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PAPER

Designing switchable near room-temperature multiferroics via the discovery of a novel magnetoelectric coupling

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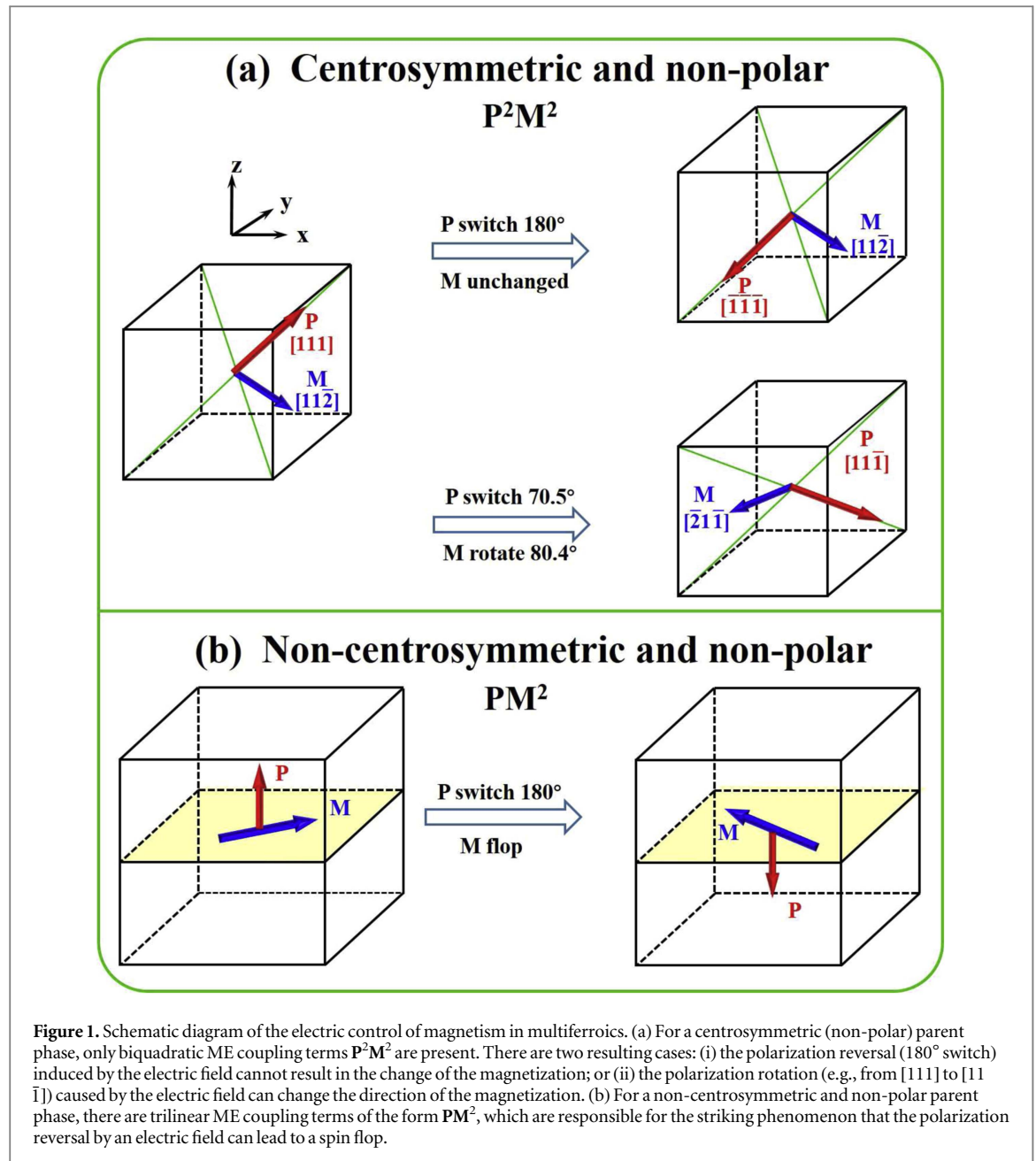
Abstract

