Ferroelectricity in spiral magnets

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It was recently observed that materials showing most striking multiferroic phenomena are frustrated spin-density-wave magnets. We present a simple phenomenological theory, which describes the orientation of the induced electric polarization for various incommensurate magnetic states, its dependence on temperature and magnetic field, and anomalies of dielectric susceptibility at magnetic transitions. We show that electric polarization can be induced at domain walls and that magnetic vortices carry electric charge.

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The recent revival of interest in materials showing strong interplay between magnetism and ferroelectricity led to the discovery of a new class of systems, which can be called ferroelectric magnets. While in 'old' multiferroics, such as BiFeO$_3$, spontaneous electric polarization appears at a much higher temperature than magnetism, in RMnO$_3$ (R = Tb, Dy, Gd) [1] and RN$_2$O$_5$ (R = Tb, Ho, Dy) [2] and Ni$_3$V$_2$O$_8$ [3] ferroelectricity is only observed in magnetically ordered states. In magnetic fields these materials show reversals and sudden flops of electric polarization vector [2] [4], and an exceptionally strong enhancement of dielectric constant (the giant magnetocapacitance effect) [3]. These remarkable multiferroic phenomena, essential for control of dielectric properties by magnetism, follow from the fact that that ferroelectricity in these materials is induced by magnetic ordering.

An intriguing feature of the new class of multiferroics is an intimate link between the spontaneously induced polarization and magnetic frustration. In RMnO$_3$ a large distortion of the cubic perovskite lattice gives rise to competing ferro- and antiferromagnetic interactions between the Mn spins [1], while in the Kagomé staircase material Ni$_3$V$_2$O$_8$ frustration originates from the lattice geometry [5]. The competing exchange interactions stabilize spin-density-wave (SDW) states with a periodically varying magnetization [1].

The relation between the ferroelectricity and incommensurate magnetism is widely used as an empirical guiding principle in the search for new multiferroic materials. In this paper we discuss a phenomenological description of ferroelectric magnets, based on general symmetry arguments. We formulate a simple continuum model, which clarifies the relation between the induced electric polarization and magnetic structure, describes anomalies of dielectric constant at magnetic transitions and qualitatively explains complex magnetic field behaviors found in these materials. We extend this analysis to domain walls and vortices. Our phenomenological approach is complimentary to the recent discussions of microscopic mechanisms of ferroelectricity in magnets [6,7].

**Induced polarization:** Incommensurate SDW states are largely insensitive to details of crystal structure and can be described by a continuum field theory of the Ginzburg-Landau type. The form of the coupling of electric polarization $\mathbf{P}$ to magnetization $\mathbf{M}$ can be found using general symmetry arguments. The invariance upon the time reversal, $t \rightarrow -t$, which transforms $\mathbf{P} \rightarrow -\mathbf{P}$ and $\mathbf{M} \rightarrow -\mathbf{M}$, requires the lowest-order coupling to be quadratic in $\mathbf{M}$ and $\mathbf{P}$. The symmetry with respect to the spatial inversion, $x \rightarrow -x$, upon which $\mathbf{P} \rightarrow -\mathbf{P}$ and $\mathbf{M} \rightarrow \mathbf{M}$, is respected when the coupling of a uniform polarization to an inhomogeneous magnetization is linear in $\mathbf{P}$ and contains one gradient of $\mathbf{M}$. Omitting vector indices the coupling term in thermodynamic potential can be written in the form

$$\Phi_{em}(\mathbf{P}, \mathbf{M}) \propto \mathbf{P} \cdot \mathbf{M} \partial \mathbf{M}.$$  \hspace{1cm} (1)

The terms linear in gradient (Lifshitz invariants) are allowed in systems with broken inversion symmetry, such as noncentrosymmetric crystals, where they can give rise to periodic spatial modulations of magnetization [8]. Such an incommensurate SDW state is observed in the ferroelectric BiFeO$_3$, where the inversion symmetry is spontaneously broken by electric polarization. The helix with the long period 620Å in BiFeO$_3$ results from the coupling between the electric polarization $\mathbf{P}$ and the G-type AFM order, which has the form Eq. (1) with the uniform magnetization $\mathbf{M}$ replaced by the slowly varying Néel vector $\mathbf{L}$ [1]. The small value of the wave vector is a consequence of the relativistic nature of the coupling [10,11].

This reasoning can be turned around to explain electric polarization in frustrated magnets, in which an incommensurate magnetic ordering results from competing exchange interactions and the SDW wave vector is, in general, not small. When the SDW order of a proper kind sets in, the coupling Eq. (1) induces a uniform electric...
polarization that breaks the inversion symmetry. The weakness of the coupling translates in this case to relatively low values of the induced polarization.

