Magnetoelectric coupling tuned by competing anisotropies in Mn$_{1-x}$Ni$_x$TiO$_3$

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A flop of electric polarization from $P\|c$ ($P_c$) to $P\|a$ ($P_a$) is observed in MnTiO$_3$ as a spin flop transition is triggered by a c-axis magnetic field, $H_{c1}=7$ T. The critical magnetic field $H_{c1}$ for $P_a$ is significantly reduced in Mn$_{1-x}$Ni$_x$TiO$_3$ (x=0.33). $P_a$ and $P_c$ have been observed with both $H_{c1}$ and $H_{a1}$. Neutron diffraction measurements revealed similar magnetic arrangements for the two compositions where the ordered spins couple antiferromagnetically with their nearest intra- and inter-planar neighbors. In the x=0.33 system, the uniaxial and planar anisotropies of Mn$^{3+}$ and Ni$^{2+}$ compete and give rise to a spin reorientation transition at $T_R$. A magnetic field, $H_{c1}$, aligns the spins along c for $T<T_R$. The rotation of the collinear spins away from the c-axis for $T<T_R$ alters the magnetic point symmetry and gives rise to a new ME susceptibility tensor form. Such linear ME response provides satisfactory explanation for the behavior of the field-induced electric polarization in both compositions. As the Ni content increases to x=0.5 and 0.68, the ME effect disappears as a new magnetic phase emerges.

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I. INTRODUCTION

The multiferroics that show strong magnetoelectric (ME) effect are among the most sought-after materials due to their multi-functionality of inducing polarization with magnetic field or magnetization with electric field. The linear ME effect occurs in a crystal when $\alpha_{ij}$ is nonzero. Here $\alpha$ is a second rank tensor which changes sign under space or time inversion, but is invariant when the occurrences of the two inversions are simultaneous. The magnetic symmetries that meet such conditions are allowed to have linear ME response. Therefore in exploring magnetoelectrics among materials with long range magnetic order, symmetry analysis serves as a reliable guide. Such predictability can be obscured when extra microscopic complications, such as magnetic anisotropy, spin frustration and spin-lattice coupling, have been introduced. However, these extra variables sometimes help to increase the magnitude of $\alpha$ or even give rise to new ME coupling mechanisms.

Mn$_{1-x}$Ni$_x$TiO$_3$ is such a system where more than one ME mechanism has emerged. MnTiO$_3$ and NiTiO$_3$ have the same ilmenite structure (Fig. 1) but different spin arrangements and easy axes which compete in the mixed compounds. Also competing are the energy loss from single ion anisotropy and that from the frustration of the exchange interactions. Various new magnetic phases including spin glass (SG) phase emerge as a result, forming a rather complex phase diagram. While the linear ME effect was observed in MnTiO$_3$ as its magnetic symmetry permits a new ME response is induced by the toroidal moments in the SG state of the mixed compounds. On both sides of the SG phase, the unexplored spin flop transitions, short range magnetic correlations and the Ti$^{4+}$ ions with empty 3d shells are all potential hosts of yet another novel ME mechanism. Although the magnetic structures of the end-member compounds have been studied, the details of the magnetic evolution in the mixed compounds and its effect on the electric polarization are still lacking. This report presents a systematic investigation of the ME effects and the magnetic orders in Mn$_{1-x}$Ni$_x$TiO$_3$. New
components of the ME tensor and an anomaly in their temperature dependence under a low magnetic field have been observed. Neutron diffraction measurement on the x=0.33 compound under an applied magnetic field reveals the effect of the field on the spin orientation and therefore, on the nature of the new ME coupling. Details of the magnetic orders in 4 typical compositions and corrections to the phase diagram are reported.