Magnetoelectric (ME) coupling is the key ingredient for realizing the cross-control of magnetism and ferroelectricity in multiferroics. However, multiferroics are not only rare, especially at room-temperature, in nature but also the overwhelming majority of known multiferroics do not exhibit highly-desired switching of the direction of magnetization when the polarization is reversed by an electric field. Here, we report group theory analysis and *ab initio* calculations demonstrating, and revealing the origin of, the existence of a novel form of ME coupling term in a specific class of materials that does allow such switching. This term naturally explains the previously observed electric field control of magnetism in the first known multiferroics, i.e., the Ni–X boracite family. It is also presently used to design a switchable near room-temperature multiferroic (namely, LaSrMnOsO₆ perovskite) having rather large ferroelectric polarization and spontaneous magnetization, as well as strong ME coupling.

Introduction

Multiferroics are attracting increasing interest due to the profound underlying physics (i.e., the coexistence and coupling of ferroelectric and magnetic orders), and the potential applications in novel multifunctional devices [1–5]. In particular, multiferroics may be used to realize nonvolatile, low-power, and high-density memory devices that combine fast electrical writing and magnetic reading [6, 7]. To make this possible, the magnetoelectric (ME) coupling between the magnetization and ferroelectric polarization should be strong.

Numerous studies [8–19] have been performed to investigate various types of ME couplings in multiferroics. Within the Landau theory, the macroscopic free energy of the ME coupling can be expressed in terms of the ferroic orders including the polarization \mathbf{P} , magnetization \mathbf{M} , antiferromagnetic vector \mathbf{L} , antiferroelectric vector \mathbf{A} and so on. Since polarization \mathbf{P} (respectively, magnetization \mathbf{M}) is directly tunable by the electric field (respectively, magnetic field), we will mainly focus on the coupling between \mathbf{P} and \mathbf{M} hereafter, unless specified. For some inhomogeneous magnetic systems, the spin current model (or inverse Dzyaloshinskii–Moriya interaction) [20–26] of the form $(\mathbf{P} \cdot [\mathbf{M}(\nabla \cdot \mathbf{M}) - (\mathbf{M} \cdot \nabla)\mathbf{M}])$ in the continuum limit, was proposed to explain the spiral spin order induced electric polarization [27–29]. For the homogeneous system with uniform \mathbf{P} and \mathbf{M} , the most common form of the ME coupling is $|\mathbf{P}|^2|\mathbf{M}|^2$ (see, e.g. [30, 31]). In fact, this biquadratic term exists in any multiferroic material regardless of symmetry. A more general biquadratic term can be written as $P_i P_j M_\alpha M_\beta$, where i, j, α, β denote the three Cartesian directions (x, y and z). For simplicity, we will refer to this term as $\mathbf{P}^2\mathbf{M}^2$. We note that both the spin current term and the $\mathbf{P}^2\mathbf{M}^2$ term satisfy both the spatial inversion and



time reversal symmetry. From thermodynamic considerations, one can see that the polarization reversal (180° switch) induced by electric field cannot result in the change of the magnetization as a result of the P^2M^2 coupling [32] (see the upper panel of figure 1(a)). However, it is possible to change the direction of the magnetization if the polarization is rotated by the electric field (see the lower panel of figure 1(a) for the case of BiFeO_3 thin-film [18, 33]) because \mathbf{P} and \mathbf{M} want to be perpendicular to each other as a result of very specific i, j, α and β indices involved in the $P_i P_j M_\alpha M_\beta$ coupling. The magnetization is switched in such a way that the free energy is conserved. A similar mechanism, involving $P_i P_j M_\alpha M_\beta$ coupling too, happens in the predicted room-temperature multiferroic $\text{Zn}_2\text{FeOsO}_6$ [34] with a strong ferrimagnetism. Nevertheless, the rotation of the polarization direction by the electric field is less convenient than the reversal of the polarization from the application point of view.

In this manuscript, we propose that a novel form of trilinear ME coupling PM^2 exists when the parent phase adopts one of the 9 non-centrosymmetry non-polar point groups (i.e., $S_4, D_2, D_3, D_4, D_6, D_{3h}, D_{2d}, T, T_d$), leading to the intriguing phenomenon that the reversal of the polarization results in a spin flop. This trilinear ME coupling is responsible for the observed and puzzling electric field control of ferromagnetism at low-temperature in the first discovered multiferroics, that are Ni–X boracites. On the basis of our finding, we further design a near room-temperature multiferroic compound by investigating the ‘double-double’ LaSrMnOsO_6 perovskite oxide.

