Spin model of magnetostricitions in multiferroic Mn perovskites

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We theoretically study origins of the ferroelectricity in the multiferroic phases of the rare-earth (R) Mn perovskites, RMnO₃, by constructing a realistic spin model including the spin-phonon coupling, which reproduces the entire experimental phase diagram in the plane of temperature and Mn-O-Mn bond angle for the first time. Surprisingly we reveal a significant contribution of the symmetric (S·S)-type magnetostriction to the ferroelectricity even in a spin-spiral-based multiferroic phase, which can be larger than the usually expected antisymmetric (S×S)-type contribution. This explains well the nontrivial behavior of the electric polarization. We also predict the noncollinear deformation of the E-type spin structure and a wide coexisting regime of the E and spiral states, which resolve several experimental puzzles.

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Frustrating spins in magnets often exhibit not only nontrivial orders but also intriguing switching and dynamical phenomena associated with phase competitions. Effective reduction of the spin-exchange energy due to the frustration increases the relative importance of other tiny interactions such as the Dzyaloshinskii-Moriya (DM) interaction, single-ion anisotropy, and spin-phonon coupling. Their fine energy balance results in keen conflict of various states. This enables us to achieve sensitive phase controls and huge responses leading to new functionalities of materials, and also provides challenging issues for fundamental science.

The rare-earth (R) Mn perovskites, RMnO₃, offer one of the most typical examples. In this class of materials, the nearest-neighbor spin exchange is very small (~1 meV) relative to that in other perovskite compounds (e.g. ~15 meV in LaTiO₃) due to the cancellation of exchange contributions from t₂g and e₉ orbital sectors [1]. Consequently the next-nearest antiferromagnetic (AFM) coupling becomes comparable to the nearest-neighbor ferromagnetic (FM) coupling. Their frustration gives rise to various competing phases including multiferroic phases where the frustration-induced nontrivial spin order generates ferroelectric polarization P [2, 3].

Recent experiments revealed spectacular magnetoelectric (ME) phenomena in these multiferroic phases, i.e., magnetic-field-induced P flops [2, 3], colossal magneto-capacitance [4, 5], and electromagnons [7, 8]. To study and/or control these cross-correlation phenomena, thorough understanding of the magnetic structures, the phase competitions, and the coupling between magnetic and ferroelectric orders based on a reliable model is essential.

However, there still remain many experimental observations, which are not understood theoretically.

(i) Multifurcation of the sinusoidal collinear phase at higher temperature (T) into four low-T phases depending on the ion R-site radius (r_R) [9].

(ii) Nontrivial r_R-dependence of the magnitude and direction of P [9].

(iii) Apparently contradicting neutron-scattering results on the magnetic commensurability in the compounds with small r_R [10, 11].

(iv) Anomalous T-dependence of |P| for YMnO₃ and ErMnO₃ [2].

In this Letter, we study theoretically the interplay of symmetric (S·S)-type magnetostriction (MS) and antisymmetric (S×S)-type MS in a realistic spin model for RMnO₃ and resolve all the puzzles listed above. We find a large (S·S) contribution to the ferroelectricity even in a spiral spin phase. This mechanism is generally expected in all the spin-spiral-based multiferroics. We start with a model in which the Mn S=2 spins are treated as classical vectors on a cubic lattice. A similar model has been examined in Refs. [11, 12] which gives the transition between two types of multiferroic spiral spin phases and explains several ME phenomena quantitatively. Here we further include the lattice degrees of freedom. This enables us to study the effect of the (S·S)-type MS as a source of the above puzzles, which has been missed thus far.

The Hamiltonian is given by

\[
\mathcal{H} = \sum_{<i,j>} J_{ij} S_i \cdot S_j + D \sum_i S_{\xi i}^2 \\
+ E \sum_i (-1)^{i_3} S_{\xi i}^x (S_{\eta i}^y - S_{\eta i}^z) \\
+ \sum_{<i,j>} d_{ij} \cdot (S_i \times S_j) + K \sum_i (\delta_{i_x+i_{\bar{x}}} + \delta_{i_y+i_{\bar{y}}}) \xi_i, (1)
\]

