Theory of magnetic switching of ferroelectricity in spiral magnets

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We propose a microscopic theory for magnetic switching of electric polarization ($P$) in the spin-spiral multiferroics by taking TbMnO$_3$ and DyMnO$_3$ as examples. We reproduce their phase diagrams under a magnetic field $H_{ex}$ by Monte-Carlo simulation of an accurate spin model and reveal that competition among the Dzyaloshinskii-Moriya interaction, spin anisotropy, and spin exchange is controlled by the applied $H_{ex}$, resulting in magnetic transitions accompanied by reorientation or vanishing of $P$. We also discuss the relevance of the proposed mechanisms to many other multiferroics such as LiCu$_2$O$_2$, MnWO$_4$, and Ni$_3$V$_2$O$_4$.

Concurrently magnetic and ferroelectric materials, i.e. multiferroics, offer prospective systems to attain magnetic control of electricity via magnetoelectric (ME) coupling $^{[1,2]}$. It was experimentally demonstrated that an external magnetic field ($H_{ex}$) can cause reorientation, emergence, and vanishing of ferroelectric polarization $P$ in many spin-spiral multiferroics such as $R$MnO$_3$ ($R$=Tb, Dy, Eu$_{1-x}$Y$_x$, etc) $^{[3,4]}$, LiCu$_2$O$_2$ $^{[5]}$, MnWO$_4$ $^{[6]}$, and Ni$_3$V$_2$O$_4$ $^{[7]}$. These ME phenomena are currently attracting enormous interest, and a thorough understanding of their mechanisms is an urgent issue. However, the number of theoretical studies is very few despite many experimental reports. Naively, the applied $H_{ex}$ can determine the direction of $P$ by controlling the conical spin structure via Zeeman coupling, but there are many examples that do not obey this simple picture.

In the spin-spiral multiferroics, inherent spin frustration as an origin of the spiral magnetism inevitably reduces the spin-exchange energy, and hence increases the relative importance of other tiny interactions, e.g. the single-ion spin anisotropy and the Dzyaloshinskii-Moriya (DM) interaction. Consequently, the magnetic switching of $P$ in this new class of multiferroics is governed by their fine energy balance tuned by $H_{ex}$, which cannot be understood from a simple interplay between Zeeman coupling and the spin exchanges.

In this Letter, by taking the Mn perovskites TbMnO$_3$ and DyMnO$_3$ as examples, we propose a microscopic theory for the magnetic control of $P$ in the spin-spiral multiferroics. Their puzzling $T$-$H_{ex}$ phase diagrams are reproduced by the Monte-Carlo (MC) analysis of an accurate spin model. Our microscopic theory reveals that the applied $H_{ex}$ controls conflicts among the spin exchanges, spin anisotropy, and DM interaction, resulting in magnetic transitions accompanied by reorientation or vanishing of $P$. The mechanisms proposed here are relevant to many other spin-spiral multiferroics such as LiCu$_2$O$_2$, MnWO$_4$, and Ni$_3$V$_2$O$_4$. We also discuss the influence of effective magnetic fields from rare-earth $f$ moments.

The ferroelectricity in these materials is described by the spin-current model $^{[8,10]}$ as given by $P \propto Q \times \chi$, where $Q$ is a propagation vector of the spiral and $\chi \propto \sum_{i,j} S_i \times S_j$ is the vector spin chirality. As shown in Fig. 1(b), the Mn spins in TbMnO$_3$ and DyMnO$_3$ are rotating within the $bc$ plane ($\chi \| a$) to form a transverse spiral with $Q \| b$ $^{[11]}$, and thus $P \| c$ is realized.