Results

Group theory analysis and novel ME coupling

Here, we first perform group theory analysis to find out the possible ME coupling forms. According to the Landau theory, the free energy \mathcal{F} of the low-temperature, low-symmetry phase with respect to the high-temperature, high-symmetry parent phase contains the ME coupling free energy \mathcal{F}_{me} . Since usually the high-symmetry parent phase is paramagnetic, the free energy (including \mathcal{F}_{me}) remains invariant under the time reversal operation, suggesting that only even order terms of \mathbf{M} might exist in \mathcal{F}_{me} . For the spatial symmetry of the parent phase, we consider all possible 32 crystal point groups. Note that since \mathbf{P} and \mathbf{M} are macroscopic physical quantities, the use of the point group instead of the full space group is enough to analyze the symmetry properties of the free energy, which greatly simplifies the derivation. Up to the fourth order, the free energy related to the ME coupling \mathcal{F}_{me} can be written as:

$$\mathcal{F}_{\text{me}} = C_{i,\alpha,\beta} P_i M_\alpha M_\beta + C_{i,j,\alpha,\beta} P_i P_j M_\alpha M_\beta, \quad (1)$$

where C s are expansion coefficients and the Einstein summation convention is used. Considering the fact that the free energy should be invariant under any operation of the point group, we derive \mathcal{F}_{me} for all 32 crystal point groups (see table S2 of supplementary material (available online at stacks.iop.org/NJP/20/053025/mmedia)). Depending on the symmetry of the parent phase, the ME coupling takes different forms: (i) If the parent phase is centrosymmetric (and thus also non-polar), there is no trilinear coupling $P_i M_\alpha M_\beta$, but rather only biquadratic couplings can exist. This is because the inversion operation changes P_i to $-P_i$, but does not change magnetization M . (ii) If the parent phase adopts one of the 11 non-centrosymmetric and non-polar point groups (C_{3h} , S_4 , D_2 , D_3 , D_4 , D_6 , D_{3h} , D_{2d} , T , T_d , O), we find that there are trilinear ME couplings $P_i M_\alpha M_\beta$ for all these point groups except the O point group (see section II of the supplementary material). For the sake of convenience in studying ME coupling, we only focus on non-centrosymmetric non-polar point group hereafter. The trilinear ME coupling suggests that the reversal of polarization may lead to a spin flop since when P_i changes sign, either M_α or M_β must change sign to keep the free energy invariant (see figure 1(b) for the case of the T_d point group). However, this is only possible if the polarization has a non-zero component along the i -axis and the magnetization has non-zero components along the α and β axes. In addition, there is another requirement for the symmetry of the low-temperature FE phase: the FE phase should adopt the appropriate point group symmetry so that the state with P_i is symmetrically equivalent to the state with an opposite polarization (i.e., $-P_i$). For all the 10 non-centrosymmetric non-polar point groups that display the trilinear ME couplings, we examine the conditions (i.e., directions of polarization and magnetization) for realizing the spin flop by reversing the polarization. All the results are listed in tables S1 and S3 in the supplementary material. We find that, if the parent phase displays one of the 9 non-centrosymmetric non-polar point groups comprising of S_4 , D_2 , D_3 , D_4 , D_6 , D_{3h} , D_{2d} , T , T_d , it is possible to manipulate the direction of magnetization by polarization reversal, which is the most important result of this manuscript. The C_{3h} point group is an exception, since, in this case, the polarization can only be along the z -axis (so that the $-P$ state is symmetrically equivalent to the P state), but there is no $P_z M_\alpha M_\beta$ coupling for the C_{3h} point group. Our above analysis is general so that the conclusion is applicable to both type-I and type-II multiferroics (in type-I multiferroics, ferroelectricity and magnetic order are caused by different mechanisms, while in type-II multiferroics, ferroelectricity appears due to the magnetic order). Note that the existence of \mathbf{PM}^2 coupling does not necessarily mean that the electric polarization is induced by the magnetization.

