Chemical doping-induced flop of ferroelectric polarization in multiferroic $\text{Mn}_{0.9}\text{Co}_{0.1}\text{WO}_4$

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We studied the multiferroic properties of the incommensurate spiral phase of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ using single-crystal neutron-diffraction and ferroelectric measurements. Whereas the rotational plane of the spin spiral is parallel to the b axis for $x \leq 0.05$, it flops by 90° for $x = 0.10$. As a result, the direction of the ferroelectric polarization also flops from the b to the a axis. These results show that the orientation of the ferroelectric polarization in MnWO_4 can be controlled via chemical doping.

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I. INTRODUCTION

Exploiting strong coupling between spin and charge degrees of freedom in complex oxides has been one of the most intensively studied topics in recent condensed-matter physics. Importance of their intimate coupling is well demonstrated in magnetotransport properties of colossal magnetoresistive manganites.¹ Nowadays a new form of magnetoelectric coupling is attracting a great deal of attention, in which long-range magnetic order is responsible for generating ferroelectricity.^{2,3} This distinct phenomenon, often called magnetoelectric multiferroics, is observed when exchange interactions produce acentric spin structures due to competitions or geometrical constraints. The ferroelectricity observed in most of long-wavelength antiferromagnets can be explained by the spin-current mechanism.⁴ In this theory, ferroelectricity arises via spin-orbit coupling between neighboring ions, and the ferroelectric polarization between two spins, $\mathbf{S}_i$ and $\mathbf{S}_j$, separated by $\mathbf{e}_{ij}$ from each other is determined by the relation $\mathbf{P}_e \propto \mathbf{e}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j)$.⁴ Noncollinear spin arrangements as well as lifting of inversion symmetry are thus critically important for the spin-current ferroelectricity to occur.⁵⁻⁷

MnWO_4 is one of the prototypical multiferroic materials exhibiting spin-current ferroelectricity.⁷ It has three antiferromagnetic phases at low temperatures: collinear sinusoidal incommensurate order below $T_N = 13.5$ K [AF3, $\mathbf{k}_3 = (-0.214, \frac{1}{2}, 0.457)$], spiral incommensurate order below $T_2 = 12.3$ K (AF2, $\mathbf{k}_2 = \mathbf{k}_3$), and collinear commensurate order below $T_1 = 8.0$ K [AF1, $\mathbf{k}_1 = (\pm\frac{1}{4}, \frac{1}{2}, \frac{1}{2})$].^{8,9} Among them,

only the AF2 phase exhibiting spiral order shows ferroelectricity.⁷ Its spiral plane is parallel to the b axis and tilted with respect to the other axes whereas the shortest exchange paths form zigzag chains along the c axis. As a result, the largest ferroelectricity is observed along the b axis as predicted by the spin-current theory.⁷ The direction of the ferroelectric polarization can be switched to a different orientation by application of external magnetic fields. For instance, the spiral plane flopped by 90° when a magnetic field was applied parallel to the b axis, which was accompanied by a simultaneous flop of the ferroelectric polarization from the b to the a axis.^{7,10} When the magnetic field was applied perpendicular to the b axis, in contrast, the AF2 phase was stabilized down to 2 K.^{10,11} This behavior is a good signature of the strong correlation between the spiral magnetic order and the ferroelectric polarization in MnWO_4 .

Its magnetic order as well as magnetoelectric properties can also be changed via chemical doping. García-Matres *et al.*¹² reported that the incommensurate AF2 phase was suppressed and the commensurate AF1 phase stabilized when Mn^{2+} ions were replaced by Fe^{2+} ions. The ferroelectric phase could then be restored by applying strong external magnetic field.¹³ Recently, our group observed an opposite behavior with Co doping. When Mn^{2+} ions were replaced by 3% or more of Co^{2+} ions, the AF2 phase was stabilized and the AF1 phase suppressed.¹⁴ When the doping level reached up to 10%, the spiral plane was observed to tilt off the b axis. This spin-flop phase was labeled as AF2' because the precise direction of the tilt could not be distinguished by analyzing the powder-diffraction data alone.