In Figs. 1(c)-(f), we briefly summarize the puzzles in $R$MnO$_3$ $^{[4]}$. The applied $H_{ex}$ induces the magnetization $M \| H_{ex}$ via Zeeman coupling, and hence forces the spin structure to be conical where $\chi \| H_{ex}$. When we apply $H_{ex} \| Q$ [see Fig. 1(c)], we expect a longitudinal conical spin order with $\chi(Q)$. In this case, $P$ should be zero within the spin-current model. Thus we expect vanishing of $P$ when we apply $H_{ex} \| b$ ($Pbnm$ setting) to TbMnO$_3$ and DyMnO$_3$. However, reorientation of $P$ from $P \| c$ to $P \| a$ is observed in reality [see Fig. 1(e)]. A neutron-scattering experiment confirmed that this $P$ reorientation results from the spin-chirality flop from $\chi \| a$ to $\chi \| c$ $^{[12,13]}$. This discrepancy has been naively attributed to the influence of $f$ moments on the rare-earth ions thus far. $^{[13,16]}$. However, a similar behavior has been observed also in LiCu$_2$O$_2$ without $f$ moments $^{[8]}$, suggesting an essentially new mechanism. Mostovoy reproduced the flop by introducing higher-order anisotropies in a phenomenological theory although their microscopic origins are unclear $^{[8]}$. On the other hand, the application of $H_{ex} \perp Q$ is expected to stabilize a transverse conical spin order with $\chi \perp Q$. As shown in Fig. 1(d), we expect the $ab$-plane transverse conical order with $P \| a$ when we apply $H_{ex} \| c$ to TbMnO$_3$ and DyMnO$_3$. However, in TbMnO$_3$, the first-order transition to paraelectric ($P=0$) phase is observed under $H_{ex} \| c$ as shown in Fig. 1(f). The $H_{ex}$-induced vanishing of $P$ is also observed in MnWO$_4$ $^{[7]}$ and Ni$_3$V$_2$O$_4$ $^{[8]}$.

To solve these puzzles, we start with a classical Heisenberg model on a cubic lattice, in which the Mn $S=2$ spins are treated as classical vectors. The Hamiltonian is given by $\mathcal{H} = \mathcal{H}_J + \mathcal{H}_{\text{dia}} + \mathcal{H}_{\text{DM}} + \mathcal{H}_{\text{Zeeman}}$. The first term $\mathcal{H}_J = \sum_{i,j} J_{ij} S_i \cdot S_j$ describes spin-exchange in-

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The second term $\mathcal{H}_{\text{sia}}$ denotes the single-ion spin anisotropy, which consists of two parts as $\mathcal{H}_{\text{sia}} = \mathcal{H}_{\text{sia}}^d + \mathcal{H}_{\text{sia}}^e$ with $\mathcal{H}_{\text{sia}}^d = D \sum \mathcal{S}_i^2$ and $\mathcal{H}_{\text{sia}}^e = E \sum \xi_i \eta_i \zeta_i$. Here, $\xi_i$, $\eta_i$, and $\zeta_i$ are the tilted local axes attached to the $i$th Mno$_6$ octahedron. The term $\mathcal{H}_{\text{sia}}^a$ causes the hard-axis anisotropy along $c$, or, equivalently, the easy-plane anisotropy in the $ab$ plane. The third term $\mathcal{H}_{\text{DM}} = \sum_{i<j} \mathbf{d}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$ represents the DM interaction where the vectors $\mathbf{d}_{ij}$ are defined on the Mn(i)-O-Mn(j) bonds, and are expressed by five DM parameters, $\alpha_{ab}$, $\beta_{ab}$, $\gamma_{ab}$, $\alpha_c$, and $\beta_c$. This term consists of two parts, $\mathcal{H}_{\text{DM}}^a$ and $\mathcal{H}_{\text{DM}}^b$, where $\mathcal{H}_{\text{DM}}^a$ is associated with the DM vectors on the in-plane (out-of-plane) Mn-O-Mn bonds. The last term, $\mathcal{H}_{\text{Zeeman}} = g \mu_B \sum \mathbf{S}_i \cdot \mathbf{H}_{\text{ex}}$, stands for the Zeeman coupling. Note that the Mn spins feel the internal magnetic field $\mathbf{H}_{\text{ex}}$, which consists of two contributions, i.e., the applied field $\mathbf{H}_{\text{ex}}$ and the effective field $\mathbf{H}_{\text{eff}}$ from the $f$ moments. This model has successfully reproduced the phase diagrams of RMnO$_3$ at $\mathbf{H}_{\text{ex}} = 0$.

We have microscopically determined the values of $J_{ab}$, $J_b$, $J_c$, $D$, and $E$, and have estimated the values of five DM parameters in Ref. [19]. We perform calculations using two sets of the model parameters (A and B) as (A) $(J_{ab}, J_b, J_c) = (-0.74, 0.64, 1.0)$, $(D, E) = (0.2, 0.25)$, $(\alpha_{ab}, \beta_{ab}, \gamma_{ab}) = (0.1, 0.1, 0.14)$ and $(\alpha_c, \beta_c) = (0.48, 0.1)$, and (B) $(J_{ab}, J_b, J_c) = (-0.7, 0.99, 1.0)$, $(D, E) = (0.22, 0.25)$, $(\alpha_{ab}, \beta_{ab}, \gamma_{ab}) = (0.1, 0.1, 0.14)$ and $(\alpha_c, \beta_c) = (0.45, 0.1)$. Here the energy unit is meV. These parameter sets give the $bc$-plane spin spirals propagating along the $b$ axis with wave numbers $Q_a = 0.3\pi$ and $Q_b = 0.47\pi$, respectively. They reproduce well the spiral spin states in TbMnO$_3$ ($Q_b = 0.28\pi$) and DyMnO$_3$ ($Q_b = 0.39\pi$) at $\mathbf{H}_{\text{ex}} = 0$.

