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Electric-field-switchable magnets: The case of $BaNiF_4$

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We show, using the antiferromagnetic ferroelectric $BaNiF_4$ as a model system, that the "weak" magnetic order arising from a polar structural distortion in a ferroelectric magnet due to the Dzyaloshinskii-Moriya interaction can be switched by an electric field. We calculate the magnitude of the resulting magnetic order parameter in $BaNiF_4$ using first-principles techniques, and we show that it is one to two orders of magnitude larger than the converse effect of "weak ferroelectricity" resulting from noncentrosymmetric magnetic ordering. Our work points the way toward the design of multiferroic devices, in which the magnetoelectric domain state can be fully controlled by both electric and magnetic fields.

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Much of the current interest in magnetic ferroelectrics stems from the possibility of cross correlations between their magnetic and dielectric properties, enabling the manipulation of magnetic properties using electric fields, and vice versa.[1] Indeed, various intriguing magnetoelectric coupling effects have been reported so far, ranging from magnetic field dependence of the dielectric permittivity in materials such as $YMnO_3$,[2] to magnetic phase control using an electric field in $HoMnO_3$,[3] and the reorientation of electric polarization by a magnetic field in $TbMnO_3$.[4]

Of particular appeal, both from the viewpoint of fundamental science and also with respect to possible applications in digital memory technologies, is the *switching* of magnetic domains by an electric field, and vice versa. This scenario is distinct from those mentioned above, in that the electric field would push the system into a different realization of the same ground state phase, so that the resulting state would be stable even when the field is removed (a basic requirement for nonvolatile data storage). In many multiferroics, however, different mechanisms drive the magnetic and ferroelectric ordering, resulting in only weak coupling between the two order parameters, and disfavoring such magnetoelectric domain switching. Therefore, despite the recent revival of interest in magnetoelectric phenomena, an early demonstration of ±90° magnetization rotation by an electric field and magnetic field switching of the polarization in $Ni_3B_7O_{13}I$ (Ref. 5) has, to our knowledge, remained the only report of magnetoelectric domain switching in a single-phase multiferroic.

In this Rapid Communication we illustrate a mechanism in which magnetic order is induced by the ferroelectricity and is therefore intimately coupled to the electric polarization, allowing controlled switching of the magnetic order parameter by switching the polarization using an electric field. We demonstrate this approach using as an example the magnetic ferroelectric $BaNiF_4$, which is representative of a whole class of multiferroic barium fluorides. We show, by using both first-principles calculations and symmetry analysis, that the polar distortion in this material gives rise to a Dzyaloshinskii-Moriya (DM) interaction,[6] and that the sign of this interaction is determined by the orientation of the ferroelectric polarization, which can be inverted with an electric field. We demonstrate that such a reversal of the polarization also leads to a reversal of the "weak" magnetism that results from the DM interaction, thus allowing switching of the corresponding magnetic order parameter with an electric field. We argue that similar magnetoelectric switching phenomena should be expected in many other multiferroics, and we therefore propose this mechanism as a very promising route toward useful magnetoelectric device applications.

All calculations presented in this work are performed using the Vienna *ab initio* simulation package[7] (VASP) employing the projector-augmented wave method.[8,9] We use a plane-wave energy cutoff of 450 eV and a Γ-centered $2\times4\times2$ **k**-point mesh (divisions with respect to the monoclinic basis vectors of the magnetic unit cell), which is sufficient to obtain converged results for all quantities under consideration. To account for the strong Coulomb interaction between the localized *d* electrons of the transition metal cations we use the local spin density approximation (LSDA)+*U* method.[10]

$BaNiF_4$ is representative of the isostructural family of barium fluorides with the chemical formula $BaMF_4$, where *M* can be Mn, Fe, Co, Ni, Zn, or Mg. These compounds crystallize in a base-centered orthorhombic structure with space group $Cmc2_1$,[11,12] which is shown in Fig. 1. $BaMnF_4$ undergoes an additional structural phase transition at around 250 K (see Ref. 13). Ferroelectric switching has been reported for *M*=Co, Ni, Zn, and Mg.[14] The systems with *M*=Mn, Fe, Co, and Ni order antiferromagnetically at Néel temperatures around 20–70 K. The magnetic structure derived experimentally for the systems with *M*=Mn, Fe, Ni is shown in Fig. 2(a).[15] The magnetic unit cell is doubled compared to the chemical unit cell, and contains four magnetic *M*

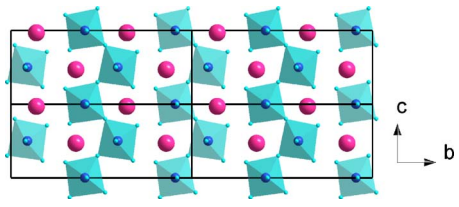

FIG. 1. (Color online) Projection of the $BaMF_4$ structure along the *a* axis. The *M* cations are surrounded by fluorine octahedra, which form puckered sheets perpendicular to the *b* axis, separated by similar sheets of Ba cations. Note that adjacent sheets are shifted relative to each other by half a lattice constant along the *a* direction.