where i_x, i_y, i_z represent the integer coordinates of the ith Mn ion with respect to the cubic x, y and z axes.
The first term describes the spin-exchange interactions as shown in Fig. 1(a). The second and third terms stand for the single-ion anisotropy. For the local axes $\xi_i$, $\eta_i$, and $\zeta_i$ attached to each MnO$_6$ octahedron, we use the structural data of DyMnO$_3$ [14]. The fourth term denotes the DM interaction. The DM vectors $d_{ij}$ are expressed using five DM parameters, $\alpha_{ab}$, $\beta_{ab}$, $\gamma_{ab}$, $\alpha_c$ and $\beta_c$, as given in Ref. [16] because of the crystal symmetry. The last term represents the lattice elastic term with $K$ being the elastic constant. Here $\delta_{ij}$ is a shift of the O ion between $i$th and $j$th Mn ions normalized by the MnO bond length. Note that the O ion in the orthorhombic lattice is already displaced from its cubic position. We consider $\delta_{ij}$ as a further shift from the position at higher $T$ in the presence of magnetic order at low $T$.

Since the nearest-neighbor FM coupling in RMnO$_3$ is sensitive to the Mn-O-Mn bonding angle, we consider the Peierls-type spin-phonon coupling $J_{ij} = J_{ab} + J_{ab}'\delta_{ij}$ for the in-plane Mn-O-Mn bonds where $J_{ab}' = \partial J_{ab}/\partial \delta$ [17]. We assume that the shift of O ion $\delta_{ij}$ occurs along the local axis $\mathbf{n}_{i,j}$ directing from its cubic position (0) to the orthorhombic position ($\Delta_o$) at higher $T$ [see Fig. 1(b)]. Then the positive (negative) shift decreases (increases) the Mn-O-Mn bond angle.

The values of $J_{ab}$, $J_c$, $J_b$, $D$, $E$, and five DM parameters have been microscopically determined in Ref. [1] for several RMnO$_3$ compounds. Except for $J_b$, they are nearly invariant upon the $R$-site variation in the vicinity of the multiferroic phases. We fix $J_{ab}=-0.8$, $J_c=1.25$, $D=0.2$, $E=0.25$, $(\alpha_{ab}, \beta_{ab}, \gamma_{ab})=(0.1, 0.1, 0.14)$, and $(\alpha_c, \beta_c)=(0.42, 0.1)$. Here the energy unit is meV. We also find that very weak FM exchange $J_a$ is necessary to produce the $E$ phase, and adopt $J_a=-0.1$. The value of $K$ is chosen to be 500 so as to reproduce the experimental $P$ in the $E$ phase [see Fig. 2(a)]. We obtain the value of $J_{ab}'$ from the $\Delta_o$ dependence of $J_{ab}$ for several $R$ species [see Fig. 2(c)], which gives $J_{ab}' = \partial J_{ab}/\partial \Delta_o = 2.5$.

We treat $J_b$ as a variable which increases (decreases) as $r_R$ decreases (increases). This is because the exchange path for $J_b$ contains two O 2$p$ orbitals, and the orthorhombic distortion, whose magnitude is controlled by $r_R$, enhances their hybridization. We find that overall features of the phase evolution upon the $R$-site variation are reproduced as a function of $J_b$ even without considering the slight $R$-dependence of other parameters.

We analyze the above model using the replica exchange Monte-Carlo (MC) method [18]. Both spins and oxygen positions are updated in the simulation, and each exchange sampling is taken after 400 standard MC steps. Typically, we perform 600 exchanges for a system of $N=48\times48=6$ sites along $x$, $y$ and $z$ axes with periodic boundaries. We identify transition points and spin structures from $T$ profiles of specific heat and spin-helicity vector $h = \frac{1}{2N} \sum_{i}\mathbf{S}_i \times \mathbf{S}_{i+\hat{z}} + \mathbf{S}_i \times \mathbf{S}_{i+\hat{y}}/S^2$. We also calculate spin correlations in the momentum space by the Fourier transformation of spin configurations.