II. EXPERIMENTAL

Single crystals of Mn$_{1-x}$Ni$_x$TiO$_3$ (x=0, 0.33, 0.50 and 0.68) were grown by the traveling-solvent floating zone technique. For electric polarization measurements, silver epoxy was pasted on the crystals cut into thin plates. The pyroelectric current was measured using a Keithley 6517A electrometer on warming after poling the crystal in an electric field of 800 kV/m while cooling down from above $T_N$. The spontaneous polarization was obtained by integration of the pyroelectric current with respect to time. The single crystal neutron diffraction measurements were carried out at the High Flux Isotope Reactor of the Oak Ridge National Laboratory. The HB-2C Wide Angle Neutron Diffractometer (WAND) with wavelength of 1.482 Å was used for reciprocal space and diffuse scattering surveys. The collections of reflections for structural determination were carried out at HB-3A four circle diffractometer where the wavelength of 1.542 Å was chosen. An assembly of permanent magnets that provides 0.7 Tesla at the sample position was employed in the magnetic field measurement on HB-3A. Closed-cycle refrigerators were used on both diffractometers. The Rietveld refinements on the crystal and magnetic structures were conducted using the FullProf Sütet.

III. RESULTS

A. Pyroelectric measurements under magnetic field

The ME effect was observed in x=0 and 0.33. In both cases the pyroelectric current anomaly signaling the onset of polarization appears only when finite magnetic field is applied along c. Fig. 2 shows the temperature dependence of the spontaneous polarization ($P_c$) under various magnetic fields for the x=0 sample. The previous study only reported the observation of $P_c$ in this compound. As shown in Fig. 2(a), $P_c$ increases monotonically with increasing field until $H_{\|c}$=6.5 T, then starts to decreases quickly and disappears above 7 T. The maximum value of $P_c$ is about 12 $\mu$C/m$^2$, which is consistent with ref. The intensity of $P_a$, on the other hand, appears and starts to grow only above 7 T, as shown in Fig. 2(b). Magnetic field of 7 T along c is where a spin flop in the magnetization was reported. The magnetic field induced $P_c$ can be attributed to linear ME effect for several reasons: (1) Polarizations for both directions are linearly dependent on $H_{\|c}$. (2) The G-type magnetic structure with spins along c belongs to 3$'$ point group which does permit a non-zero $\alpha_{zz}$. (3) A dielectric anomaly appears in the vicinity of $T_N$. The switch of polarization from $P_c$ to $P_a$ signifies the change of the ME tensor, and therefore of the magnetic symmetry. The ME coefficient $\alpha_{xx}$ and $\alpha_{zz}$, deduced from the slope of the $P-H$ curve, are $4.44\times10^{-6}$ and $5.1\times10^{-5}$ (CGS unit), respectively. These values are about an order of magnitude smaller than those of Cr$_2$O$_3$. In the x=0.33 compound, the magnetic field induced polarization persists, but its behavior differs from that in undoped compound. The threshold of field $H_{\|c}$ for $P_a$ disappears. Both $P_c$ and $P_a$ start to increase as soon as $H_{\|c}$ is turned on, as shown in Fig. 3(a) and (b). $P_a$ linearly increases with $H_{\|c}$ (Fig. 3(b)), but $P_c$ increases first then decreases to 1 $\mu$C/m$^2$ and remains unchanged from 4 T to 7 T (Fig. 3(a)). The polarizations along the two
different $E$ directions also have different temperature dependence. The onset temperature of $P_a$ is at about 20 K while that of $P_c$ is 27 K. Moreover, at $H_{\parallel c} = 1$ T the initial increase of $P_c$ on cooling is considerably suppressed below 20 K, as shown by the red circle in Fig.3(a). Such an anomaly is absent for higher fields. Additionally, the $P_a$ and $P_c$ can also be induced by $H_{\parallel a}$ (Fig. 3(c) and (d)), which does not give rise to any polarization in the $x=0$ compound. Compared to the $H_{\parallel c}$-induced polarizations, the onset temperature for the palmarizatoin with $a$-axis field is different though. In Fig.3(c) and (d), $P_c$ and $P_a$ both appear below 17.5 K. Different critical values of $H_{\parallel a}$ are required for $P_c$ and $P_a$, which are around 2 Tesla and 4 Tesla, respectively. Above the critical $H_{\parallel a}$, the polarization increases with the $H_{\parallel a}$ in both cases. The polarization was not observed in the $x=0.50$ and 0.68 crystals regardless of the directions and magnitudes of the applied magnetic field. The knowledge of detailed spin structures in these mixed compounds and their evolution with temperature and magnetic field is needed to understand the coupling of the ferroelectric order with the magnetic one.

