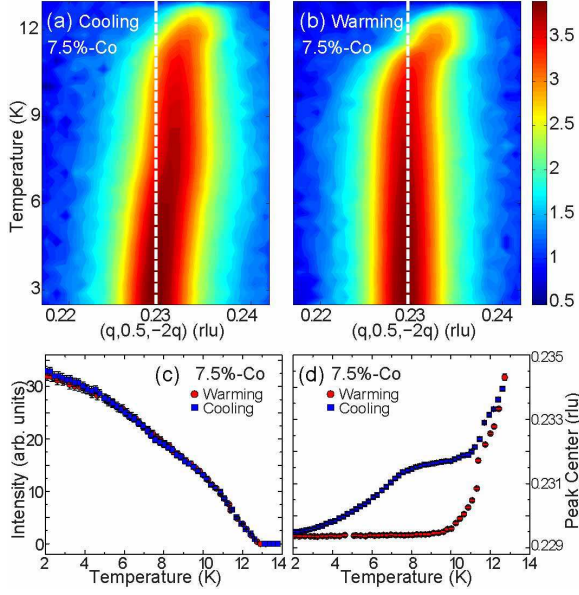


FIG. 7. (Color online) The T -dependence of the wavevector scans of the ICM magnetic peak for $x = 0.075$ sample upon (a) cooling and (b) warming. The dashed lines in (a)-(b) are guides the eyes to illustrate the locked in peak position at the lowest temperature probed. Panels (c)-(d) display the T -dependence of the integrated intensity and the peak center of the ICM scattering.

jected moments of the spin helix along a and c . This prediction only agree partially with the experimental observation where both P_a and P_c develop below 10 K.⁴⁷ To explain the presence of P_c , we have to consider the interchain magnetic interactions along the a axis. Recent spin wave measurements in MnWO_4 have revealed that the interchain magnetic interactions are of the same order as the intrachain exchange coupling in its collinear spin state.²⁰ Although the obtained results are for the collinear spin structure, it is expected they will have similar strength when the system enters the noncollinear AF2 phase, based on what has been found in the pure CuFeO_2 and the multiferroic $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$.^{48,49} Taking the interchain magnetic interactions into account, the contribution to the electric polarization has the form of $P_c = C_2 m_a m_c \sin 2\pi q_x \vec{e}_z$. This prediction of small polarization along c is in accordance with the bulk polarization measurement.

With the sample cooled below 8 K, it was found that both P_a and P_c are suppressed. Such feature suggests a gradual change of the spin structure that might be due to either the distortion of the elliptical envelope or the rotation of the spiral plane. Since both polarizations are proportional to $m_a m_c$ for an ac spiral structure, the increased eccentricity of the spiral ellipse could certainly yield a reduced bulk polarization. On the other hand, the rotation of the spiral plane away from the ac plane can also lead to the suppression of polarization along both directions. The spin structure determination with data

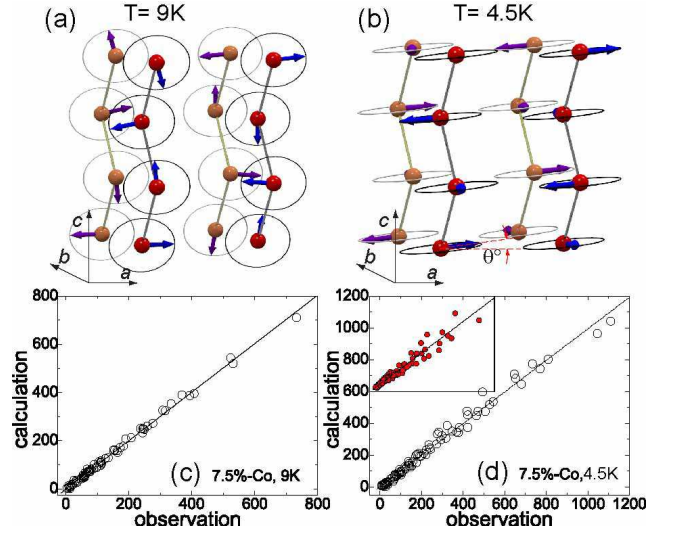


FIG. 8. (Color online) The refined spin structure for $x=0.075$ sample at (a) 9 K and (b) 4.5 K. The corresponding agreement plots of the refinements are plotted on (c) and (d). Inset of panel (d) shows the agreement plot at $T = 4.5$ K using the same elliptical spiral at 9 K. The scattered data points indicate a poor description of the spin configuration.

collected at 4.5 K provides a definitive answer to separate those two possibilities. As shown in Fig. 8(b), the system at base temperature shows a completely different spin structure from the one at 9 K. It possesses the configuration similar to the low Co concentration with the short axis of the spin ellipse along the b axis and the long axis residing in the ac plane. The canted angle θ between the spiral plane normal vector \vec{n} and the c axis is $\sim 5.5^\circ$. The result reveals that the $x = 0.075$ sample is located near the boundary between distinct spin configurations of the low- x spiral and the ac spiral structure.