We first display the theoretical $T$-$J_b$ phase diagram in Fig. 2 which successfully reproduces the experimentally observed phase evolutions [10]. More concretely, the following four phases successively emerge at low $T$ as $J_b$ decreases: the $A$, $ab$-spiral, $bc$-spiral, and $E$ phases. In the $A$ ($E$) phase, the FM (up-up-down-down) Mn-spin layers stack antiferromagnetically, while in the $ab$ ($bc$) spiral phase, the Mn spins rotate within the $ab$ ($bc$) plane ($Pbnm$ setting) to form transverse cycloids [20, 21]. As $T$ decreases, these four phases emerge with multiferroic from the sinusoidal collinear phase at higher $T$ where the collinear Mn spins are sinusoidally modulated in amplitude. The spin structure is commensurate (C) with $q_b=0.5$ in the $E$ phase, whereas it is incommensurate (IC) in the $ab$ and $bc$ spiral phases. Importantly, the sinusoidal collinear state is also IC even above the $E$
FIG. 3: (Color online) (a) Polarizations vs $J_\parallel$ at $T \to 0$, i.e., $(S \cdot S)$ contribution $P_3$, $(S \times S)$ contribution $P_{3\text{M}}$, and experimentally measured $P$ in Eu$_{1-x}$Y$_x$MnO$_3$ and Y$_{1-y}$Lu$_y$MnO$_3$ 
[4, 5]. The summation $P_3 + P_{3\text{M}}$ reproduces the experimental $P$ well. 
(b) Alternation of the spin angles in the $ab$ spiral state due to the staggered DM vectors is illustrated in an exaggerated manner where $\hat{\phi} (\hat{\phi}^*)$ denotes the positive (negative) $c$-component of the vector. Shifts of the O ions due to the $(S \cdot S)$-type magnetostriction are shown by gray arrows.

phase (e.g., $q_\parallel = 0.458$ for $J_\parallel = 2.4$), and the spin-phonon coupling is a source of the IC-C transition with lowering $T$.

In the $ab$ ($bc$) spiral phase, this has been naively believed that the antisymmetric $(S \times S)$-type MS induces the ferroelectric polarization $P || a$ ($P || c$) 
[22, 24]. However, the observed $P$ in the $ab$ spiral phase is much larger than that in the $bc$ spiral phase. For instance, the $P_a$ in the $ab$ spiral phase of DyMnO$_3$ under $H || b$ is 2.5 times larger than $P_c$ in the $bc$ spiral phase at $H = 0$ 
[4, 6]. Moreover, in Eu$_{0.4}$Y$_{0.4}$MnO$_3$, the $P_a$ at $H = 0$ is approximately 10 times larger than $P_c$ under $H || a$, which excludes the influence of $f$ moments as its origin because of their absence 
[22]. This is quite puzzling since we expect nearly identical strength of the $(S \times S)$-type MS in these two phases. Recent first-principles study also suggested different mechanisms of $P$ between the two spiral phases 
[26]. To solve this issue, we calculate the polarization due to the $(S \cdot S)$-type MS, $P_3 = (\tilde{P}_a, \tilde{P}_b, \tilde{P}_c)$ from the oxygen shifts. Because of the staggered local axes $n_{i,j}$ on the zigzag Mn-O chain, $\tilde{\gamma}_i$ ($\gamma = a, b, c$) is given by

$$\tilde{\gamma}_i = -\frac{\Gamma_i}{N} \sum_j [(1)^{i + 1}_{i+1} + n^{\delta_{i+x} + 1}_{i+1} + (1)^{i + 1}_{i+1} + n^{\delta_{i+y} + 1}_{i+1}],$$

where $(m, n) = (0, 0)$ for $\gamma = a$, $(m, n) = (1, 0)$ for $\gamma = b$, and $(m, n) = (i + 1, 1, i + 1)$ for $\gamma = c$. Here the constant $\Pi_i$ is calculated to be $4.6 \times 10^5 \mu C/m^2$ for $\gamma = a$ and $b$, and $3.3 \times 10^5 \mu C/m^2$ for $\gamma = c$ from lattice parameters using the charge model.

In Fig. 3(a), we plot calculated $P_3$ at $T \to 0$ as functions of $J_\parallel$. Surprisingly we find a finite $P_3$ in the $ab$ spiral phase (e.g., $P_3 \sim 500 \mu C/m^2$ for $J_\parallel = 0.7$), while it is zero in the $bc$ spiral phase. This can be understood as follows [see also Fig. 3(b)]. On the in-plane chains, the $c$-axis components of the DM vectors are arranged in the staggered way. As a result, the spin rotation angles in the $ab$ spiral become subject to an alternate modulation 
[24]. Then the O ions between two spins with a smaller angle of $\phi - \Delta \phi$ (a larger angle of $\phi + \Delta \phi$) shift negatively (positively) to strengthen (weaken) the FM exchange through increasing (decreasing) the Mn-O-Mn bond angle. These shifts generate a uniform component resulting in the ferroelectric polarization. In fact, the spin rotation angles in the $bc$ spiral are also subject to the alternate modulation because of the staggered $a$-axis components of the DM vectors. However the induced O shifts are opposite between neighboring $ab$ planes, which results in their perfect cancellation.