B. The Ni – doping dependence of magnetic order

1. The G-type AFM phase

The structural refinements show that the 4 compositions of $\text{Mn}_{1-x}\text{Ni}_x\text{TiO}_3$ compounds all crystallize in space group $R3$. Their ilmenite structure and the two generalized spin configurations are depicted in Fig.1. Along the $c$-axis of the hexagonal lattice, $\text{Mn}^{2+}/\text{Ni}^{2+}$ and $\text{Ti}^{4+}$ layers alternate and every third octahedral site is vacant. The magnetic structure of $\text{MnTiO}_3$ is G-type where nearest inter- and intra-planar neighbor spins are antiparallel which has the propagation wave vector $\vec{q}=(0,0,0)$. The magnetic peaks coincide with the allowed nuclear ones (-$H+K+L=3n$, $n$ is integer). The contour plots of the magnetic diffraction in the $(HOL)$ scattering plane, obtained by subtracting the high temperature (140 K) data as background, are shown in Fig. 4(a-d). The temperature dependence of the (1,0,1) position gives the Néel temperature $T_N \sim 64\pm 2.4$ K. The absence of peaks along [0,0,L] implies that the Mn$^{2+}$ moments are along $c$. The ridge-like diffuse scattering along $c$ starts to develop around 90 K. Fig.4(d) show the diffuse peaks at 75 K, which center on the magnetic Bragg peak positions such as (1,0,1), instead of (1,0,0). On cooling the diffuse scattering intensity reaches its maximum at $T_N$, then quickly decreases. Before Lorentzian peaks completely disappear at 4 K, they coexist with the Gaussian line shape, suggesting the coexistence of long-range AFM order and short-range 2D AFM correlations.

The spin structure of $x=0.33$ system remains G-type as suggested by the unchanged magnetic peak positions in Fig. 4(c). The onset temperature of the AFM order is suppressed by Ni-doping to 27.6 K (Fig. 5(a) and Fig. 6(a)). However, the temperature dependence of the magnetic peaks, shown in Fig.5(a) and Fig.6(a), indicates an extra phase transition at $T_R=17.5$ K. Both (0,1,2) and (1,0,1) show a kink at this temperature and (0,0,3) suddenly gains intensity below $T_R$ suggesting the spins rotate away from the $c$-axis and obtain the component of the moment perpendicular to the wavevector. To accurately characterize the magnetic configuration and monitor the changing spin directions, 116 magnetic Bragg peaks were collected for every 1 K between 5 K and $T_N$. In the magnetic structure refinement using FullProf, three equivalent magnetic domains were taken into account, only one of which is presented here. The component of the ordered moment in the $ab$-plane at all measured temperatures lies in the $a$-direction. So the spin directions are specified by...
FIG. 6: (Color online) Temperature dependence of (a) various magnetic reflections of the x=0.33 compound without magnetic field, (b) magnetic peaks with applied external magnetic field of 0.7 T, (c) the refined ordered moment and (d) the angle $\phi$ between the ordered spins and $c$.

