Symmetry and magnetically driven ferroelectricity in rare-earth manganites $R\mathrm{MnO_3}$ (R=Gd,Tb,Dy)

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This work investigates the magnetically driven ferroelectricity in orthorhombic manganites $R\mathrm{MnO_3}$ (R=Gd, Dy, or Tb) from the point of view of the symmetry. The method adopted generalizes the one used to characterize the polar properties of displacive modulated structures to the case of an irreducible magnetic order parameter. The symmetry conditions for magnetically induced ferroelectricity are established, and the Landau-Devonshire free energy functionals are derived from general symmetry considerations. The ferroelectric polarization observed in $\mathrm{DyMnO_3}$ and $\mathrm{TbMnO_3}$ at zero magnetic field is explained in terms of the symmetry of a reducible magnetic order parameter. The polarization rotation induced in these compounds by external magnetic fields and the stabilization of a ferroelectric phase in $\mathrm{GdMnO_3}$ are accounted for by a mechanism in which magnetization and polarization are secondary order parameters that are not directly coupled but compete with each other through their coupling to competing primary modulated order parameters.

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I. INTRODUCTION

In the last decades, the search for novel materials displaying enhanced magnetoelectric effect has attracted a great interest due to the potential technological application that can be envisaged and the subtlety of the physical mechanisms involved.[1,2] Until recently, the magnetoelectric coupling in insulating and single phase materials has been explored mainly in the few known multiferroic compounds.[3–5] In materials of this type, such as $\mathrm{BiFeO_3}$ (Refs. 6 and 7) or $\mathrm{BiMnO_3}$,[8] the coexistence of ferroelectric and magnetic cooperative orders in the same phase might prompt one to posit a relatively efficient coupling between the polar and magnetic degrees of freedom. However, because of the quite different critical temperatures associated with the magnetic and polar ordering, the experimentally observed magnetoelectric coupling in these systems is weak and only very small signatures of the lower temperature magnetic phase are seen in the dielectric properties. In this respect, the behavior observed may be considered similar to that found in antiferromagnetic and ferroelectric hexagonal manganites of the $\mathrm{YMnO_3}$ family.[9–11]

The situation has been dramatically altered with the discovery of magnetically induced ferroelectricity in several frustrated magnets, such as the perovskites $R\mathrm{MnO_3}$ and $R\mathrm{Mn_2O_5}$ (R=rare-earth element), $\mathrm{Ni_3V_2O_8}$, delafossite $\mathrm{CuFeO_2}$, spinel $\mathrm{CoCr_2O_4}$, $\mathrm{MnWO_4}$, and hexagonal ferrites $(\mathrm{Ba,Sr})_2\mathrm{Zn_2Fe_{12}O_{22}}$.[12–20] Here, in contrast to the conventional multiferroics, the paramagnetic phase is also paraelectric, and the spontaneous ferroelectric polarization appears to be directly driven by a transition to a magnetic modulated phase. Not surprisingly, the observed magnetoelectric coupling is much stronger and gives rise to a wealth of fascinating phenomena that are currently being investigated.

From a perspective based on symmetry and group theory, the idea of improper ferroelectricity driven by the condensation of a primary order parameter of a magnetic nature raises interesting questions. In the case of the novel frustrated magnets, a key point is to know under which circumstances a modulated magnetic order parameter can induce ferroelectricity. Improper ferroelectricity driven by displacive lattice modulation has been extensively investigated over two decades ago in molecular systems such as $\mathrm{RbZn_2Cl_4}$, $(\mathrm{C(NH_3)_4})_2\mathrm{CoCl_4}$, or $(\mathrm{CH_3})_3\mathrm{NCH_2COO\cdot CaCl_2\cdot 2H_2O}$ (BCCD). In these cases, it has been possible to take advantage of the simple crystallographic structure and irreducible nature of the modulated order parameter to obtain, from general symmetry considerations, common pictures of the structural phase transitions and precise predictions for the polar or nonpolar character of a given modulated phase.[21–23] Particularly interesting is the case of BCCD, a compound that shares with the orthorhombic manganites $R\mathrm{MnO_3}$ the same reference space group *Pnma* (in this work, the standard setting *Pnma* is adopted for the $R\mathrm{MnO_3}$ compounds, as opposed to the *Pbnm* setting used in some articles) and displays a wealth of structurally commensurate or incommensurate modulated phases. Here, a definite relationship between the modulation wave number and the direction of the electric polarization could be established.[23]