We also show $J_\parallel$-dependence of $P_{3\text{M}}$ of $(S \times S)$ origin at $T \to 0$ in Fig. 3(a). Since the $P_{3\text{M}}$ consists of two contributions, i.e., the electronic and the lattice-mediated ones 
[26] and the former one is difficult to evaluate by the spin model, we calculate $P_{3\text{M}}$ from the spin helicity $h$. Note that $P_{3\text{M}}$ is proportional to $|h|$ and the observed $P$ in the $bc$ spiral phase is purely of $(S \times S)$ origin. In addition, we plot the experimentally measured $P$ of Eu$_{1-x}$Y$_x$MnO$_3$ and Y$_{1-y}$Lu$_y$MnO$_3$ for comparison 
[4, 9], whose $P$ originates purely from the Mn-spin order because of the absence of $f$ moments 
[28]. Effective $r_R$ and $J_\parallel$ of these solid solutions are evaluated by interpolations.

We find that the summation $P_3 + P_{3\text{M}}$ reproduces well the experimental $P$. Here we emphasize that only the elastic constant $K$ is an uncertain parameter in our model, and once we determine its value so as to reproduce the experimental $P$ in the $E$ phase, the behaviors of $P$ in the spiral phases are reproduced almost perfectly. Moreover it turns out that the $(S \cdot S)$ contribution $P_3$ can be comparable to or even larger than the $(S \times S)$ contribution $P_{3\text{M}}$ in the $ab$ spiral phase. This explains why $P$ in the $ab$ spiral phase is much larger than that in the $bc$ spiral phase.

Next we discuss the $E$ phase. Interestingly we find a finite $c$ component of the spin-helicity vector $h$ in this phase, indicating that its spin structure is not collinear in contrast to what we have believed so far, but its up-up-down-down structure is subject to a spiral modulation within the $ab$ plane. The inset of Fig. 2 illustrates the real-space spin configuration of the $E$ phase, which indeed shows the elliptically deformed $ab$-plane cycloid. Calculating the $T$-dependence of the expectation value for each term in the Hamiltonian, we find that the single-ion anisotropy or alternation of the in-plane easy magnetization axes due to the $d_{3xz}d_{2yz}$ or $d_{3yz}d_{2xz}$ orbital ordering is an origin of the cycloidal deformation. This predicted deformation should be confirmed in a future polarized neutron-scattering experiment.

With dominant up-up-down-down spin $b$-axis components, the O ions between nearly (anti)parallel Mn-spin
This seems as if the spin structure were IC components have very small peaks as shown in Fig. 4(a). qponent has sharp peaks at $3$ in the MC calculation. We find only the spin results [10–13], we calculate the spin-correlation functions which leads to the confusion. Observations of the IC wave numbers which can be attributed to this coexisting state, while a report $E$ state disappears as $T$ decreases. In this case, an anomaly in YMnO$_3$ and ErMnO$_3$ [9], which strongly evidences the coexistence. The coexistence together with the $(S \cdot S)$ contribution in the $E$ phase should be seriously considered also when we interpret the experimental results for RMnO$_3$ with $R$=Y, Ho, ....Lu, like the strange electromagnon spectra in the optical spectroscopy [31].

In summary, we have theoretically studied the magnetic structures and the ME coupling in RMnO$_3$ by using a realistic spin model including the spin-phonon coupling. We have succeeded in reproducing the entire phase diagram of RMnO$_3$ for the first time, and have revealed the cooperative contributions of symmetric $(S \cdot S)$-type and antisymmetric $(S \times S)$-type MSs to the ferroelectricity in the $ab$ spiral phase. This mechanism is generic and is relevant to all the spin-spiral multiferroics. We have also found the cycloidal spin deformation in the $E$ phase, and the coexistence of the $E$ and ICS states. On these basis, the nontrivial behavior of $P$ and several puzzles in the experiments have been explained. Our model gives a firm basis for studying and controlling the intriguing cross-correlation phenomena in RMnO$_3$.

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