To understand the spin flop transition near $x_c = 0.075$, we recall that the spiral spin order allows the coupling linear in gradient of the magnetic order parameter (also known as Lifshitz invariant) with broken inversion symmetry and induces a uniform electric polarization according to the Ginzburg-Landau approach.⁴⁵ The energy gain originating from the nonlinear coupling between \vec{P} and \vec{M} ($\sim \gamma \vec{P} \cdot [\vec{M}(\nabla \cdot \vec{M}) - (\vec{M} \cdot \nabla)\vec{M}]$) and the corresponding electric polarization is proportional to the angle θ . With increasing Co concentration, both the electric polarization \vec{P} and the energy gain decrease because of the decreasing angle. It is not surprising that there exists a critical concentration x_c , around which the system can no longer gain energy to maintain the magnetic structure. Such instability will then bring about a spin flop transition to the observed ac spiral which can reduce the free energy further because of the sizable polarization. Compared to other multiferroics, the continuous change in the magnetic wavevector from the transition between different spin configurations of the Co doped MnWO_4 appears rather rare. The gradual transition highlights

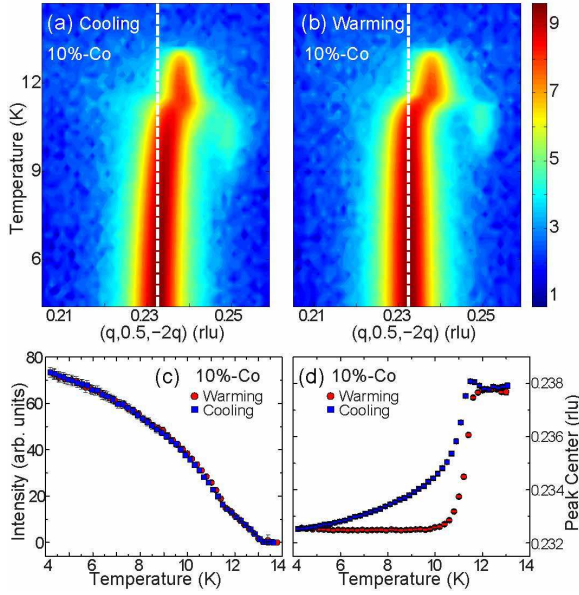


FIG. 9. (Color online) The T -dependence of the wavevector scans of the ICM magnetic peak for $x = 0.10$ sample upon (a) cooling and (b) warming. Notice the weak commensurate AF1 reflections at $\vec{q} = (0.25, 0.5, -0.5)$ is present near 11 K for both cooling and warming protocols. Panels (c)-(d) display the T -dependence of the integrated intensity and the peak center of the ICM scattering.

that the high- T spiral and the low- T ac spiral spin structures are nearly degenerate in energy such that a small change in temperature would drive the system between competing magnetic states characterized by a continuous rotation of the spiral plane.

Figs. 9(a)-(d) show the neutron diffraction results on the $x = 0.10$ sample. The hysteresis of the magnetic order upon thermal cycling is still discernable. However, the shift of the magnetic wavevector is much smoother upon cooling and does not show the plateau as seen at $x = 0.075$. Accordingly, electric polarizations show continuous growth upon cooling. The saturated P_a and P_c reach 100 and 30 $\mu\text{C}/\text{m}^2$ at 4 K, respectively. P_a exceed the maximum b -axis polarization of MnWO_4 by nearly a factor of two. With warming, the low- T spin structure remains till 11 K and a transition to the high- T collinear AF3 phase occurs. The lack of abrupt change in the ICM wavevector suggests the modification of the spin structure is not as drastic as the $x = 0.075$ sample and the same ICM spin structure is preserved to the lowest temperature. In a recent neutron diffraction study on the $x = 0.10$ sample, Urcelay-Olabarria *et al.* obtained similar result and found that the magnetic spins remain in the ac plane at all temperatures while the eccentricity reduces from $\epsilon = 0.66$ at 9 K to 0.42 at 2 K, suggesting the spiral ellipse becomes more circular at lower temperature.⁴⁰ Another noteworthy feature in the $x = 0.10$ sample is that the energy of the ac spiral structure is close to other competing state includ-