In this follow-up work, we present the result of single-crystal neutron diffraction and report that the spiral plane flops by 90° for $x=0.10$. We also report that the ferroelectric polarization in this phase shows the largest value along the a axis.

II. EXPERIMENTAL

Single-crystal samples of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ ($x=0, 0.05$, and 0.10) were grown by floating-zone method. Magnetic susceptibility was measured using a vibrating sample magnetometry, and ferroelectric polarization was measured by integrating the pyroelectric current. Neutron-diffraction measurements were performed using two instruments. Temperature dependence of the magnetic Bragg reflections were measured at SPINS cold neutron triple-axis spectrometer of the NIST Center for Neutron Research ($\lambda=4.14$ Å). The data for magnetic structure refinement were collected using the TriCS four-circle diffractometer¹⁵ at Swiss Spallation Source (SINQ) (Ref. 16) of the Paul Scherrer Institute [$\lambda=2.32(1)$ Å]. The magnetic structure refinement was performed using the FULLPROF suite.¹⁷

III. RESULTS AND DISCUSSIONS

A. Magnetization and order parameter

Figures 1(a) and 1(b) show the magnetic susceptibilities ($\chi=M/B$) of $\text{Mn}_{0.9}\text{Co}_{0.1}\text{WO}_4$ along three different crystallographic orientations and their temperature derivatives ($d\chi/dT$), respectively. Two magnetic phase transitions are clearly identified at low temperatures.⁷ The transition at $T=T_N=13.1$ K shows up as changes in slopes in the susceptibilities along all three directions. This change appears most sharply for χ_a , suggesting that the ordered spins are oriented close to the a axis. In contrast, the transition at $T=T_2=11.4$ K is not clearly visible in χ_b , but weakly noticeable in χ_a or χ_c . This transition is more easily noticed in the temperature derivatives, in which stepwise changes are observed toward opposite directions between the two curves [see Fig. 1(b)]. The initial transition at T_N corresponds to the onset of the collinear sinusoidal AF3 order whereas the one at T_2 to the spiral AF2' order as described in the Ref. 14. The transition from the AF2 to the AF1 at T_1 is apparently absent, which is in contrast to MnWO_4 .

The magnetic Bragg reflections also show consistent behaviors. Figure 1(c) shows the intensity of the $(0.221, -\frac{1}{2}, -0.472)$ magnetic Bragg peak as a function of temperature. The intensity initially appears at T_N , and a small kink is observed in its intensity as the temperature is reduced through T_2 indicating the changes in the magnetic structure factor. Nevertheless, it continues to increase down to the lowest temperature and shows no sign of an additional transition.

B. Magnetic structure refinement

Magnetic neutron-scattering intensity from ordered spins depends not only on their internal correlations but also spatial orientations with respect to the momentum transfer wave

FIG. 1. (Color online) Temperature dependence of (a) magnetic susceptibilities ($B=1000$ Oe), (b) their temperature derivatives, and (c) integrated intensity of the magnetic Bragg peak of $\text{Mn}_{0.9}\text{Co}_{0.1}\text{WO}_4$. In (a), the susceptibility of MnWO_4 powder is also shown for comparison. Also shown in (c) with smaller symbols is the temperature dependence of the magnetic Bragg-peak intensity of MnWO_4 . The solid lines are guide to the eyes.

vector, $\mathbf{Q}$. Therefore, magnetic interaction vectors, $\mathbf{F}_\perp(\mathbf{Q}) = \hat{\mathbf{Q}} \times \mathbf{F}(\mathbf{Q}) \times \hat{\mathbf{Q}}$, should be used in place of magnetic structure factors, $\mathbf{F}(\mathbf{Q}) = \sum_j \mathbf{S}(\mathbf{R}_j) e^{i\mathbf{Q} \cdot \mathbf{R}_j}$, for intensity calculations, such that $I(\mathbf{Q}) \propto |\mathbf{F}_\perp(\mathbf{Q})|^2$.¹⁸ It is for this reason that one can determine the spatial orientations of the spins from neutron-diffraction data. When the spins form elliptical spiral order characterized by the propagation vector $\mathbf{k}_2$, a spin vector located at $\mathbf{R}=\mathbf{R}_j$ can be expressed using the following equation:

$$\mathbf{S}(\mathbf{R}_j) = \mathbf{p} \cos(\mathbf{k}_2 \cdot \mathbf{R}_j + \phi) + \mathbf{q} \sin(\mathbf{k}_2 \cdot \mathbf{R}_j + \phi). \quad (1)$$