In Figs. 2(a) and (b) we display theoretically obtained $T-H_{\text{in}}$ phase diagrams of TbMnO$_3$ and DyMnO$_3$ for $H_{\text{in}} || b$, respectively. They successfully reproduce the observed reorientation of $P$ from $P || c$ to $P || a$ as a flop of the spin chirality from $\chi || a$ to $\chi || c$. We determine the transition points and the spin structures by calculating the $T$ dependence of specific heat $C(T)$ and spin chiralities $\chi_\gamma(T)$ using $C(T) = \frac{1}{4T} \partial \langle H \rangle / \partial (k_B T)$ and spin chiralities $\chi_\gamma(T) = \frac{1}{S^2} \langle (\sum (\mathbf{S}_i \times \mathbf{S}_{i+1})_c) \rangle$ ($\gamma = a, b, c$). Here the brackets denote thermal averages. Concerning the spin chiralities, the $\chi_\gamma(T)$ [ $\chi_c(T)$] has a large value, while other two components are nearly zero in the $bc$-plane [ab-plane] spiral or conical phases. Figure 2(c) shows $C(T)$ and $\chi_\gamma(T)$ at $T=0$ or $8$ T. (d) Spin structure in the $bc$-plane spiral state at $H_{\text{in}} = 0$, and arrangement of the $a$-axis components of DM vectors on the out-of-plane Mn-O-Mn bonds. The symbols $\circ$ and $\otimes$ express their signs, i.e., positive and negative, respectively. In the inset, the arrows (dashed lines) show the spin directions in the presence (absence) of DM interaction.
but alternate along the c axis, while their magnitudes are all equal to $\alpha \phi_c$ [see Fig. 2(d)]. Without DM interaction, angles between adjacent two spins along the c axis are uniformly $\phi_c=\pi$ because of the strong antiferromagnetic (AFM) coupling $J_c$. In the presence of DM interaction, the angles alternate between $\pi + \Delta \phi_c$ and $\pi - \Delta \phi_c$ with $\Delta \phi_c>0$ [see the inset of Fig. 2(d)]. We can derive a gain of the DM energy due to this angle modulation as $\Delta E_{\text{DM}}^c/N = -\alpha S^2 \cos \phi_c \Delta \phi_c$. Without $H_{\text{in}}$, the gain $\Delta E_{\text{DM}}^c$ in the bc-plane spiral dominates over the easy-(ab)-plane [or the hard-(c)-axis] spin anisotropy from $H_{\text{D}}^b$, which favors the ab-plane spiral with $\chi || c$. Note that the value of $|\cos \phi_c|$ is maximum ($=1$) at $\phi_c=\pi$, but decreases as $\phi_c$ decreases. This means that the application of $H_{\text{in}}||b$ suppresses this energy gain since it destroys the interplane AFM coupling and reduces the angle $\phi_c$ from $\pi$. The bc-plane spiral becomes destabilized when the reduced energy gain $\Delta E_{\text{DM}}^c$ is defeated by the easy-(ab)-plane anisotropy $H_{\text{D}}^b$, resulting in the spiral-plane (chirality) flop from bc ($\chi || a$) to ab ($\chi || c$). Note that in RMnO$_3$, the ac-plane spiral or conical is unfavorable. This is because it can energetically benefit neither from $H_{\text{D}}^a$ nor from $H_{\text{D}}^c$, whereas the ab- and bc-plane spirals can take advantage of one of these two. We expect that the above mechanism is relevant also to the $H_{\text{ex}}||b$ induced P flop from $P||c$ to $P||a$ in LiCu$_2$O$_2$ [4] in terms of the role of $H_{\text{ex}}$, which destabilizes the spin spiral with $P||c$ [14] through destroying the AFM coupling along c. Note that the single-ion anisotropy $H_{\text{D}}^a$ cannot work in this quantum S=1/2 spin system in contrast to RMnO$_3$ with S=2 spins. We expect that the spin spiral with $P||a$ under $H_{\text{ex}}$ (possibly the ab-plane spiral) is stabilized by the other interaction, and the DM coupling with the c-axis components of DM vectors is a possible candidate.