$\text{Ni}_3\text{B}_7\text{O}_{13}\text{X}$ boracite crystal structure

We find that the above mechanism is applicable to the first multiferroic compounds $\text{Ni}_3\text{B}_7\text{O}_{13}\text{X}$ (referred to as Ni-X hereafter) discovered by Schmid *et al* [35–37], where X represents a halogen atom (Cl, Br, or I). The high-temperature parent phase of $\text{Ni}_3\text{B}_7\text{O}_{13}\text{X}$ can be viewed as a cubic AMO_3 perovskite structure where B_7O_{13} , X , and Ni play the role of A, M, and O, respectively. Note that the high-symmetry parent phase with the $F\bar{4}3c$ space group and T_d point group is non-centrosymmetric and non-polar, different from the usual perovskite systems, due to the presence of asymmetric B_7O_{13} clusters. Ni-X compounds were found to display ferroelectricity and weak ferromagnetism at low-temperature. In the low-temperature ferroelectric structure with the $Pca2_1$ space group, the originally equally spaced $-X\text{--Ni--X--Ni--}$ chain along each of the three pseudocubic orthogonal directions undergoes a Peierls-like distortion to the $\cdots X\text{--Ni} \cdots X\text{--Ni} \cdots$ chain with alternative Ni-X bond lengths, resulting in XNi_3 pyramids as illustrated in figure S1 of the supplementary material. Interestingly, the electrical switching of the ferroelectric polarization from $[001]_c$ to $[00\bar{1}]_c$ was observed to result in a 90° change of magnetization from $[110]_c$ to $[1\bar{1}0]_c$ [35]. The complicated magnetic structures of Ni-X compounds were difficult to be fully resolved experimentally. Fortunately, the magnetic space group (magnetic point group) of Ni-Cl [38–40] is unambiguously determined to be $\text{Pc}'a_2'$ ($m'm2'$) [41]. Hereafter, we will mainly focus on Ni-Cl to study ferroelectric and magnetic properties, as well as ME coupling.