$\phi$, the angle between the spin and the $c$-direction in the $ac$-plane, as shown in Fig.1(b). The blue up-triangles in Fig.6(d) show the spin orientation $\phi$ as a function of temperature. The ordered spins between $T_N$ and $T_R$ are close to but not quite along $c$ ($\phi=14.26^\circ$ at 20.5 K). Cooling across $T_R$ the spins abruptly rotate by more than 60 degrees toward $a$. The angle $\phi$ reaches 80.1$^\circ$ at 4 K. These results are different from the established phase diagram which shows spins lying exactly along $a$ between $T_N$ and $T_R$ and exactly along $c$ below $T_R$. Fig. 6(c) shows the refined ordered moment as a function of temperature, which is a smooth decrease and proves that the kinks of the magnetic peak intensities at 20 K in Fig. 6(a) are solely caused by the reorientation of the spins.

The diffuse scattering at this composition becomes more prevalent: The ridge along $c$ persists to the lowest measured temperature, extends high above $T_N$, and becomes broader than the undoped system (Fig.4(g)). The integrated intensity of the diffuse component around (1,0,1) also reaches its maximum at $T_N$ and decreases quickly on both sides (Fig.5(b)). In addition, the Lorentzian line width does decrease on cooling. The inter-plane spin correlation length $\xi$ is smaller than the nearest neighbour interlayer distance above $T_N$, implying the short range order is basically 2-dimensionl (2D). The crossover from 2D to 3D occurs close to $T_N$ when the correlation length becomes bigger than the distance between neighbouring Mn/Ni layers. $\xi$ does not diverge at $T_N$ but continues to increase on cooling to the base temperature. With some short-range correlated spins participating in the establishment of 3-dimensional long range order, some remain short-ranged at low temperature.

2. Magnetic field effect on the AFM order ($x=0.33$)

The onsets of $P_a$ and $P_c$ occur at $T_R$ and $T_N$, respectively. The anomalous suppression of $P_c$ under low field also coincides with $T_R$. Given that there is no detectable structural transitions at these temperatures, the electric polarization in the x=0.33 system apparently originates from the magnetic order. To investigate if this is linear or higher order ME effect, it is critical to know the effect of $c$-direction magnetic field on the symmetry of the AFM order. The same crystal was aligned and mounted in the permanent magnet set which were mounted in a CCR with the $c$-axis parallel to the field direction. The selected magnets provided a field of 0.7 T at the sample position, which was measured by Gauss meter. The actual angle between $c$ and the field was determined to be 6$^\circ$ using the observed angle $\chi$ of the Bragg peak (0,0,6). The temperature dependence of the magnetic peak intensities is shown in Fig.6(b). Due to the geometrical restrictions imposed by the magnets, fewer magnetic peaks were accessible, but enough were collected for an unambiguous refinement of the spin structure at each temperature. The field kept the spin structure and $T_N$ intact, but increased $T_R$ from 17.5 K to about 20 K, making the same as the onset temperature for $P_a$. The result of spin structure refinements shows that the spins were pulled toward $c$ by the field, both below and above $T_R$. $\phi$ is reduced to about 5$^\circ$ above $T_R$ and around 30$^\circ$ below. It is reasonable to assume that the spins would have been aligned along the $c$-axis had a higher field been perfectly applied along $c$. The spin-rotation transition is made sharper by the small field. Another effect of this field is suppressing the moment as shown in Fig. 6(c).

3. A-type AFM structure ($x=0.50$ and 0.68)

The SG state forms between $x=0.4$ and 0.48 according to the established phase diagram. The contour plot of the (H,0,L) scattering plane collected at 4 K with the 25 K data subtracted as the background. The visible $(0,0,3)$ and $(0,0,6)$ peaks do not show temperature dependence. The temperature dependence of the magnetic peak (1,0,2.5) for the (b) $x=0.5$ and (c) $x=0.68$ compound.
order has taken over at this composition. There is no sign of diffuse scattering along \( c \). The Bragg peak \((1,0,2,5)\), shown in Fig. 7(b), decreases smoothly in intensity without an abrupt transition and completely vanishes above 15 K. The smeared transition also shows hysteresis on cooling suggesting the spin glass phase still lingers at this composition. This is consistent with the magnetization measurement.\(^{32}\) The coexistence of long range AFM order with the spin glass order has been predicted in such a magnetically non-diluted system. Similar phenomena have been observed in \( \text{Mn}_{1-x}\text{Fe}_x\text{TiO}_3 \), where the dominant nearest neighbor interactions compete with each other and give rise to a strong magnetic frustration within the honeycomb layer.\(^{33}\) The spin structure refinement agrees with the A-type model with the spins lying along \( a \)-axis, as shown by Fig. 1(c). As the nickel content increases to 0.68, the arrangement of the ordered moments remains A-type. Both the Néel temperature and the size of the ordered magnetic moment at low temperature increase. \( T_N \) increases to 21.5 K and the transition is abrupt and first-order like, contrasting with a temperature increase.