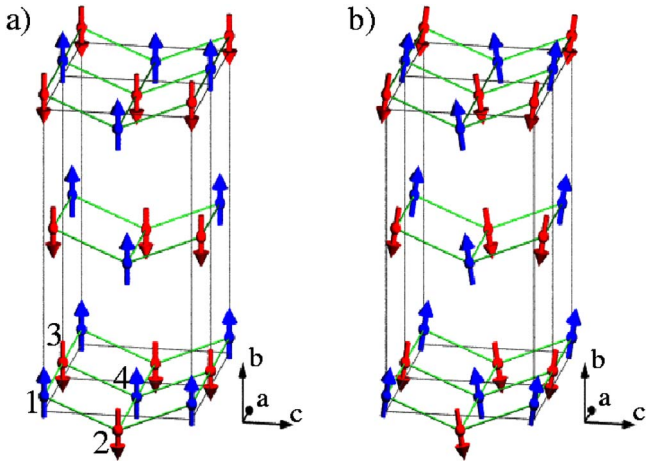

FIG. 2. (Color online) Magnetic structures (not to scale) of $BaNiF_4$ derived from the experimental observations (a) and from our calculation including spin-orbit coupling (b). The conventional orthorhombic unit cell is outlined, and the puckered sheets perpendicular to the *b* direction are also shown; numbers in (a) indicate the four magnetic ions in the unit cell.

cations, which are arranged in sheets perpendicular to the *b* axis. Within each sheet the cations form a puckered rectangular grid, with the magnetic moments of neighboring cations oriented antiferromagnetically, and all moments aligned parallel to the *b* axis. The coupling between different sheets is weak, leading to low magnetic ordering temperatures and pronounced two-dimensional behavior.[16] The corresponding magnetic space group is P_a2_1.

First we perform a full structural optimization of $BaNiF_4$ within the experimentally observed $Cmc2_1$ symmetry, using typical values of $U=4$ eV for the Hubbard U and $J=1$ eV for the intra-atomic exchange parameter of the LSDA+U method; the structural parameters we obtain agree well with available experimental data.[17] To confirm the experimentally reported magnetic structure we then calculate the energy differences for different relative orientations of the four magnetic sublattices corresponding to the four magnetic ions in the unit cell and extract the Heisenberg nearest-neighbor coupling constants. In these calculations the spin-orbit coupling is neglected. We obtain strong antiferromagnetic nearest-neighbor coupling within the buckled planes, $J_a=4.4$ meV, $J_c=3.3$ meV,[18] consistent with the experimentally observed structure. However, when spin-orbit coupling is included in the calculation, we observe that the collinear spin configuration shown in Fig. 2(a), with all spins aligned along the *b* direction, is unstable, and that instead the magnetic moments assume a noncollinear configuration where all spins are slightly tilted toward the $\pm c$ direction as shown in Fig. 2(b). The tilting angle obtained from the calculation is about 3°.

Figure 3 shows the U and J dependence of the canting angle between the magnetic moments of the Ni cations and the *b* direction. In order to obtain local magnetic moments we integrate the spin density within spheres of radius 1.2 Å centered at the Ni sites. Our test calculations show that for this radius the integrated spin density adopts a saturated value of about $1.7\mu_B$ per Ni. It can be seen that there is only

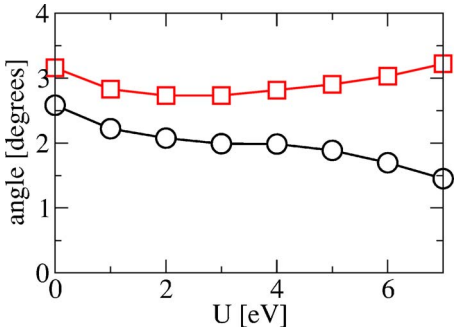

FIG. 3. (Color online) Dependence of canting angle on the LSDA+U parameters. Circles correspond to $J=0$ and squares to $J=1$ eV.

a moderate U dependence of the canting angle between $U=2$ and 6 eV, whereas it is slightly suppressed by decreasing J. This J dependence is a consequence of the spin-nondiagonal elements introduced into the effective potential by the LSDA+U energy in its most general form,[19] which is rotationally invariant with respect to both orbital and spin quantum numbers. It follows from Fig. 3 that within the physically reasonable parameter range of $U=2-6$ eV and $J=0-1$ eV the canting angle is $2°-3°$.