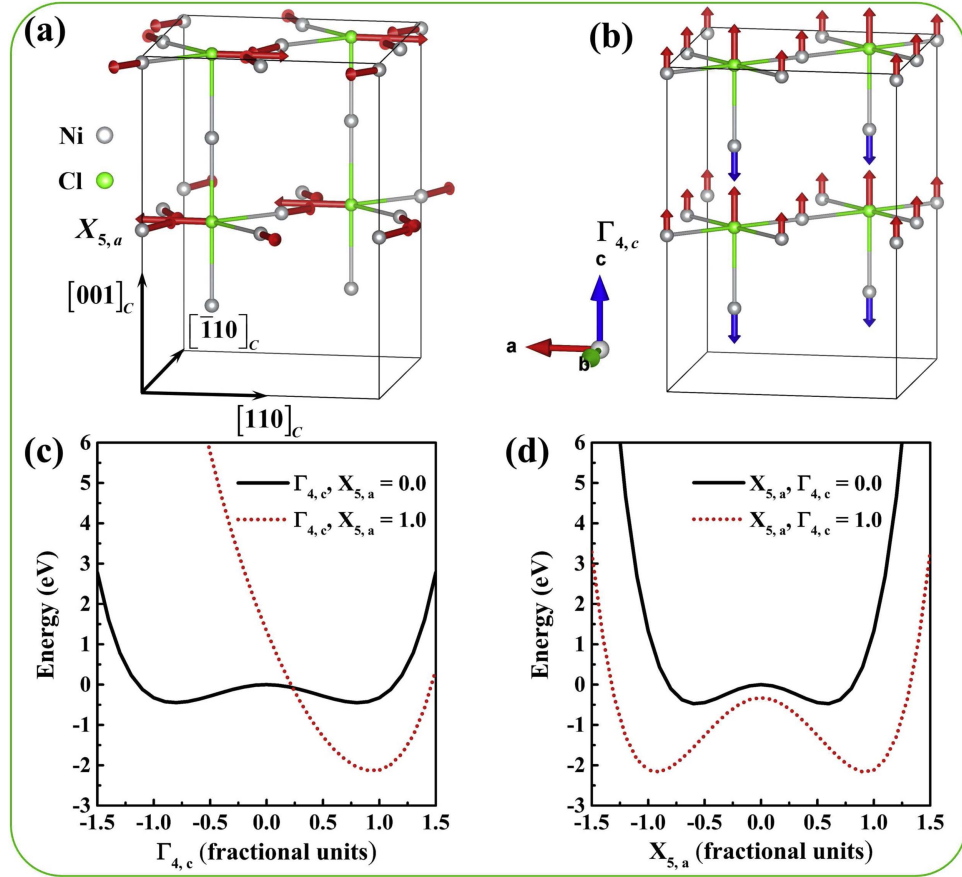


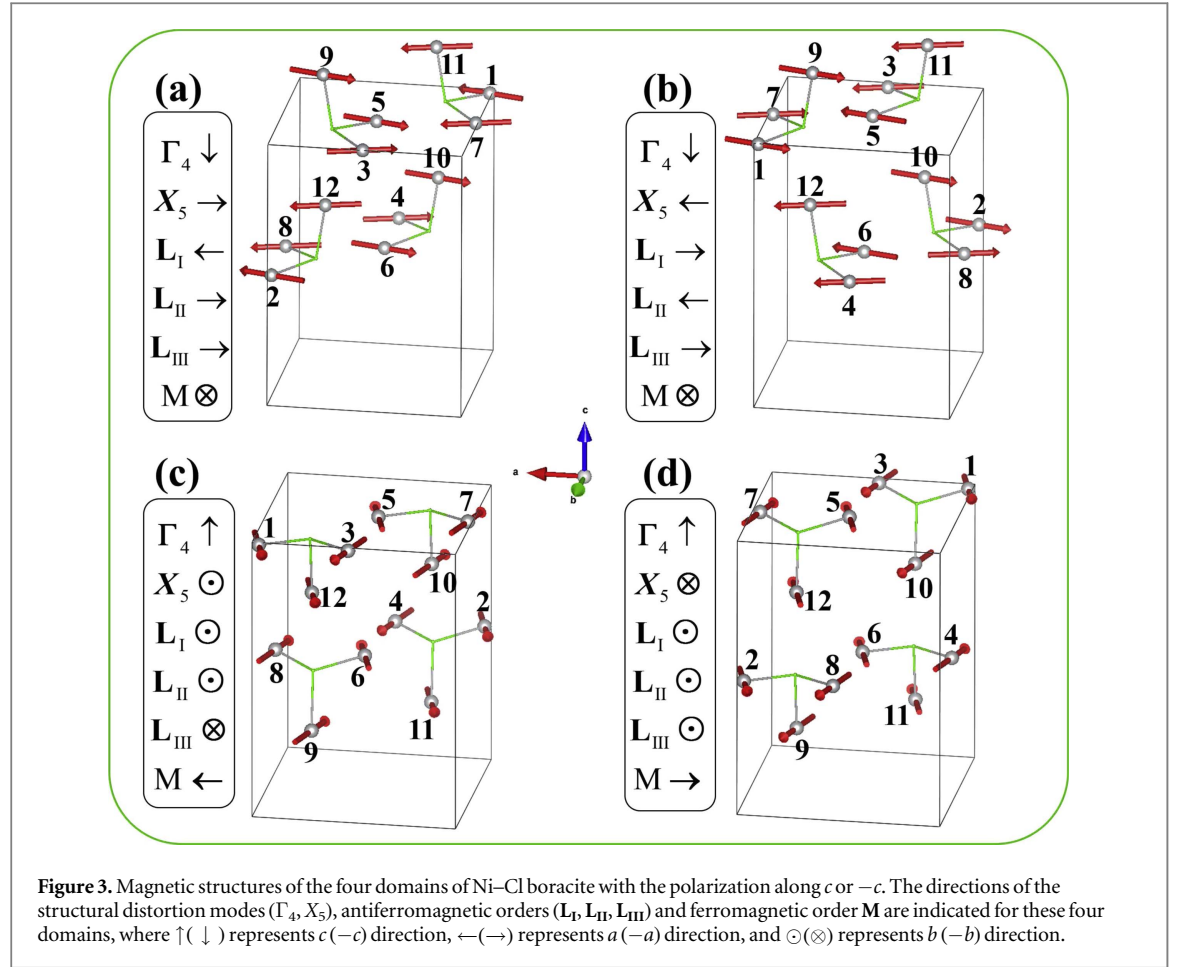
Figure 2. Two dominant structural modes of $\text{Ni}_3\text{B}_7\text{O}_{13}\text{Cl}$ that drive the cubic phase ($F\bar{4}3c$) into the orthorhombic phase ($Pca2_1$) and the coupling between these two modes. (a) The $X_{5,a}$ mode and (b) the $\Gamma_{4,c}$ mode (which is ferroelectric). Note that the displacements of boron and oxygen atoms are not shown since they are not relevant to the magnetic property and ME coupling. (c) Total energy with respect to the cubic phase as a function of the amplitude of the $\Gamma_{4,c}$ mode when the $X_{5,a}$ mode amplitude is fixed to 0 (solid line) or 1 (dashed line), respectively. (d) Same as (c), but now the $X_{5,a}$ mode amplitude is varied and the $\Gamma_{4,c}$ mode amplitude is fixed to 0 (solid line) or 1 (dashed line), respectively.