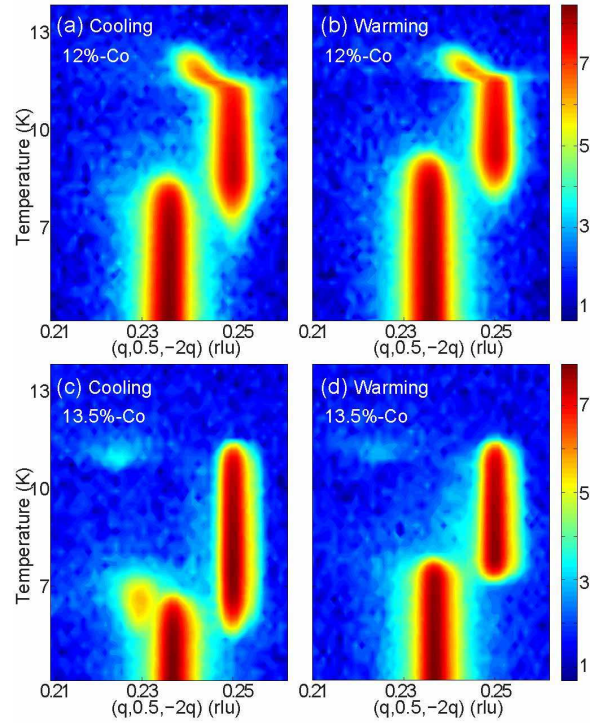


FIG. 10. (Color online) The T -dependence of the wavevector scans of the magnetic peaks for $x = 0.12$ sample upon (a) cooling and (b) warming. The system undergoes ICM AF3, CM AF1, and ICM AF5 phases as cooling. Similar scans on the $x = 0.135$ sample are presented on (c) and (d). Only CM AF1 and ICM AF5 orders appear as the major phases. In panel (c), a minor AF2 phase with $\vec{q} = (0.23, 0.5, -0.46)$ appears at $5.8 \text{ K} < T < 7.6 \text{ K}$.

ing the collinear AF1 phase. This can be appreciated by the weak magnetic reflection at the CM wavevector $\vec{q} = (0.25, 0.5, -0.5)$ near 11 K [Figs. 9(a)-(b)].

The evolution to other competing magnetic orders is manifested at higher Co concentration. Figure 10 displays the T -dependence of the wavevector scans for two samples with $x = 0.12$ and $x = 0.135$. At $x = 0.12$, the first magnetic order present in the scattering plane consisting of the $[1, 0, -2]$ and the $[0, 1, 0]$ directions is the collinear AF3 phase, which locks into the commensurate AF1 phase at lower temperature. With the sample cooled below 9.0 K, the previously observed AF5 phase sets in and extends to the lowest temperature without any noticeable shift of the magnetic wavevector. There is narrow range of temperature window that both the AF1 and AF5 phases are present between $6.8 \text{ K} < T < 9.0 \text{ K}$. On warming, reverse order of the magnetic phases is observed except the coexisting region shifts up to $7.5 \text{ K} < T < 9.3 \text{ K}$. Interestingly, the order of appearance for the commensurate AF1 and the multiferroic AF5 phases is exactly opposite to the pure MnWO_4 , where the AF1 phase occurs at lower temperature. At $x = 0.135$, the transition between the collinear AF3 and the AF1 phases vanishes.

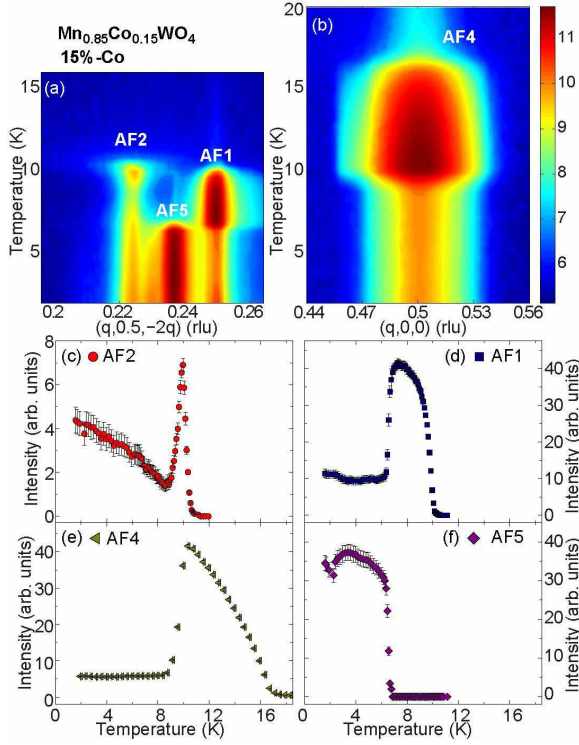


FIG. 11. (Color online) The T -dependence of wavevector scan near the magnetic orders of the $x = 0.15$ sample along (a) the $[H, 0.5, -2H]$ and (b) the $[H, 0, 0]$ directions. Panels (c)-(f) are the T -dependence of integrated intensities for the AF2, AF1, AF4, and AF5 phases.

There is very weak scattering near the ICM wavevector $\vec{q} = (0.225, 0.5, -0.45)$ that exists in a very narrow range of $10.7 \text{ K} < T < 11.3 \text{ K}$, which was later identified as the AF2 phase. The strongest intensity is only one percent of that for the AF1 phase and is too weak to induce any detectable polarization signal. We also observed the coexistence of the multiferroic AF5 phase and collinear AF1 phase. The coexisting region downshifts to $5.5 \text{ K} < T < 7.2 \text{ K}$ for cooling and $7.0 \text{ K} < T < 7.8 \text{ K}$ for warming. At lower temperature, the AF1 phase is completely suppressed.