Above, $\mathbf{p}$ and $\mathbf{q}$ are mutually orthogonal spin vectors, and ϕ is the phase factor. Then, the magnetic neutron-scattering intensity should depend on the angle (η) between the momentum transfer wave vector and the vector normal to the spiral plane. Then the equation for magnetic intensity can be rewritten as

$$I(\mathbf{Q}) \propto \cos^2 \eta (|\mathbf{p}|^2 + |\mathbf{q}|^2) \left| \sum_j f_j \exp(i\mathbf{Q} \cdot \mathbf{R}_j + \phi) \right|^2, \quad (2)$$

where f_j is the magnetic form factor.

The diagram shown in Fig. 2 is useful in explaining the reason why single-crystal diffraction is necessary in order to understand the precise orientation of the spiral plane in the

FIG. 2. (Color online) Geometry for the pair of scattering wave vectors ($\mathbf{Q}$ and $\mathbf{Q}'$) versus spiral planes. The propagation vector is $\mathbf{k}_2 = (k_h, \frac{1}{2}, k_l)$. The gray circles mark the positions for nuclear Bragg peaks whereas the gray or hatched ellipses represent spiral planes. In this example, note that $|\mathbf{Q}| = |\mathbf{Q}'|$ and $\cos^2 \eta_1 = \cos^2 \eta'_1$ but $\cos^2 \eta_2 \neq \cos^2 \eta'_2$.

AF2 phase. The incommensurate propagation vector of the AF2 phase is $\mathbf{k}_2 = (k_h, k_k, k_l) \approx (-0.221, \frac{1}{2}, 0.471)$. Since $k_k = 1 - k_h$, every magnetic Bragg peak shares the equal magnitude of momentum transfer wave vector with another. For instance, a reflection at $\mathbf{Q} = (h, k, l) + \mathbf{k}_2 = (h + k_h, k + \frac{1}{2}, l + k_l)$ has the same magnitude of wave vector as $\mathbf{Q}' = (h, -k-1, l) + \mathbf{k}_2 = (h + k_h, -k - \frac{1}{2}, l + k_l)$ because $|\mathbf{Q}|^2 = |\mathbf{Q}'|^2 = (h + k_h)^2 \mathbf{a}^* + (l + k_l)^2 \mathbf{c}^* + (k + \frac{1}{2})^2 \mathbf{b}^*$. (Note that $\alpha = \gamma = 90^\circ$ and $\beta \neq 90^\circ$.) The difference in angles between the spiral plane and these two wave vectors, respectively, should produce different intensities at the corresponding magnetic Bragg peaks. (See the case of hatched spiral planes in Fig. 2.) In powder diffraction, however, these two peaks will be observed at the same scattering angle (2θ) resulting in uncertainties during the intensity analysis. Such unfortunate overlaps are avoided in single-crystal diffraction, in which the precise orientation of the spiral plane can be easily revealed by observing the two reflections independently.

Figure 3 summarizes the results of the magnetic structure refinement performed in the AF2(AF2') phases of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ ($x=0.0, 0.05$, and 0.10). For $x=0.0$ and 0.05 , the magnetic intensities can be well reproduced using the previously known elliptical spiral spin structure, in which the spiral plane is parallel to the b axis.⁹ This structure is marked as $\mathbf{p} \parallel \mathbf{b}$ in Fig. 3. The angle between the a axis and the spiral plane is smaller for $x=0.05$ (15.8°) than $x=0.0$ (34.1°), which is consistent with our previous powder-diffraction study.¹⁴ Figure 3(c) shows, however, that the calculation based on the same model fails to reproduce the observed intensity for $x=0.10$, indicating that the spiral plane is tilted off the b axis. We took a similar approach as in the previous study and tried out two other spiral spin models: one with the plane parallel to the a ($\mathbf{p} \parallel \mathbf{a}$), and the other to the c axis ($\mathbf{p} \parallel \mathbf{c}$). Commonly in both cases, we found that the spin components parallel to the b axis is approximately 0.5% of the total moment, and thus negligible. Therefore, one can safely conclude that the