The small tilting of the magnetic ions can be explained by the DM interaction,[6] $E_{ij}^{DM}=d_{ij}\cdot(s_i\times s_j)$, where s_i is the spin of ion i and d_{ij} is the coupling vector corresponding to this antisymmetric exchange interaction between ions i and j. This interaction occurs only for certain low symmetries and can give rise to "weak ferromagnetism" in otherwise antiferromagnetic materials, where a canting of the two (or more) sublattice magnetizations away from the ideal collinear antiferromagnetic orientation gives rise to a small net magnetization.[6,20] In the case of $BaNiF_4$ the magnetic space group does not allow the occurrence of weak ferromagnetism but nevertheless there is a nonzero DM interaction d_c between magnetic nearest neighbors along the *c* direction,[21] whereas the DM interaction between neighboring cations along the *a* direction vanishes by symmetry.

The canting due to the DM interaction leads to a weak antiferromagnetic order parameter $L_c=s_1+s_2-s_3-s_4$, in addition to the experimentally observed (primary) antiferromagnetic order parameter $L_{ab}=s_1-s_2-s_3+s_4$. On a macroscopic level the DM interaction leads to a coupling between L_{ab} and L_c of the form

$$E_{\text{macro}}^{\text{DM}}=D\cdot(L_{ab}\times L_c), \tag{1}$$

where $D=d_c/2$. If we neglect the magnetic single-ion anisotropy contribution to the total energy, the canting angle is given by $\alpha\approx D/4J_c$, from which we obtain a value for D of about 0.7 meV (using $U=4$ eV, $J=1$ eV). We note that since both D and J scale with the strength of the superexchange interaction, α is not correlated with the magnetic ordering temperature.

Note that a term of the form (1) can also be caused by different orientations of the easy axes for the magnetic moments on different sites. This mechanism is also allowed within the crystallographic and magnetic symmetry of

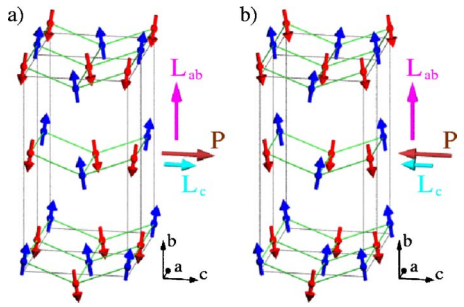

FIG. 4. (Color online) Magnetoelectric switching in $BaNiF_4$. The weak antiferromagnetic order parameter L_c is coupled to the polarization P. Reversal of the polarization from (a) to (b) leads to a reversal of the canting of the magnetic moments and thus to a reversal of L_c.

$BaNiF_4$, in addition to the DM interaction described above. Since the following analysis of the magnetoelectric domain switching is independent of the actual microscopic mechanism leading to the term (1), we do not separate these two effects further.

In order to analyze the possibility of magnetoelectric domain switching in $BaNiF_4$ we need to know the symmetry of the corresponding "prototype" phase.[20,22] Although the paraelectric states of the $BaMF_4$ systems are not accessible experimentally, since all crystals melt before undergoing a ferroelectric phase transition, a nonpolar reference structure has been suggested and used to discuss the ferroelectric switching properties of these systems.[23] This structure has the nonpolar space group *Cmcm* and can be obtained from the ground-state $Cmc2_1$ structure by enforcing a mirror symmetry perpendicular to the c axis. Within this symmetry no canting of the magnetic moments is allowed and the resulting magnetic order corresponds to the collinear spin arrangement shown in Fig. 2(a) with the magnetic space group P_a2_1/m'. The absence of canting in the centrosymmetric reference structure indicates an intimate connection between the structural distortion and the weak antiferromagnetic order parameter L_c.

From the above symmetry groups it follows that two different orientations of the ferroelectric polarization are possible in $BaNiF_4$. In addition, there are two twin variants resulting from the antiferromagnetic ordering, which reduces the symmetry from orthorhombic to monoclinic. These twin variants can be classified as ferroelastic domains, even though the corresponding lattice distortion is negligible. Together with the two opposite orientations of the antiferromagnetic order parameter L_{ab} this gives a total of eight possible domain states for this system.[24] If we invert the ferroelectric polarization P in our calculation, we observe that for fixed orientation of L_{ab} and within the same twin variant the orientation of L_c is determined by P (see Fig. 4). This means that a reversal of P by an electric field is accompanied by a reversal of L_c, if during the polarization switching the other order parameters are preserved. Energetically, a reversal of L_c is much more favorable than reversal of L_{ab}, since the latter requires the magnetic moments to rotate by $\sim 180°$ through the hard magnetic axis, whereas the reversal of L_c requires only a slight reorientation of the magnetic moments through the easy axis. The same holds true for a switching of the ferroelastic domain, which requires 180° rotations of half of the spins in the system. We therefore predict that the ferroelectric switching in $BaNiF_4$ will be accompanied by a reversal of the weak antiferromagnetic order parameter.