The $x = 0.15$ sample is probably the most complex system with a minimum of five coexisting magnetic phases.⁴¹ Fig. 11 summarizes the thermal evolution of the various magnetic orders probed at two scattering planes. Panel (a) shows the T -dependence of wavevector scans along the $[H, 0.5, -2H]$ direction where the AF1, AF2, and AF5 can be surveyed. Panel (b) displays the scans along the $[H, 0, 0]$ direction where the commensurate AF4 magnetic order with $\vec{q} = (0.5, 0, 0)$ can be examined. Upon cooling, the AF4 phase first appears around 17 K and the intensity increases continuously till 10 K. A sharp drop in its intensity is accompanied by the simultaneous development of the commensurate AF1 and multiferroic AF2 phases. With the sample cooled below 6.6 K, the CM AF1 phase is also suppressed and ad-

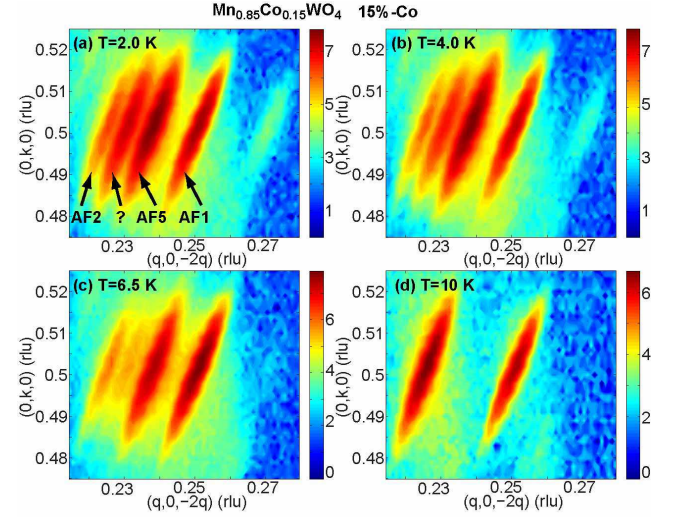


FIG. 12. (Color online) The reciprocal space mapping near the CM and ICM magnetic reflections at (a) 2 K, (b) 4 K, (c) 6.5 K and (d) 10 K. At least four distinct magnetic reflections are observed in this scattering plane at low temperatures.

ditional ICM AF5 phase develops at lower temperature. Figs. 11(c)-(f) summarize the T -dependence of integrated intensities for the four major magnetic (the commensurate AF1, AF4 and incommensurate AF2, AF5) phases in the $x = 0.15$ sample. Since the magnetic intensity of AF2 phase closely follows the b axis polarization P_b , it is speculated that such state has a spiral spin structure similar to the $x \leq 0.05$ samples. Notice even at the lowest temperature, there are finite magnetic scattering from the commensurate AF1 and AF4 phases.

To confirm the coexistence of various magnetic orders, we have performed extensive survey in the reciprocal space at selected temperatures at 2.0, 4.0, 6.5, and 10 K as shown in Figure 12. The appearance and disappearance of competing magnetic orders is evident. At 10 K, only the AF2 with $\vec{q}_2 = (0.225, 0.5, -0.45)$ and AF1 with $\vec{q}_1 = (0.25, 0.5, -0.5)$ phases are present, while more magnetic Bragg peaks appear at lower temperature. A distinct magnetic reflection appearing as the shoulder of the AF5 Bragg peak becomes visible in the low- T mapping [Fig. 12(a)-(b)]. The peak is located between the AF2 and AF5 phases with wavevector $\vec{q} = (0.23, 0.5, -0.46)$. The exact nature of this magnetic order remains unknown since its reflection is too close to the neighboring AF2 and AF5 Bragg peaks. It is worth to point out this unknown magnetic phase is already present at $x = 0.135$, but only exists within a very narrow temperature range [Fig. 10(c)]. This magnetic fluctuation continues to grow in intensity upon cooling at $x = 0.15$. Together with the already identified commensurate AF1, AF4 phases and incommensurate AF2, AF5 phases, there are five magnetic orders at the lowest temperature. Such remarkable coexistence of many competing magnetic phases marks the $x = 0.15$ sample as the most frustrated system.

Table II lists the refined magnetic structures for the $x = 0.075, 0.10, 0.12$, and 0.135 samples in the AF5 phase as well as the commensurate AF1 and AF4 phases for the $x = 0.135$ sample. As mentioned in Sec. III, the $x = 0.075$ sample is located near the phase boundary between the low- x spiral and the ac spiral structures; its magnetic structure can be refined as an ac spiral configuration only for $T > 8$ K. In contrast, the magnetic ground states of the $x = 0.10, 0.12$ samples are well described by the same ac spiral structure at low temperatures. Although the ICM magnetic order seems to be the only low- T phase for the $x = 0.135$ sample, it cannot be refined by a pure ac spiral structure implying the deviation from that configuration. To get a good agreement between the observation and model calculation, we chose a combined low- x spiral and ac spiral structure to fit the experimental data and yield satisfactory result. The spin structure is best characterized as modified ac helical structure that the normal vector of the spiral plane tilts way from the b axis. Such spin order result in a reduction of electric polarization and is consistent with the bulk measurement that both P_a and P_c decrease for $x > 0.10$.⁴⁷