FIG. 3. (Color online) (a)–(c) Results of magnetic structure refinement in the AF2(AF2') phases of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$. The measurement temperatures were $T=9$ K for $x=0.0$, and 4 K for $x=0.05$ and 0.10 . (d) Observed and calculated neutron diffraction profiles for $x=0.10$ using the spiral plane perpendicular to the b axis.

spiral plane becomes perpendicular to the b axis. We then applied this model ($\mathbf{p} \perp \mathbf{b}$) to the previous powder-diffraction data and obtained an excellent agreement between the observed and the calculated intensities [see Fig. 3(d)].

Finally, the obtained magnetic structures of the AF2/AF2' phases are depicted in Fig. 4. The angle between the spiral plane and the a axis initially decreases upon Co doping at $x=0.05$. For $x=0.10$, the spiral plane becomes perpendicular to the b axis, and is composed of magnetic vectors $|\mathbf{p}| = 5.02 \pm 0.05 \mu_B$ and $|\mathbf{q}| = 4.58 \pm 0.05 \mu_B$. Its ellipticity is smaller than the AF2 phase of the undoped compound. The analysis of the nuclear-diffraction data, either powder or single crystal, revealed no particular changes in crystallographic structures as functions of Co doping, except mono-

FIG. 4. (Color online) Magnetic structures of the AF2 phases of (a) MnWO_4 and (b) $\text{Mn}_{0.95}\text{Co}_{0.05}\text{WO}_4$, and the AF2' phase of (c) $\text{Mn}_{0.9}\text{Co}_{0.1}\text{WO}_4$ obtained by single-crystal neutron diffraction. Only the Mn sites and the bonds forming zigzag chains are shown. Also shown are the vectors associated with the spin-current ferroelectric polarization.

FIG. 5. (Color online) (a) Temperature dependence of ferroelectric polarization measured along three crystallographic orientations. Data shown with empty circles are the $(0.221 \ -\frac{1}{2} \ -0.472)$ magnetic Bragg-peak intensity that is scaled to overlap with the ferroelectric polarization. (b)–(d) The ferroelectric polarization along the a axis, P_a under the field applied along three different crystallographic orientations, respectively. (e) and (f) P_b under the field $H \parallel a$ and $H \parallel b$, respectively.

tonic decreases in the lattice parameters or anomalous temperature coefficient of the b axis parameter for $x < 0.1$.¹⁴ Therefore, the same spin-current model is expected to work for the Co-doped AF2' phase. Figure 4 also shows the orientations of the vectors associated with the spin-current ferroelectric polarization. It shows that the ferroelectric polarization of $\text{Mn}_{0.9}\text{Co}_{0.1}\text{WO}_4$ should appear primarily along the a axis instead of the b according to the spin-current theory.⁴ Furthermore, since the spiral plane normal vector is at right angle with respect to the c axis, an enhancement in polarization strength is also expected. The relevant results are discussed in the next section.

C. Ferroelectric polarization

In order to verify the ferroelectric polarization flop due to the Co doping, pyroelectric current was measured along three crystallographic orientations, from which ferroelectric polarization was obtained. The suspected flop of the ferroelectric polarization is confirmed by the data shown in Fig. 5(a). First, it shows that the polarization is observed only

below T_2 , which is in the AF2' phase. Second, the polarization observed along the a axis is substantially larger than those along other directions. Therefore, the flop of the spiral plane is indeed accompanied by the flop of the ferroelectric polarization. Figure 5(a) also shows that the magnitude of the polarization continues to rise as the temperature is lowered down to 2 K. The polarization observed at 2 K ($P_a \approx 90 \ \mu\text{C}/\text{m}^2$) is nearly two times larger than the value observed in the AF2 phase of the undoped compound. It is partially because the angular relation between the spiral plane and the zigzag spin chain is changed in such a way to maximize the spin current. Another reason is that the size of the spin moment continues to increase at low temperatures. In fact, the temperature dependence of the ferroelectric polarization precisely follow the growth of the magnetic moment. In Fig. 5(a), the $(0.221 \ -\frac{1}{2} \ -0.472)$ magnetic Bragg-peak intensity is rescaled and plotted over P_a , which shows that the two data closely overlap with each other. Since the propagation vector barely changes within the AF2' phase, the magnitude of the ferroelectric polarization must be directly determined by the size of the magnetic moment.