Now we compare our results with experimental ones. Between Figs. 1(c) and Fig. 2(b), there are a few discrepancies. First, threshold fields for the P reorientation are different; i.e., the calculated threshold value of $H_{\text{in}}^P$ for DyMnO$_3$ is approximately 18 T, whereas the experimental value of $H_{\text{ex}}^c$ is 1-4 T. Second, the slope of the phase boundary is very steep in the theoretical $T$-$H_{\text{ex}}$ diagram of Fig. 2(b), while in the experimental $T$-$H_{\text{ex}}$ diagram of Fig. 1(c), it is rather gradual. These discrepancies are solved by considering the effective magnetic field $H_{\text{fd}}$ generated by the rare-earth f moments, which acts on the Mn spins via the f-d coupling $J_{f-d}$. Because of the AFM $J_{f-d}$, $H_{\text{fd}}$ and $H_{\text{ex}}^c$ are antiparallel, and the internal field $H_{\text{in}}^c (\gamma = a, b, c)$ is given by $H_{\text{in}}^c = H_{\text{ex}}^c - H_{\text{fd}}$. Here $H_{\text{fd}}^c$ is written using the f-electron magnetization $m_f$ as a function of $T$ and $H_{\text{ex}}^c$ as $H_{\text{fd}}^c(T, H_{\text{ex}}^c) = z J_{f-d} m_f (T, H_{\text{ex}}^c)$. Here $z (=8)$ is the coordination number of R ions around the Mn ion. We assume $J_{f-d} = 0.45$ T/µB for DyMnO$_3$. Figure 3(a) displays a color plot of the internal magnetic field $H_{\text{in}}^c$ in the $T$-$H_{\text{ex}}$ plane calculated using the experimental magnetization data. A solid line on which $H_{\text{in}}^c$ is
equal to the calculated threshold value is drawn. This figure coincides with the experimental diagram of DyMnO$_3$ in Fig. 1(e). A similar analysis for TbMnO$_3$ has also reproduced the experimental diagram (not shown). The roles of the $f$-$d$ coupling in RMnO$_3$ at $H_{\text{ex}}=0$ have been studied by recent neutron-scattering experiments [13, 14]. We find that the switching of $P$ can be qualitatively understood even without considering the $f$-$d$ coupling, but it should be taken into account for quantitative discussion.

Next we discuss the case of $H_{\text{ex}} \parallel c$. The theoretical $T$-$H_{\text{in}}^c$ phase diagrams of TbMnO$_3$ and DyMnO$_3$ are displayed in Figs. 1(a) and (b). In Fig. 1(a), we find the transition to a coplanar spin state with $P=0$ for TbMnO$_3$ at $H_{\text{in}}^c \approx 3$ T, which coincides with the experimental observation of paraelectric phase under $H_{\text{ex}} \parallel c$. For its magnetic structure, see Fig. 1(c). Again, there are a few discrepancies between the theoretical and experimental results [compare Figs. 1(f) and Fig. 1(a)]. They are resolved by considering the influence of Tb moments.

In Fig. 2(b), we display the $T$ and $H_{\text{ex}}^c$ dependence of the internal field $H_{\text{in}}^c$ calculated from the experimental magnetization data. Here we assume $J_{pd}=0.65$ T/$\mu_B$ for TbMnO$_3$. Solid lines on which $H_{\text{in}}^c$ is equal to the calculated threshold value are drawn. This figure coincides well with the experimental diagram of TbMnO$_3$ in Fig. 1(f). On the other hand, the transition to the ab-plane transverse conical state with $P \parallel a$ [see Fig. 1(d)] is found for DyMnO$_3$ in Fig. 2(b), which has not been observed in experiments up to $H_{\text{ex}}^c=9$ T. The required $H_{\text{ex}}^c$ for this transition deviates from the calculated critical value of $H_{\text{in}}^c$ by the field $H_{fd}$ from the Dy $f$ moments antiparallel to $H_{\text{ex}}$. Hopefully, the reorientation of $P$ will be observed in DyMnO$_3$ under a higher $H_{\text{ex}}^c$.