**TABLE I**: The lattice parameters, atom parameters, magnetic structures, magnetic phase transition temperatures, the ordered moments of the magnetic orders, and the \( R \) factors of the structure refinements in various \( \text{Mn}^{2+} \) compounds. \( m_a \) and \( m_c \) denote the projected moment on the hexagonal \( a \)- and \( c \)-axes respectively. \( R_{p2} \) is calculated by \( R_{p2}=100 \sum_n\left|G_{obs}^2 - G_{calc}^2\right|/\sum_n G_{obs}^2 \), where \( G \) is the structure factor and \( n \) the number of reflections used.

| refined \( x \) | \( x=0.00^{[32]} \) | \( x=0.33 \) | \( x=0.50 \) | \( x=0.68 \) | \( x=1.00^{[30]} \) |
|---|---|---|---|---|---|
| \( a \) | 5.14 | 5.12 | 5.06 | 5.05 | 5.04 |
| \( c \) | 14.28 | 14.15 | 13.91 | 13.91 | 13.81 |
| \( Mn_z/Ni_z \) | 0.3600 | 0.347(2) | 0.347(2) | 0.3509(5) | 0.3509 |
| \( Ti_z \) | 1.0476 | 1.0504(5) | 1.0466(2) | 1.0426(8) | 1.0450 |
| \( O_x \) | 0.3189 | 0.3188(6) | 0.3166(2) | 0.3161(8) | 0.3142 |
| \( O_y \) | 0.031 | 0.0264(8) | 0.0246(3) | 0.0205(7) | 0.016 |
| \( O_z \) | 0.2439 | 0.2449(3) | 0.2459(1) | 0.2458(3) | 0.2465 |
| magn. struc. | G-type | G-type | A-type | A-type | A-type |
| \( T_N \) | 64 | 27.6 | 15 | 21.5 | 21.4\(^{[30]} \) |
| \( T_{k} \) | – | 17.51 | – | – | – |
| \( m_a (\mu_B) \) | 0 | 2.86(2) | 1.36(3) | 2.06(3) | 2.23\(^{[32]} \) |
| \( m_c (\mu_B) \) | 4.55\(^{[32]} \) | 0.5(1) | 0 | 0 | 0 |
| Nucl. \( R_{p2} \) | 7.77 | 6.33 | 8.05 | – | – |
| Magn. \( R_{p2} \) | 3.97 | 15.2 | 9.6 | – | – |