Ferroelectricity of Ni–Cl

The spontaneous polarization of the low-temperature phase of Ni–Cl is calculated to be about $1.391 \mu\text{C cm}^{-2}$ along the $[001]_c$ polar axis of the $Pca2_1$ space group. To seek the microscopic mechanism of ferroelectricity in Ni–Cl, we performed modes decomposition [42] of the low-symmetry phase with respect to the cubic high-symmetry phase. We find there are two dominant modes, i.e., X_5 and Γ_4 (see figures 2(a) and (b)). The Γ_4 mode is ferroelectric, and Ni and Cl ions' motions participate to the formation of the polarization along the $[001]_c$ axis. On the other hand, the non-ferroelectric X_5 mode involves the in-plane displacements of Ni and Cl ions in $(001)_c$ planes, with the displacements in two adjacent planes being opposite. Our DFT calculations show that the Γ_4 mode itself is unstable (figure 2(c)), indicating that the ferroelectricity is of proper nature (therefore indicating that polarization in our system does not originate, e.g., from magnetic moments). However, we find that the X_5 mode is also unstable (figure 2(d)) and the coupling $\Gamma_{4,c}X_{5,a}^2$ (where a, b, c of the orthorhombic coordinate system are along the $[\bar{1}\bar{1}0]_c$, $[1\bar{1}0]_c$, $[001]_c$ directions, respectively) between the two modes is rather strong, suggesting that there is a significant, additional, improper contribution arising from the coupling of polarization with the X_5 mode. The system is rather unusual, in the sense that it exhibits improper characteristics (see figure 2(c)) but also possesses intrinsic polar instabilities.

Magnetic property of Ni–Cl

To determine the directions of magnetic moments in the magnetic ground state, we consider 27 possible magnetic structures that are compatible with the experimentally determined $Pc'a_2'$ magnetic space group [41]. There are three different Ni Wyckoff positions [Ni–A(1,2,3,4), Ni–B(5,6,7,8), Ni–C(9,10,11,12) in figure 3] in the unit cell of the low-temperature structure; to be compatible with the $Pc'a_2'$ magnetic space group, Ni–A and Ni–B (respectively, Ni–C) may take one of the three possible magnetic structures C_a, F_b, G_c (respectively, G_a, F_b, C_c). Our DFT + U + SOC calculations show that the nearly collinear magnetic structure shown in figure 3(a) has the lowest energy among all these 27 magnetic configurations: the Ni magnetic moments almost adopt a perfect



antiferromagnetic arrangement along the a axis, while there is a small canting ferromagnetic moment along the b axis in agreement with experiment [40]. Our predicted magnetic structure is not exactly the same as the proposed non-collinear magnetic structure from a neutron diffraction study on the powder sample [40]; in our proposed magnetic structure, the magnetic moments inside each Ni_3Cl pyramid are almost ferromagnetically aligned, which is different from the previously proposed magnetic structure. In fact, our DFT calculations show that the experimentally proposed magnetic structure has a higher energy by 2.18 meV/f.u. than ours. In order to further verify our results, we computed the exchange parameters J (see table S5 and figure S3 of the supplementary material) in the $Pca2_1$ structure, and found that the computed exchange parameters are consistent with the predicted magnetic structure (see section III.A of the supplementary material).