TABLE II. Refined parameters of the magnetic structures at $x = 0.075, 0.10, 0.12$, and 0.135 . The spin configurations of the $x = 0.075$ sample at 9 K and the $x = 0.10, 0.12$ samples at 5 K can be refined as an ac spiral structure with its principle axes aligning along the a and c directions. The $x = 0.135$ sample is refined to be the AF4 phase at 12 K, the AF1 phase at 9 K and the modified AF5 phase at 5 K. The moment direction has a angle of -33° with respect to the a axis in the AF1 phase and -52° to the a axis in the AF4 phase. At the AF5 phase, the spin helix has one of its two principle axes in the ac plane and the other in the bc plane.

x	phase	moment (μ_B)		R_{F^2}	
0.135	AF4	$m_a : 0.817(8)$	$m_c : -1.051(9)$	11.33	
0.135	AF1	$m_a : 3.13(3)$	$m_c : -2.07(4)$	8.08	
		Real	Imaginary	ϵ	
0.075	AF5	$m_a : 3.45(4)$	$m_c : 2.67(4)$	0.63	4.81
0.10	AF5	$m_a : 4.05(4)$	$m_c : 3.14(5)$	0.63	7.41
0.12	AF5	$m_a : 4.04(6)$	$m_c : 3.56(7)$	0.46	5.83
0.135	AF5	$m_a : 4.03(4)$	$m_c : 3.53(5)$	7.06	
		$m_c : -0.81(7)$	$m_b : -0.10(7)$		

With Co concentration $x > 0.10$, we have observed the expansion of both commensurate AF1 and AF4 phases as shown in Figure 13. Overall, samples in this doping region form the commensurate AF4 spin structure with $\vec{q}_4 = (0.5, 0, 0)$ at higher temperature and enter directly the collinear AF1 phase upon cooling, which is different from pure MnWO_4 . With increasing x , the transition to the AF1 state moves to lower temperature while the transition to the AF4 phase shifts to higher one. Although both phases at $x = 0.10, 0.12, 0.135$ are completely suppressed at low- T , they survive for the $x = 0.15$ sam-

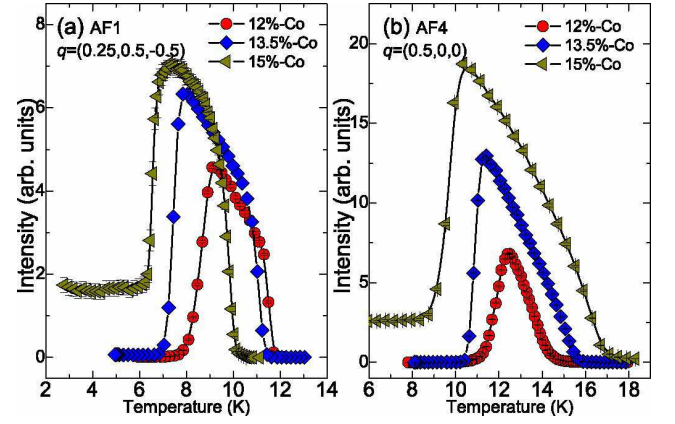


FIG. 13. (Color online) The T -dependence of integrated intensity for (a) the AF1 phase with $\vec{q} = (0.25, 0.5, -0.5)$ and (b) the AF4 phase with $\vec{q} = (0.5, 0, 0)$ at $x = 0.12, 0.135$, and 0.15 . Both the AF1 and AF4 states survive at low temperature for the $x = 0.15$ sample.

ple indicating the collinear spin structures gradually become the stable magnetic ground state at large x . Magnetic structure refinements in this doping range reveal that the spin moments in the AF4 phase are confined in the ac plane, with an angle of -50° towards the a axis (Tab. II). This spin reorientation is again due to the strong anisotropy of Co^{2+} ions^{42,50} that locks the Mn^{2+} spins in the same direction and makes the collinear spin structure more favorable with increasing x . We further note that the spins in the collinear AF1 phase have a angle of -33° with respect to the a axis, which is different from pure MnWO_4 , and is probably due to the pinning of the high- T AF4 magnetic structure.