This mechanism does not require a special kind of crystal lattice. In the simplest case of cubic symmetry the coupling term has the form

$$\Phi_{\text{em}}(P, M) = \gamma P \cdot [M (\nabla \cdot M) - (M \cdot \nabla) M + \ldots]. \quad (2)$$

The omitted terms can be written as the total derivative, \(\nabla f(M)\), and do not contribute to the uniform polarization. Assuming that in absence of magnetism the system shows no instability towards ferroelectricity, we only keep the quadratic term in the ‘electric part’ of the thermodynamic potential, \(\Phi_e(P) = \frac{f^2}{2\chi_e}\), where \(\chi_e\) is the dielectric susceptibility in absence of magnetism. The variation of \(\Phi_e + \Phi_{\text{em}}\) with respect to \(P\) then gives

$$P = \gamma \chi_e [(M \cdot \nabla) M - M (\nabla \cdot M)]. \quad (3)$$

![FIG. 1: The sinusoidal SDW [panel (a)] does not induce a uniform electric polarization, while for a helicoidal SDW [panel (b)] the electric polarization vector \(P\) lies in the spin rotation plane (with the normal vector \(e_3\)) and is transverse to the wave vector \(Q\) of the helix.](image)

Consider now a SDW state with the wave vector \(Q\),

$$M = M_1 e_1 \cos \phi + M_2 e_2 \sin \phi + M_3 e_3, \quad (4)$$

where \(\phi = Q \cdot x\) and the unit vectors \(e_i, i = 1, 2, 3\) form an orthogonal basis. If only \(M_1\) or \(M_2\) is nonzero, this state is the sinusoidal wave (see Fig. 1a), while for \(M_1, M_2 \neq 0\) it is an (elliptical) helix with the spin rotation axis \(e_3\). If also \(M_3 \neq 0\), then the helix is conical. Using Eq. 3, we find that the average polarization is transverse both to the spin rotation axis \(e_3\) and the wave vector \(Q\) of the helix (see Fig. 1b), and is independent of \(M_3\):

$$\bar{P} = \frac{1}{V} \int d^3 x P = \gamma \chi_e M_1 M_2 [ e_1 \times Q]. \quad (5)$$

For the sinusoidal SDW the induced polarization is 0: such an ordering does not break the inversion symmetry at the sites where the magnetization reaches maximum or minimum (e.g., the points on the dashed line in Fig. 1b) and, therefore, it cannot induce an average electric polarization. Equation 5 also holds for the orthorombic crystal symmetry, provided that \(e_3\) and \(Q\) are parallel to crystal axes.

This explains why the transition at \(T_S = 41K\) to the sinusoidal SDW state in TbMnO$_3$ [2] does not give rise to ferroelectricity. The polarization is only induced below the so-called lock-in transition at \(T_H = 28K\), when the sinusoidal SDW is replaced by the helix with the propagation vector \(Q\) parallel to the \(b\) axis and the \(M\) spins rotating in the \(bc\) plane (\(e_3 \parallel a\)) [13], so that according to Eq. 5 the polarization is induced along the \(c\) axis in agreement with experiment. Similarly, the polarization is absent in the high-temperature incommensurate phase of Ni$_3$V$_2$O$_8$, which is the sinusoidal SDW state [7]. The helix with \(Q \parallel a\) and the spin rotation axis \(e_3 \parallel c\), which appears in the low-temperature incommensurate phase, induces polarization along the \(b\) axis.

We note that the spiral ordering can be considered as a particular case of a magnetic ordering with two non-collinear SDWs with equal wave vectors,

$$M = M_1 e_1 \cos (Q \cdot x + \phi_1) + M_2 e_2 \cos (Q \cdot x + \phi_2),$$

such as the one recently found in RMn$_2$O$_5$ [14, 15]. Although a single sinusoidal SDW does not induce polarization, the interference between the two SDWs gives

$$\bar{P} = \gamma \chi_e M_1 M_2 \sin (\phi_2 - \phi_1) [Q \times (e_1 \times e_2)]. \quad (6)$$

**Magnetic textures:** Electric polarization can also be induced in nonfrustrated magnets near magnetic defects, e.g., domain walls or in inhomogeneous ground states stabilized by magnetostatic interactions, e.g., vortices in nanodisks [10]. In many cases the integrated quantities, such as the total polarization per unit area of a domain wall, only depend on topology of spin textures. For walls with collinear spins and the ones with spins rotating around the axis normal to the wall, the total polarization is 0, while the wall, in which spins rotate around an axis parallel to the wall, \(M = M [\cos (\phi(x_1) e_1 + \sin (\phi(x_1)) e_2]\), has the total polarization that depends on the total rotation angle

$$\int_{-\infty}^{+\infty} dx_1 P = 2 \gamma \chi_e M^2 [e_2 [\phi(+\infty) - \phi(-\infty)]]. \quad (7)$$