The contrasting behaviors of $P$ under $H_{\text{ex}} \parallel c$ between DyMnO$_3$ and TbMnO$_3$ can be attributed to the difference in magnitude of the in-plane spin-exchange $J_p$. TbMnO$_3$ has much smaller $J_p=0.64$ meV than DyMnO$_3$ with $J_p=0.99$ meV. At $H_{\text{ex}}=0$, the Mn spins form a spiral order to minimize the spin-exchange energy in both compounds. Once we apply $H_{\text{ex}} \parallel c$, the ferromagnetic moment is induced along the $c$ axis, and hence rotating components of the spins become reduced. Then in TbMnO$_3$ with a small $J_p$, the spiral and conical spin orders no longer take advantage of the spin exchanges under $H_{\text{ex}} \parallel c$, resulting in the first-order transition to the coplanar state as shown in Fig. 1(c). This state can benefit from all of the large $a$-axis components of the DM vectors on the out-of-plane bonds, which are perpendicular to the coplanar spin plane. The $H_{\text{ex}}$-induced ferroelectric-to-paraelectric transition with sudden vanishing of $P$ has also been observed in many other spin-spiral multiferroics, e.g., Ni$_3$V$_2$O$_8$ [8] and MnWO$_3$ [9]. We expect that the above mechanism is relevant also to them.

In summary, we have theoretically studied the puzzling $T$-$H_{\text{ex}}$ phase diagrams of the spin-spiral multiferroic RMnO$_3$ ($R=$Tb and Dy) and have revealed new mechanisms for the magnetic control of $P$ by analyzing a microscopic spin model using the MC technique. We have shown that the applied $H_{\text{ex}} \parallel Q$ (parallel in the present case) reduces the DM energy through modulating the interplane spin angles, and thereby controls a competition between $H_{\text{DM}}^c$ and other interaction ($H_{\text{dia}}$ in the present case), which results in the spiral-plane or spin-chirality flop with reorientation of $P$. On the other hand, the applied $H_{\text{ex}} \perp Q$ (perpendicular in the present case) suppresses the spin-exchange energy through reducing the rotating components of spins, and thereby causes a competition between the spin exchanges $H_{\text{ex}}$ and other interaction ($H_{\text{DM}}^c$ in the present case). As a result, the first-order transition from spiral to coplanar spin phases occurs in TbMnO$_3$ with a rather small $J_p$ accompanied by the sudden disappearance of $P$. We have discussed that the proposed mechanisms are also applicable to many other spin-spiral multiferroics. Additionally, we have found that the experimental results can be quantitatively reproduced by considering the effective field $H_{fd}$ from the rare-earth $f$ moments.

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[1] T. Kimura et al., Nature (London) 426, 55 (2003).
[2] Y. Tokura, J. Magn. Magn. Mater. 310, 1145 (2007); S.-W. Cheong and M. Mostovoy, Nat. Mater. 6, 13 (2007).
[3] T. Kimura, Annu. Rev. Mater. Res. 37, 387 (2007).
[4] T. Kimura, G. Lawes, T. Goto, Y. Tokura, and A. P. Ramirez, Phys. Rev. B 71, 224425 (2005).
[5] H. Murakawa et al., Phys. Rev. Lett. 101, 197207 (2008).
[6] S. Park, Y. J. Choi, C. L. Zhang, and S.-W. Cheong, Phys. Rev. Lett. 98, 057601 (2007).
[7] K. Taniguchi et al., Phys. Rev. B 77, 064408 (2008).
[8] M. Kenzelmann et al., Phys. Rev. B 74, 014429 (2006).
[9] M. Mostovoy, Phys. Rev. Lett. 96, 067601 (2006).
[10] H. Katsura, N. Nagaosa, and A. V. Balatsky, Phys. Rev. Lett. 95, 057205 (2005).
[11] M. Kenzelmann et al., Phys. Rev. Lett. 95, 087206 (2005).
[12] N. Aliouane et al., Phys. Rev. Lett. 102, 207205 (2009).
[13] Y. Hamada, K. Terakura et al., Phys. Rev. Lett. 101, 097204 (2008).
[14] Y. Kobayashi et al., J. Phys. Soc. Jpn. 78, 084721 (2009).
[15] O. Prokhnenko et al., Phys. Rev. Lett. 98, 057206 (2007).
[16] O. Prokhnenko et al., Phys. Rev. Lett. 99, 177206 (2007).
[17] For their direction vectors, we use the structural data of TbMnO$_3$ and DyMnO$_3$; see J. A. Alonso, M. J. Martinez-Lope, M. T. Casais, and M. T. Fernández-Díaz, Inorg. Chem. 39, 917 (2000).
[18] I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev.
Lett. 76, 4825 (1996).
[19] M. Mochizuki, and N. Furukawa, Phys. Rev. B 80, 134416 (2009).
[20] K. Hukushima and K. Nemoto, J. Phys. Soc. Jpn. 65, 1604 (1996).