IV. MAGNETIC ORDER AT HIGH CONCENTRATION ($0.17 \leq x \leq 0.30$)

Finally, we focus on the magnetic structures for $x \geq 0.17$. The bulk polarization measurements show no detectable P_a and P_c . Instead, the polarization is pointing to the b axis, the same direction as observed at lower Co concentration. Thus, the switch of the polarization suggests another major modification of the spin structure. Fig. 14 compares of T -dependence of wavevector scans across the ICM peak of four Co doped samples with $x = 0.17, 0.20, 0.25$, and 0.30 . The scattering profile in this doping regime exhibits different character. Unlike the coexistence of various competing magnetic orders in the intermediate doping regime, there is only one ICM magnetic reflection at the wavevector of $\vec{q} \approx (0.22, 0.5, -0.44)$. The transition temperature decreases from 9.6 K at $x = 0.17$ to 4.4 K at $x = 0.30$. The scattering intensity of the ICM magnetic order is also suppressed with increasing x as displayed in Fig. 15(a). Further survey in reciprocal space reveals that there is one strong collinear AF4 phase that is established at

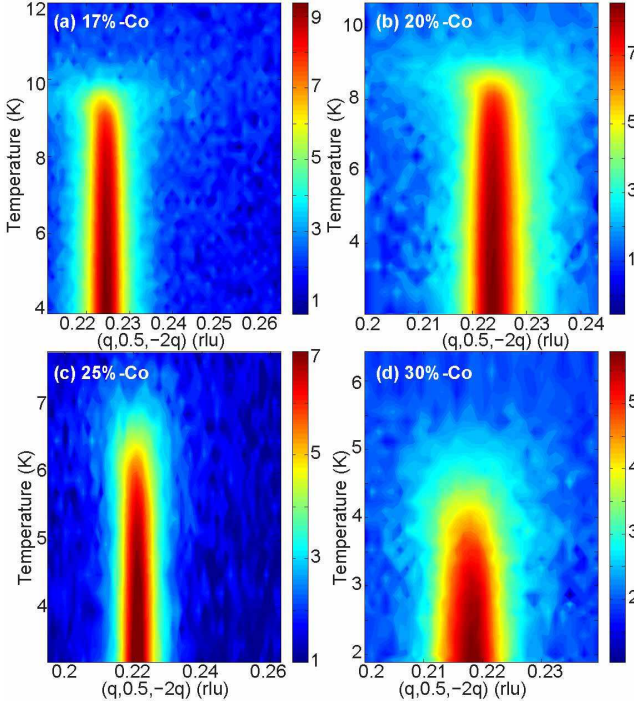


FIG. 14. (Color online) (a) The T -dependence of the wavevector scans of the magnetic orders along the $(H, 0, -2H)$ direction for $x = 0.17, 0.20, 0.25$, and 0.30 .

higher temperatures and persist to the lowest temperatures [Fig. 15(b)]. The transition temperature increases sharply with Co concentration and reaches 25 K for the $x = 0.30$ sample. For all samples studied, the magnetic intensities of the AF4 phase exhibit a kink at temperatures corresponding to the onset of the mentioned ICM magnetic order indicating a strong interplay between the CM and ICM phases.

TABLE III. Magnetic structure parameters at $x = 0.17$. The sample has collinear AF4 phase with $\vec{q} = (0.5, 0, 0)$ at 11 K and 5 K. At $T = 5$ K, additional AF2 spiral structure is formed. m_a and m_c are the spin components along the a and c axes in the collinear phase. The real $m_{\perp b}$ and imaginary m_b denote the projected moments of the long and short spiral ellipse lying in the ac plane and along the b axis. θ is the angle of the $m_{\perp b}$ with respect to the a axis.

phase	T	moment (μ_B)		θ	R_{F2}
AF4	11 K	$m_a : 1.47(3)$	$m_c : -1.86(2)$	-51.6°	6.47
AF4	5 K	$m_a : 1.47(1)$	$m_c : -1.90(1)$	-52.3°	6.25
		Real	Imaginary	ϵ	
AF2	5 K	$m_{\perp b} : 2.92(7)$	$m_b : 2.36(4)$	0.39	5.11

Since all samples in this doping region show similar magnetic properties except the transition temperature, we chose the $x = 0.17$ sample for the crystal and magnetic structure refinement and expect the other doped samples have smooth evolution of the spin structure. As

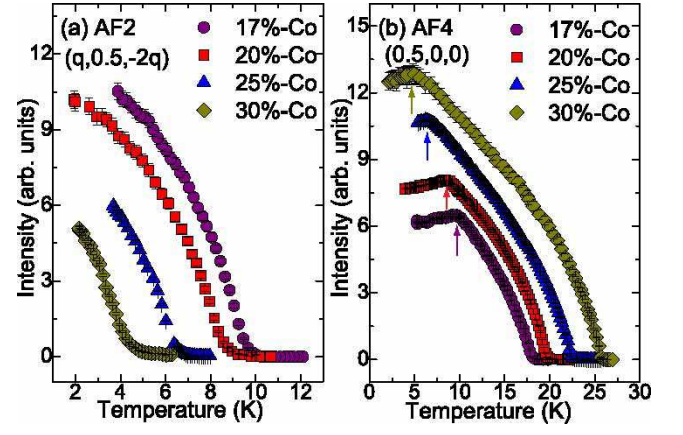


FIG. 15. (Color online) (a) The T -dependence of the integrated intensities of the AF2 phase for $x = 0.17, 0.20, 0.25$, and 0.30 . (b) The T -dependence of the integrated intensities of the AF4 phase with $\vec{q} = (0.5, 0, 0)$ for the same samples. Arrows label the transitions where the low- T AF2 phases set in. The magnetic scattering intensities are normalized to the intensities from the nuclear reflections for comparison.