Using Eq. 8 one can also show that the vortex

$$M = M [\cos(\phi + \phi_0) e_1 + \sin(\phi + \phi_0) e_2],$$

where \(\phi = \arctan \frac{x}{y}\) and \(\phi_0\) is an arbitrary phase, has quantized electric charge located at the vortex core: \(q_n = n q_1\), where \(q_1 = 4 \gamma \chi_e M^2\) and \(n\) is the winding number of the vortex. An applied electric field will move magnetic vortices and anti-vortices in opposite directions.
Sinusoidal-helical transition: We now turn to the phase diagram of ferroelectric SDW magnets. Using the values of the induced polarization ($10^{-2} - 10^{-3} \mu C \text{ m}^{-2}$) and magnetic transition temperatures ($5-40K$) for these materials, we find that the energy gain related to the induced polarization is small compared to the magnetic energy gain. Therefore, the temperature and magnetic field dependence of the polarization merely reflects the changes in magnetic ordering, which can be described using the Ginzburg-Landau thermodynamic potential

$$\Phi_m(M) = \sum_{i=x,y,z} \frac{\alpha_i}{2} (M_i)^2 + \frac{b}{4} M^4 + \frac{c}{2} M \left( \frac{d^2}{dx^2} + Q^2 \right)^2 M.$$  \hspace{1cm} (8)

In what follows we assume that $a_x < a_y < a_z$ (easy axis along the $x$ direction) and first neglect higher-order anisotropies. The last term in Eq.(8) favors a periodic axis along the $-P$ direction.

A down-shift of the ferroelectric transition with respect to the magnetic one, found in all magnetic ferroelectrics, is a consequence of magnetic anisotropy. While for an isotropic system the ground state is a helix with a constant $M$, an anisotropic system first undergoes a transition to the sinusoidal SDW state with $M$ along the easy axis, $M = M_x \cos Q x$, at temperature $T_{S} : a_x(T_{S}) = 0$. As temperature is lowered and the amplitude of the order parameter grows, the system undergoes a second transition at some $T_H < T_S$ to the elliptical helix state, $M = M_x \cos Q x + M_y \sin Q x$, provided that the anisotropy parameter $\Delta = a_y - a_z$ is not too large. When the two transitions occur at close temperatures, the higher harmonics in the SDW state are small and the helix appears at $a_y = a_z/3$. For $a_x(T) = \alpha(T - T_S)$ we then obtain

$$T_H = T_S - \frac{3\Delta}{2\alpha}.$$ \hspace{1cm} (9)

The average electric polarization only appears in the helicoidal state and for spins rotating in the $xy$ plane and $Q \parallel x$ it is parallel to the $y$ axis:

$$P_y = \alpha \gamma \chi e Q \sqrt{(T_H - T)(T_S - \Delta/2\alpha - T)}.$$ \hspace{1cm} (10)

Note that since $P_y \propto M_x M_y$ [see Eq.(5)], it has the square root anomaly at the ferroelectric transition, even though it is not a primary order parameter. Furthermore, as in proper ferroelectrics, the dielectric constant $\varepsilon_{yy}$ diverges at $T_H$ and obeys ‘the 1/2-law’ \[12]:

$$\varepsilon_{yy} \approx \begin{cases} \frac{A}{T-T_H}, & \text{for } T > T_H, \\ \frac{A}{(T_H-T)}, & \text{for } T < T_H, \end{cases}$$ \hspace{1cm} (11)

where $A = 6\Delta(\gamma \chi e Q)^2/(\alpha b)$. Although $P_y$ vanishes in the sinusoidal SDW state, the magnetic contribution to $\varepsilon_{yy}$ is nonzero up to $T = T_S$:

$$\varepsilon_{yy} = \frac{(2\gamma \chi e)^2}{b} \frac{(T_S - T)}{(T - T_H)}, \text{ for } T_H < T < T_S.$$ \hspace{1cm} (12)

Behavior in magnetic field: The salient feature of ferroelectric magnets, important for technological applications, is the strong sensitivity of their dielectric properties to magnetic field, which can suppress electric polarization or change its direction \[4,7]. We first discuss polarization flops in the model Eq.5. In weak fields spins rotate in the $xy$ plane, so that the spin rotation axis $e_3$ of the helix is parallel to the ‘hard’ $z$ axis. For $Q \parallel x$ electric polarization is oriented along the $y$ axis. In strong magnetic fields spins form a conical helix with $e_3 \parallel H$, e.g., $H_z$ will force the spins to rotate in the $yz$ plane (see Fig.2a). Such a spin flop will suppress electric polarization, since for the $zy$-helix $e_3 \parallel Q$ and according to Eq.(5) $P = 0$. On the other hand, magnetic field in the $y$ direction favors the rotation of spins in the $xz$ plane, in which case $P \parallel z$ (see Fig.2b).