ME coupling of Ni-Cl

We are now in position to discuss the ME coupling in Ni-Cl. Since the parent phase takes the T_d symmetry, the trilinear ME coupling adopts the form of:

$$\mathcal{F}_{\text{me}} = C(M_x M_y P_z + M_y M_z P_x + M_x M_z P_y), \quad (2)$$

where C is a coupling constant. By symmetry, there are six possible ferroelectric domains with polarization along $[100]_c$, $[\bar{1}00]_c$, $[010]_c$, $[0\bar{1}0]_c$, $[001]_c$, $[00\bar{1}]_c$ respectively. Without loss of generality, we consider the ferroelectric domains with the polarization along $[001]_c$ or $[00\bar{1}]_c$ where the magnetization is along $[110]_c$ or $[1\bar{1}0]_c$ respectively. The ME coupling can be simply written as $\mathcal{F}_{\text{me}} = CM_x M_y P_z$. It is now immediately clear that when the polarization is reversed, either M_x or M_y must change sign to make the free energy unchanged. Thus, the reversal of polarization by an electric field will lead to a rotation of the magnetization by 90° or -90° . We note that the existence of the $M_x M_y P_z$ term in Ni-X was noticed by Schmid *et al* [37]. However, why and how the trilinear ME coupling arises were not addressed there. Furthermore, the significance and the generality of the trilinear ME coupling was not realized either.

The Landau theory provides a general way to analyze the ME coupling in multiferroics. In order to gain deep insight into the mechanism of the ME coupling, below, we will investigate how the $M_x M_y P_z$ ME coupling is realized in Ni-Cl. First, symmetry analysis shows that there are eight domains with polarization along $[001]_c$ or $[00\bar{1}]_c$. Four of these eight domains are shown in figure 3, while the other four domains can be obtained by reversing all the local magnetic moments of Ni ions with the time reversal operation. Note that these domains

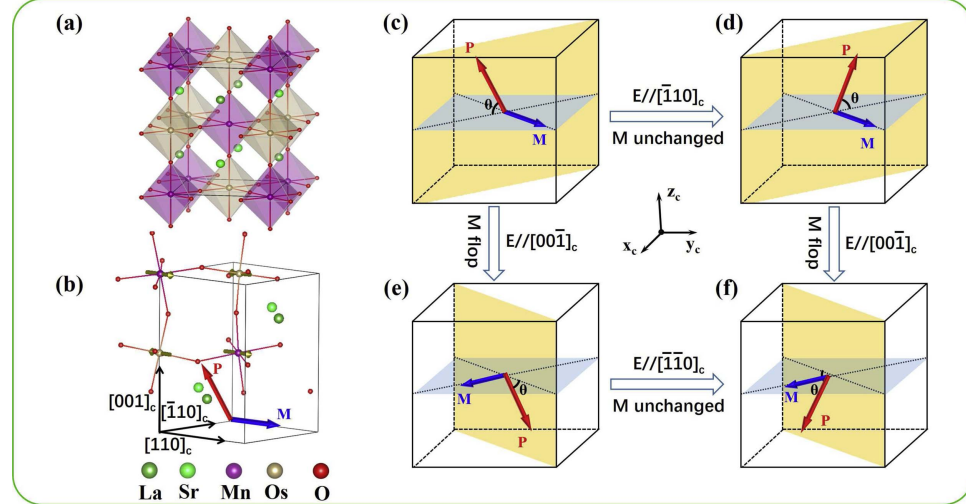


Figure 4. (a) Crystal structure of the parent phase of LaSrMnOsO₆. (b) Crystal and magnetic structures of low-symmetry LaSrMnOsO₆. (c)–(f) show the polarization and magnetization in four domains of LaSrMnOsO₆. The angle θ is used to characterize the direction of polarization ($\theta \sim 45^\circ$). It is possible to switch the direction of magnetization by 90° via the application of an electric field along $[00\bar{1}]_c$.