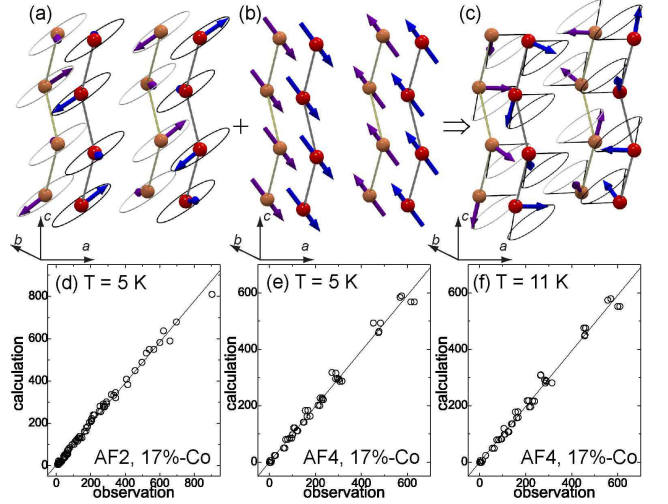


FIG. 16. (Color online) The spin configurations of (a) the low- T incommensurate AF2 phase, (b) the high- T incommensurate AF4 phase, and (c) the conical spin order resulting from the superposition of the AF2 and AF4 phases. Agreement plots for (d) the incommensurate AF2 phase at 5 K, (e) the commensurate AF4 phase at 5 K, and (f) the commensurate AF4 phase at 11 K.

demonstrated in Figs. 14-15, there are two major magnetic phases with ICM and CM wavevectors for $x = 0.17$. We collected 193 nuclear reflections at 5 K for the structural determination. One set of magnetic reflections for the low- T ICM magnetic structure were collected to refine the spin structure and two sets of magnetic reflections with $\vec{q} = (0.5, 0, 0)$ are collected at 5 K and 11 K separately to investigate how the collinear AF4 phase is affected by the low- T ICM magnetic order. Figs. 16(a)-(b) show the corresponding magnetic structures of the

ICM spiral order and the CM AF4 phase. At 11 K, only the collinear AF4 phase exists, the magnetic spins form in a configuration identical to CoWO_4 , where the moments lie in the ac -plane, with a angle of $\theta \approx -50^\circ$ towards the a axis. With the sample cooled below 10 K where the ICM order sets in, the magnetic structure of the collinear spin order is not modified; the spins remain in the same direction and the total moment of $2.42(4)\mu_B/\text{site}$ at 5 K is almost the same as $2.39(3)\mu_B/\text{site}$ at 11 K (Tab. III). On the other hand, attempting to refine the low- T ICM order using the ac spiral structure gives poor fit to the collected data. We adopted the spin configuration at low Co concentration because such spin structure provides an electric polarization along the b axis. As shown in Fig. 16(d), this model provides a good description of the experimental data. The spin moment of the spiral state varies from $2.36\mu_B$ to $2.92\mu_B$ which is comparable with the moment size at the AF4 phase. The observation of spiral order with the helix plane similar to the low- x case implies that the $x = 0.17$ sample is located at another phase boundary where the system undergoes a second spin flop transition consistent with $\vec{P} \parallel b$. However, there is one apparent difference between the $x \leq 0.05$ and $x \geq 0.17$ samples. There is only one ICM AF2 phase in the low Co concentration samples, while the ICM AF2 phase appearing in the high- x samples coexists with the commensurate AF4 phase that is established at higher temperature. The simultaneous presence of two magnetic phases is similar to the colossal magnetoresistance related manganite $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (PCMO), in which both the ferromagnetic and antiferromagnetic components are observed at low temperature.⁵¹ This can be interpreted either as a canted antiferromagnetic structure or coexisting FM and AFM phases. Similarly, neutron diffraction data alone can not differentiate whether the observed coexistence of AF2 and AF4 orders in $\text{Mn}_{0.83}\text{Co}_{0.17}\text{WO}_4$ arises from two separated phases, each with distinct magnetic wavevector; or if they originate from one single phase with two- k magnetic structure. One definite identification would be the spatial sensitive probe in conjunction with the electric polarization measurement. Our neutron diffraction result at $x = 0.17$ is consistent with recent study on the $x = 0.20$ sample, where the coexisting collinear AF4 and multiferroic AF2 phases are revealed.⁵² The authors concluded that the superposition of the competing AF4 and AF2 magnetic structures leads to a conical antiferromagnetic order that is depicted in Fig. 16(c).