A canted antiferromagnetic structure caused by the DM interaction was also proposed in the seminal paper by Moriya for $CuCl_2 \cdot 2H_2O$,[6] and was subsequently confirmed by several experimental methods.[25–27] This shows that a "hidden" order parameter such as L_c can be detected experimentally. However, in order to observe our predicted reversal of L_c by an electric field, an experimental technique is required that allows the distinction between different antiferromagnetic 180° domains. One such technique, which in addition allows imaging of the antiferromagnetic domain topology, is second-harmonic generation,[28] which, in fact, has already successfully detected weak antiferromagnetism in $YMnO_3$.[29] We therefore hope that our work will stimulate experimental efforts to measure the predicted magnetoelectric domain switching in $BaNiF_4$ and related materials.

The occurrence of weak magnetic order, both ferromagnetic and antiferromagnetic, resulting from the DM interaction, should be expected to be a very common phenomenon in magnetic ferroelectrics, since this interaction can occur whenever the midpoint between two magnetic ions is not an inversion center.[6] Indeed, magnetic order induced by ferroelectricity via the magnetoelectric effect has been suggested for the related system $BaMnF_4$, based on macroscopic symmetry considerations.[30] In $BaMnF_4$ an additional structural phase transition lowers the symmetry so as to allow the linear magnetoelectric effect, which is symmetry forbidden in $BaNiF_4$. Nevertheless, the microscopic mechanism governing magnetoelectric behavior could be the same in both systems (although a rigorous microscopic study is required to show this unambiguously). The weak antiferromagnetism in $BaNiF_4$ would then be classified as an "antimagnetoelectric effect,"[1] mediated by the DM interaction. A related scenario has also been reported recently for multiferroic $BiFeO_3$, where the DM interaction leads to weak ferromagnetism.[20] Although the linear magnetoelectric effect is symmetry allowed in this system,[31] first-principles calculations show that the weak ferromagnetic moment in $BiFeO_3$ is in fact not induced by the ferroelectricity, but is coupled to a nonpolar structural mode.[20] This exemplifies that symmetry considerations alone cannot provide full insight into the exact coupling mechanism of magnetoelectric systems. Our case study of $BaNiF_4$ and our previous work on $BiFeO_3$,[19] on the other hand, show that it is possible to identify a unique structural mode that is causing the antisymmetric exchange, and that reversing this mode inverts the sign of the magnetic interaction. If this mode is polar, it can be controlled by an electric field, thus leading to an electric-field-switchable magnetic order parameter.

Our results show that the amplitude of the corresponding order parameters are typically of the order of $0.1\mu_B$ per magnetic ion, which is about 10% of a typical strong magnetic order parameter ($\sim 1\mu_B$ per magnetic ion), which is easy to measure with modern experimental techniques. Finally, we compare this with a somewhat converse effect, which is cur-

rently attracting a lot of attention, namely, the appearance of a small electric polarization in materials where the magnetic order breaks the inversion symmetry of the system.[4,32] The resulting polarization is then intimately coupled to the magnetic properties. Although the underlying microscopic mechanism is not yet understood, the important role that symmetry plays for this effect is similar to the case of the weak magnetic order discussed in this paper. The magnitude of the resulting electric polarization is around 0.01 $\mu C/cm^2$,[4,32] which is two to three orders of magnitude smaller than the spontaneous polarization in typical strong ferroelectrics ($\sim 1-10$ $\mu C/cm^2$). From this it becomes clear that the weak magnetic order that is caused by structural distortions is in comparison a rather large effect and therefore provides a very promising route for achieving practical magnetoelectric coupling effects. In addition, the individual driving forces for the ferroelectric and the primary magnetic ordering do not have to be related to each other, since coupling between the weak magnetic order and the ferroelectricity arises due to the *symmetry* of the corresponding crystal structure. As a result, the ferroelectric and magnetic ordering temperatures do not have to be close together.

In summary, we have shown, using the multiferroic system $BaNiF_4$ as an example, that magnetic ferroelectrics can exhibit weak magnetic order whose orientation is determined by the polar distortion, and can be reversed by reversing the ferroelectric polarization using an electric field. This phenomenon can be expected to occur in many magnetic ferroelectrics. The amplitude of the weak magnetic order parameter is non-negligible, about 10% of a typical primary magnetic order parameter. We therefore propose this mechanism as a promising route for achieving magnetoelectric switching behavior in ferroelectric magnets.

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