The magnetic field behavior observed in orthorombic manganites is somewhat more involved. If we identify the $x$, $y$, and $z$ axes used in this paper with, respectively, the $b$, $c$, and $a$ axes of the $Pbnm$ crystal structure of TbMnO$_3$, then magnetic field applied in the $x$ and $z$ directions changes the direction of the electric polarization of TbMnO$_3$ from $y$ to $z$. According to Eq.(1), this corresponds to the change of the rotation plane from $xy$ to $xz$. It is the flop shown in Fig.2d, but induced by magnetic fields with ‘wrong’ orientations.

This unusual behavior is most likely related to the flops of the strongly anisotropic rare earth spins, coupled to Mn spins \[2,12]. It can be described phenomenologically by adding the higher-order anisotropies to Eq.(5), e.g.,

$$\Delta \Phi_m(M) = b_{xy} (M_x)^2 (M_y)^2 + b_{xy} (M_x)^2 \left( \frac{dM_y}{dx} \right)^2 + b_{yz} (M_y)^2 (M_z)^2.$$ \hspace{1cm} (13)

For positive coefficients the first two terms suppress the rotation in the $xy$ plane, when magnetic field is applied in the $x$ or $y$ direction, while the last term suppresses the rotation in the $yz$ plane. This gives rise to phase transitions occurring at close temperatures, the higher harmonics in the SDW state are small and the helix appears at $a_y = a_z/3$. For $a_x(T) = \alpha(T - T_S)$ we then obtain

$$T_H = T_S - \frac{3\Delta}{2\alpha}.$$ \hspace{1cm} (9)

The average electric polarization only appears in the helicoidal state and for spins rotating in the $xy$ plane and $Q \parallel x$ it is parallel to the $y$ axis:

$$P_y = \alpha \gamma \chi e Q \sqrt{(T_H - T)(T_S - \Delta/2\alpha - T)}.$$ \hspace{1cm} (10)

Note that since $P_y \propto M_x M_y$ [see Eq.(5)], it has the square root anomaly at the ferroelectric transition, even though it is not a primary order parameter. Furthermore, as in proper ferroelectrics, the dielectric constant $\varepsilon_{yy}$ diverges at $T_H$ and obeys ‘the 1/2-law’ \[12]:

$$\varepsilon_{yy} \approx \begin{cases} \frac{A}{T-T_H}, & \text{for } T > T_H, \\ \frac{A}{3(T_H-T)}, & \text{for } T < T_H, \end{cases}$$ \hspace{1cm} (11)

where $A = 6\Delta(\gamma \chi e Q)^2/(\alpha b)$. Although $P_y$ vanishes in the sinusoidal SDW state, the magnetic contribution to $\varepsilon_{yy}$ is nonzero up to $T = T_S$:

$$\varepsilon_{yy} = \frac{(2\gamma \chi e)^2}{b} \frac{(T_S - T)}{(T - T_H)}, \text{ for } T_H < T < T_S.$$ \hspace{1cm} (12)

FIG. 2: Magnetic field behavior of electric polarization for the model Eq.(5). In zero field spins rotate in the $xy$ plane and $P \parallel y$. Magnetic field in the $z$ direction suppresses the polarization, while $H_y$ orients $P$ in the $z$ direction.
diagrams, shown in Fig. 3, which are similar to the ones found for TbMnO$_3$. The nonlinear terms also result in a magnetic field dependence of the helicoidal transition temperature, which together with the divergency of dielectric constant at $T_H$ makes $\varepsilon$ strongly field-dependent (the giant magnetocapacitance effect). The result of the numerical calculation of $P(H_x)$, using the Ginzburg-Landau expansion similar to Eq. (5), is shown in Fig. 4.

![FIG. 4: Predicted magnetic field dependence of the electric polarization $|P^y| = |P^x|$ of CaFeO$_3$ for $H \parallel x$.](image)

In conclusion, we used simple symmetry arguments to explain ferroelectric properties and thermodynamics of spiral magnets. Taking into account the complexity of exchange interactions and spin orders in these materials, this phenomenological approach works surprisingly well.

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