Whereas the simple picture of zigzag spin chains expects the polarization only along the a axis, small polarizations are observed along the other two directions. [See Fig. 5(a) for P_b and P_c .] A similar observation has been reported for MnWO_4 as well.⁷ We suppose it is partially due to errors in cutting the crystal for ferroelectric measurements, which could result in leakages of the primary polarization observed along other directions. We do not rule out, however, that it is also due to the fact that the magnetic exchange of MnWO_4 is not truly one-dimensional along the c axis. In fact, the magnetic excitations observed in MnWO_4 were reported to involve nine different exchange constants.¹⁹ If magnetoelectric coupling exists through bonds, for instance, along the a axis, it may produce a nonzero polarization along the c axis. This argument is not applicable to P_b , which seems to be solely due to the error in sample preparation. Figure 5(a) indeed shows that the magnitude of P_c is much larger than P_b .

The field dependence of P_a is also summarized in Figs. 5(b)–5(d). It is apparent that the polarization is hardly changed under the field up to 9 T applied parallel to the b axis. In contrast, the field applied along other directions eventually leads to the reduction in P_a . The change is more drastic when the field applied along the c axis indicating that the spins are relatively more stable along the a axis. The onset of the ferroelectric polarization ($T = T_2$), however, is independent of the strength and direction of the field. This behavior is different from MnWO_4 , in which the temperature range for the ferroelectric phase shrink before the spin-flop transition occurred when the field was applied parallel to the spiral plane.⁷ It also indicates that the AF2' phase in $\text{Mn}_{0.9}\text{Co}_{0.1}\text{WO}_4$ is a stable ground state whereas the AF2 in MnWO_4 is not. It has already been pointed out in our previous powder-diffraction study that the structural lattice of MnWO_4 show a negative temperature coefficient of the parameter b at low temperatures.¹⁴ Such anomalous behavior can be understood if the bond angles along the zigzag chains become smaller as the temperature is lowered. (See Fig. 4 for the zigzag chains.) Such lattice behavior can selectively affect particular exchange interactions, for instance, between

the second-nearest neighbors. Note that the MnO_6 octahedra in MnWO_4 are largely distorted due to the relatively large radii of Mn^{2+} ions, which can easily accommodate the angle changes within the zigzag chain. This anomaly disappears when Co doping level is 10% or larger.¹⁴ Probably the role of Co doping is in making the zigzag chains more rigid and thus maintaining the balance among various exchange interactions.

We have not observed a clear spin-flop transition up to 9 T in $\text{Mn}_{0.9}\text{Co}_{0.1}\text{WO}_4$ but the data seems to suggest that it is probably approaching the boundary for a similar transition. Figure 5(e) shows that the magnitude of P_b increases substantially when the field along the a axis is at 9 T. This change can be understood if the angle between the a axis and the spiral plane starts to increase between 7 and 9 T. The apparent reversal of sign is probably related to the specific details of the tilt direction. Nevertheless, the magnitude of polarization is always the largest along the a axis regardless of the direction and strength of the field.

IV. SUMMARY AND CONCLUSION

We have used single-crystal diffraction to show that the incommensurate spin spiral plane of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ flop from being parallel to the b axis ($x \leq 0.05$) to being perpendicular to it ($x = 0.10$). This spin-flop transition is accompa-

nied by a subsequent flop of the ferroelectric polarization from the b to the a axis, which agrees with the prediction by the spin-current mechanism. The result presented in this work is a good example in which the direction of ferroelectric polarization of a magnetoelectric material can be controlled via chemical doping.

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