**IV. DISCUSSION AND CONCLUSION**

The ionic radius of \( \text{Ni}^{2+} \) (0.70 Å) is smaller than that of \( \text{Mn}^{2+} \) (0.80 Å), so the effect of increasing \( \text{Ni}^{2+} \) content on the nuclear structure is to be expected. As exhibited in Table 1, \( a \) and \( c \) both decrease with increasing Ni-doping, so do the \( z \) values of the atoms on 6c sites (Mn, Ni, and Ti). The value of \( O_y \) for the oxygen site, already small in \( \text{MnTiO}_3 \) (0.031), is systematically reduced by the Ni-replacement and becomes 0.016 in \( \text{NiTiO}_3 \). However, its minuscule value keeps the crystal from having mirror planes, so is important for the crystallographic symmetry and consequently for the magnetic symmetry. The effective moment for \( \text{Mn}^{2+} \) in \( \text{MnTiO}_3 \), 4.55 \( \mu_B \), is smaller than the spin-only value. This can be ascribed to the incomplete ordering of Mn and Ti or the existence of \( \text{Mn}^{4+} \). Both the effective moment and the Néel temperature change with Ni concentration as a result of the competing anisotropies and frustrated exchange interactions. This change is more rapid on the Mn-rich region. Both values are considerably reduced at \( x=0.5 \), which is compatible with the observed spin glass behavior. In the \( x=0.68 \) compound, the intra-layer exchange interactions among the \( \text{Ni}^{2+} \) ions become so dominant that \( T_N \) and the ordered moment are very close to those in the pure \( \text{NiTiO}_3 \). Because of the similar radii of Ni and Ti ions, more incomplete ordering exists in \( \text{NiTiO}_3 \) which is mainly responsible for the less-than-expected moment size of \( \text{Ni}^{2+} \).\(^{[33]} \)

The \( \text{Mn}^{2+} \) and \( \text{Ni}^{2+} \) ions have distinct single ion anisotropies as manifested by their different easy axes in the ilmenites and other compounds such as barium fluorides \( \text{BaMnF}_4 \) and \( \text{BaNiF}_4 \). The added Ni cations randomly replace Mn on the octahedral sites and weaken the spin correlations, more so in the inter-planar direction, as indicated by the enhanced diffuse scattering in the \( x=0.33 \) system. Although the spin correlation starts to form high above \( T_N \), the electric polarization does not occur until the long range G-type magnetic order is established. When the spins are parallel to the \( c \)-axis, the magnetic group symmetry is \( R3' \) and the point symmetry is \( 3' \). As the collinear AFM moments tilt away from the \( c \)-axis, the emerged \( a \)-axis components in the hexagonal layer loses the 3-fold rotation symmetry. The magnetic space group then becomes \( P1 \) and the magnetic point symmetry becomes \( 1' \). Since the nonzero \( O_y \) value keeps the crystal from having 2-fold rotation axis and mirror planes. Even if the spins completely lie in the \( a \)-axis, the point group of the magnetic symmetry is not \( 2'/m \) as it appears to be. The restrictions from the non-magnetic anion sites must be obeyed as the Neumann’s principle requires the physical property tensor be invariant under all the permissible operations of the crystallographic symmetry.\(^{[33]}\)

This observation is the key to understand the observed electric polarizations summarized in Fig. 2 and Fig. 3 for \( x=0 \) and 0.33, respectively. Both \( 3' \) and \( 1' \) are among the 58 magnetic point groups that have non-zero elements in their ME susceptibility tensors.\(^{[33]}\) The former has both diagonal \( \alpha_{xx}, \alpha_{yy}, \alpha_{zz} \) and off-diagonal components \( \alpha_{xy}=-\alpha_{yx} \), while the latter does not impose any restrictions on the form of ME tensor and all tensor components are non-zero. The G-type structure with \( c \)-axis spins (\( \phi=0 \)) in \( \text{MnTiO}_3 \), permits \( \alpha_{yz} \) as indeed observed. In the \( x=0.33 \) system, the spins tilt away from \( c \) while maintaining the G-type structure and lowers the symmetry to...
The symmetry remains as $\bar{1}'$ even for $T_R < T < T_N$ unless a $c$-direction magnetic field pull the spins back along $c$ (Fig. 6(d)), which enables the recovery of the $3'$ symmetry in this temperature range. This explains why $\alpha_{zz}$, allowed by both symmetries, exist in the entire $T<T_N$ range. Cooling across $T_R$ at 20 K, $\bar{1}'$ arising from the collinear spin rotation triggers $\alpha_{zz}$, which is prohibited by $3'$. At the same temperature, $\alpha_{zz}$ exhibits considerable suppression due to the reduced $c$-component of the moment, as shown by the red triangle in Fig.6(d). The change of magnetic point symmetry satisfactorily explains the temperature dependence of the observed $P_a$ and $P_c$. It is clear that coupling of the ferroelectric order and magnetic order is due to the linear ME effect. The case of $x=0.33$ system is different from a normal linear ME effect, as in $x=0$, in that the spin directions vary with external magnetic field, which fails the linear dependence of the polarization on magnetic field.