V. DISCUSSION AND CONCLUSIONS

The comprehensive single-crystal neutron diffraction measurement, in combination with the magnetic property and polarization measurements, make it possible to construct the phase diagram of the $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ as function of Co concentration and temperature. Unlike other transition metal ion doped MnWO_4 , where only one type of spin configuration is stabilized, a rich va-

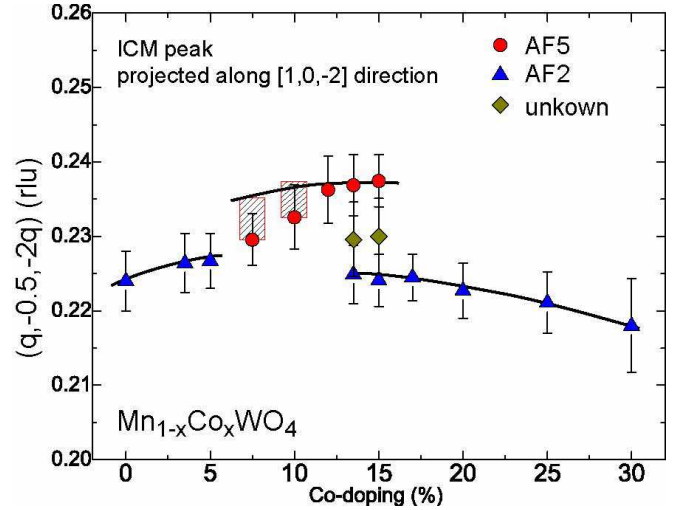


FIG. 17. (Color online) The doping dependence of incommensurability of the low- T magnetic structures. The low- T spin orders are labeled with different symbols. The shadow region for the $x = 0.075$ and $x = 0.10$ samples indicates the samples undergo continuous change of the magnetic wavevectors upon cooling. Solid lines are guides to the eye. For $x = 0.15$ and 0.17 , there are additional magnetic Bragg reflection between the known AF2 and AF5 phases.

riety of spin structures and complex evolution between different phases are observed as the Co concentration is increased. It is noted that the spin anisotropy of the Co ions plays a vital role in defining the low- T magnetic structures. Although confined in the same ac plane, the spin easy axis in CoWO_4 is -45° from the a axis, and is nearly 90° away from the easy axis direction in MnWO_4 .^{42,53} With increasing x , the long axis of the spiral ellipse that initially has a positive angle towards the a axis will tilt gradually to the negative direction due to the single ion anisotropy of the Co^{2+} . The rotation of the spin helix plane leads to decrease of the electric polarization $|\vec{P}|$ that is compatible with the magnetic symmetry, as well as the energy gain that is coupled to the $|\vec{P}|$. At the critical concentration of $x = 0.075$, the system cannot gain enough energy to maintain the multiferroic phase, thus results in the spin flop transition. The new ac spiral structure helps the system lower the free energy because of the large value of the ferroelectric polarization. For $0.075 \leq x \leq 0.15$, the presence of the P_a and P_c instead of P_b is consistent with an ac spiral spin structure, and highlights the significant intrachain as well as the interchain interactions. Although the samples in the intermediate doping exhibit similar spiral structure, the maxima of the electric polarizations only occur near $x = 0.10$. It results mainly from the rotation of the spiral plane as exemplified by the neutron diffraction data from the $x = 0.075, 0.135$ samples. The perfect ac spiral order is realized at $x \approx 0.10$ that induces the largest polarization. Further increasing x not only causes the deviation from a pure ac spiral configuration, but also introduces

collinear AF1 and AF4 spin orders that reduce the effective moment of the spiral structure responsible for the polarization. A second spin flop transition takes place with $x \geq 0.17$ and leads to the same spiral structure as in the low Co concentration. This phase coexists with a CM collinear AF4 phase with spin configuration similar to CoWO_4 .

The phase diagram is characterized by three well-defined regions distinguished by different spin spirals. However, the evolution of the magnetic spin structure within individual region is gradual. This can be better appreciated by examining the concentration dependence of the incommensurability of the low- T noncollinear order, as shown in Fig. 17. The magnetic wavevector of the ICM order does not exhibit a lock-in value over the wide range of Co concentration. Instead, it varies smoothly within each of the three regions. For the samples near the $x = 0.075$ phase boundary, the ICM magnetic structure is unstable such that a small temperature variation will cause the rotation as well as the periodicity change of the spiral structure. All these observations reinforce that the magnetic structure results from the delicate balance between the competing exchange interactions and spin anisotropy of the transition metal ions.

Without chemical substitution, MnWO_4 appears to be a highly frustrated system where the magnetic and ferroelectric properties can be tuned by external stimuli like the magnetic and electric field.^{54–60} The introduction of Co ions with distinct spin anisotropy also serves a parameter to fine tune the magnetic ground states. This is very similar to the rare-earth multiferroic manganite RMnO_3 , in which the ferroelectric polarization is enhanced by the magnetic order of rare earth elements,⁶¹ except that the tuning parameter is on the same magnetic site in the case of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$. We hope the current experimental study would inspire further theoretical effort to understand the magnetic and ferroelectric order parameters in this doped system. Most importantly, such work would provide a new pathway to design and synthesize magnetoelectric-control materials with multiple magnetic and ferroelectric ground states.

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