are equivalent by symmetry, i.e., they have the same free energy. For all domains, Ni spins along each of the three pseudocubic –Ni–Cl–Ni– chains adopt an antiferromagnetic arrangement, thus we define three antiferromagnetic orders L_I , L_{II} , L_{III} . L_I is for the $[010]_c$ chain, L_{II} is for the $[100]_c$ chain, and L_{III} is for the $[001]_c$ chain. To be more specific, the three antiferromagnetic orders are defined as (see figure 3)

$$L_I = S_1 + S_2 - S_5 - S_6, L_{II} = S_3 + S_4 - S_7 - S_8, \text{ and } L_{III} = S_9 + S_{10} - S_{11} - S_{12}.$$

To characterize the four domains, we also use other order parameters (i.e., Γ_4 , X_5 , \mathbf{M}) besides the antiferromagnetic order parameters. Our analysis shows that the $\Gamma_{4,c}(L_{III,a}M_b + L_{III,b}M_a)$ ME coupling is the key to realize the macroscopic ME coupling $M_xM_yP_z$ in Ni–Cl (see section III.B of the supplementary material). More precisely, the ME coupling is microscopically realized in the following way. In domain(a), $\Gamma_{4,c} < 0$, $L_{III,a} < 0$, $M_b < 0$, while $L_{III,b} = M_a = 0$. When one applies an electric field along the c -axis to domain(a) (shown as figure 3(a)), this domain(a) can change to domain(c) (for which $\Gamma_{4,c} > 0$, $L_{III,b} < 0$, $M_a > 0$, while $L_{III,a} = M_b = 0$) or domain(d) to maintain invariant the free energy.

Designing multiferroics based on the novel ME coupling

The trilinear ME coupling can thus explain the electric field-induced observed spin flop in the Ni–X multiferroics, but can also be utilized to design new multiferroics. For that, we propose the following general design principle: (i) first, one should start from a non-centrosymmetric non-polar parent phase. One way to achieve this is by element mixing; (ii) there should be ferroelectric instability in the parent phase below a critical temperature. The ferroelectricity can be proper or improper; and (iii) there should exist spontaneous magnetization that is compatible with the ferroelectricity.

Hereafter, we will take the AMO₃ perovskite structure as an example to illustrate this idea. In particular, the cubic double-double perovskite $AA'BB'O_6$ structure with a checkboard arrangement at both A and B sites is non-centrosymmetric and non-polar (T_d point group). This atomic ordering can also be seen as a superlattice along the $[111]_c$ direction, which may be grown with the molecular beam epitaxy method or the pulse laser deposition. As an example, we find that LaSrMnOsO₆ adopts a common $a^-a^-c^+$ tilt pattern (Glazer's notation [43]) as confirmed from the genetic algorithm simulation [44]. Because of the octahedral tilt, LaSrMnOsO₆ becomes ferroelectric with the P_c space group (C_{1h} point group), similar to the case of hybrid improper ferroelectricity [45–50].

The electric polarization of the LaSrMnOsO₆ is calculated to be $3.58 \mu\text{C cm}^{-2}$ along the $[\sqrt{2}/2, -\sqrt{2}/2, 1]_c$ direction. The magnetic ground state is found to be ferrimagnetic, with a $2 \mu_B/\text{f.u.}$ net magnetization and a magnetic easy axis being along the $[110]_c$ direction. Our first-principles molecule dynamics simulations indicate that the polar phase of LaSrMnOsO₆ is stable at room-temperature (see section IV.A of the supplementary material). The Curie temperature is estimated to be 310 K (see section IV.A of the supplementary material).

The ferrimagnetism and ferroelectricity in double-double perovskite LaSrMnOsO₆ are also strongly coupled to each other, as similar to the Ni–Cl case. We find that the reversal of the $[001]_c$ component of the polarization will lead to a spin flop, while the reversal of the in-plane polarization will not change the direction of the magnetization (see figure 4).

Therefore, we predict that LaSrMnOsO_6 is a promising multiferroic with a large polarization, strong magnetization, high transition temperature, and strong ME coupling. Although we mainly discuss the ME coupling in the T_d case, the main conclusion is applicable to other non-centrosymmetric non-polar point groups.

Summary

To summarize, we report and document a novel ME coupling of the PM^2 form, when the parent phase is non-centrosymmetric and non-polar. Our work not only reveals the mechanism behind such novel ME coupling, but also paves a new way to design/search novel high-performance multiferroics.

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