With the ties between the two orders established, one can use the polarization to predict the spin structures at higher fields, as they are difficult to determine experimentally. The representation analysis using SARAh program suggests that for the space group $R3$ with magnetic propagation vector $k=(0,0,0)$, the $G$-type is the only possible AFM spin arrangement. So if one assumes the magnetic wave vector remains unchanged, $\phi$ alone should be sufficient to describe all the spin structures under moderate magnetic field. With higher $H_{||c}$ in the $x=0.33$ compound, $\phi$ remains different in the two temperature regions. The fact that $P_a$ only exists below $T_R$ (Fig.2(d)) suggests that up to $H_{||c}=7$ T, $\phi=0$ for $T_R < T < T_N$ and that $\phi \neq 0$ for $T<T_R$. As the magnetic field is applied along $a$, the observed $\alpha_{zz}$ (Fig.3(d)), prohibited by $3'$, suggests the $\bar{1}'$ magnetic point symmetry.

The electric polarization flop has been observed in a few multiferroic materials, including rare-earth manganeseites $\text{RMn}_3O_7^{52,53}$ $\text{RMn}_2O_4^{54}$ and the mineral hübnerite $\text{MnWO}_4^{55}$ which generally have incommensurate noncollinear spiral spin structures. In these materials the $P$-flop is typically caused by the flop of spiral or cycloid plane. $\text{MnTiO}_3$ is a rare case of magnetic field induced $P$-flop with a collinear magnetic structure. In the $x=0.33$ system, the polarizations in the two directions are turned on together with $P_a$ and $P_c$ and their different on-set temperatures makes it a unique type of ME control. The Co-doped $\text{MnWO}_4$ is another case of $P$-flop caused by the competing single ion anisotropies, which is achieved by the flop of the spin helix. But the magnetic frustration and complex magnetic structure make this type of control difficult to repeat in other compounds in terms of materials design. In comparison, the collinear spin rotation in $\text{Mn}_{1-x}\text{Ni}_x\text{TiO}_3$ can be easily created for a random mixture of two antiferromagnets with orthogonal easy axes. A new intermediate phase whose easy axis tilts oblique to the easy axes of the pure systems, and two second order transitions are all predicted by mean field approximation. Such predictions have also been fulfilled in other random mixtures such as $\text{K}_2\text{Mn}_{1-x}\text{Fe}_x\text{P}_4^{56}$ and $\text{Co}_{1-x}\text{Fe}_x\text{Cl}_2\text{H}_2\text{O}^{57}$

**V. SUMMARY**

The structural, magnetic and electric properties have been studied for 4 typical compositions of $\text{Mn}_{1-x}\text{Ni}_x\text{TiO}_3$. Magnetic field induced electric polarizations have been observed in the compositions $x=0$ and $0.33$, both of which have the G-type magnetic order. In the $x=0$ system, the polarizatio flops from $P_a$ to $P_c$ as the spin flop transition is triggered at $H_{||c}=7$ T. In $x=0.33$, $P_a$ is turned on together with $P_c$ by $H_{||c}$. Additionally, $P_a$ and $P_c$ can also be induced by $H_{||a}$. By studying the magnetic structure and phase transition with and without magnetic field, the occurrence of the new ME coupling is attributed to the emergent point group symmetry as the antiferromagnetically coupled spins tilt collinearly toward the $a$-axis. Such spin rotation results from the strong competition of single ion anisotropy of the transition metal elements and provides a new way to tune electric polarizations. The magnetic structure of the $x=0.5$ and $0.68$ systems is the same as that of the NiTiO$_3$. No polarization was observed.

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