A question naturally arises if the method of analysis used to investigate the polar properties of modulated displacive systems can be adapted to the case of the magnetoelectric compounds and to a situation where the primary order parameter is of magnetic nature. The case of BCCD, for example, has been used to suggest a possible mechanism[24] for the magnetic field induced rotation of the electric polarization observed in $\mathrm{TbMnO_3}$ and $\mathrm{DyMnO_2}$.[24–26] According to this suggestion, the electric polarization in these compounds would result from the secondary lattice modulation (of a displacive nature) magnetoelastically induced by the primary magnetic modulation. Consequently, a magnetic field could, by tuning the primary magnetic modulation, modify the secondary lattice modulation and, as a result, induce a rotation of the polarization. However, this key role of the lattice modulation is inconsistent with the well known fact that it is the primary order parameter that determines the symmetry of the ordered phase.[27,28] Hence, the displacive lattice modulation and the electric polarization must be both seen as sec-

ondary parameters whose direct coupling to the primary magnetic order parameter is restricted by general symmetry conditions.

In general, the complexity of the magnetic structures of most of the novel magnetoelectric compounds makes the investigation of their magnetoelectric properties using symmetry considerations a difficult task. Among this set of materials, the rare-earth manganites $R\mathrm{MnO_3}$ (R=Gd, Tb, or Dy) are relatively simple from a crystallographic point of view and their properties are well characterized experimentally. They therefore represent appropriate model systems to investigate further the mechanisms of the remarkable magnetoelectric coupling observed in the class of frustrated magnets.[20,24–26,29–31]

This work analyzes the symmetry conditions that allow for the magnetically induced ferroelectricity observed in the orthorhombic rare-earth manganites $R\mathrm{MnO_3}$ (R=Gd, Tb, or Dy). From this analysis, we derive adequate and symmetry based free energy functionals capable of describing both the ferroelectricity observed in $\mathrm{TbMnO_3}$ and $\mathrm{DyMnO_3}$ at zero magnetic field, the polarization rotation induced in these compounds by external magnetic fields, and the ferroelectric phase induced in $\mathrm{GdMnO_3}$ by an external magnetic field.

This paper is organized as follows. In Sec. II, we will briefly review the essential phenomenology of the magnetoelectric effect in the $R\mathrm{MnO_3}$ compounds. Section III analyzes some general aspects related to the compatibility between a modulated magnetic order and a spontaneous polarization and establishes the methods of the analysis to be made. In Sec. IV, we will adapt the analysis made in Ref. 23 for BCCD to the case of a magnetic order parameter and use the complete irreducible corepresentations of the magnetic space group of the reference phase to obtain the possible magnetic space groups of the commensurate phases that can be originated from the condensation of a magnetic irreducible order parameter. Sections V and VI analyze the possible translational invariants that can be constructed from the order parameter components and derive symmetry based Landau free energy functionals that are capable of describing the behavior experimentally observed in the orthorhombic manganites.

II. MAGNETOELECTRIC EFFECT IN THE RARE-EARTH MANGANITES $R\mathrm{MnO_3}$

The rare-earth manganites $R\mathrm{MnO_3}$ (R=Gd, Tb, or Dy) are remarkable examples of the novel family of magnetoelectric materials.[12,24,32–34] At room temperature, these compounds are paraelectric and paramagnetic with a distorted perovskite structure of orthorhombic symmetry (space group $Pnma$). All the three compounds undergo a phase transition to a magnetic incommensurate phase with a modulation wave vector directed along the a axis ($\vec{k}=[\delta;0;0]$, $\delta(T_i)\approx 0.24$ (Gd), $\delta(T_i)\approx 0.28$ (Tb), $\delta(T_i)\approx 0.36$ (Dy); $T_i\approx 40$ K).[32–34] This incommensurate modulation corresponds to a collinear arrangement of the Mn magnetic momenta. With further cooling of the Tb and Dy compounds, under zero magnetic field, $\delta(T)$ approaches and enters into quasicommensurate plateaus ($T\approx 20$ K) corresponding approximately to the values $\delta\approx 0.275$ and $\delta\approx 0.375$ for $\mathrm{TbMnO_3}$ and $\mathrm{DyMnO_3}$, respectively. The onset of these plateaus marks a transition from a collinear to a cycloidal modulation of the Mn magnetic momenta. This modulation remains directed along the same axis ($\vec{k}=[\delta;0;0]$) and gives rise to a ferroelectric polarization directed along the $\vec{b}$ crystallographic axis.[12,24,35,36]

At zero magnetic field, $\mathrm{GdMnO_3}$ remains paraelectric. The modulated magnetic order below T_i remains collinear until the system enters into an A-type antiferromagnetic phase at about 27 K. The application of a strong magnetic field ($H\geqslant 5$ T) along the a axis induces in this compound a ferroelectric phase with a polarization oriented along the c axis. Structural studies indicate that this magnetically induced ferroelectric phase is accompanied by a commensurate modulation of the Mn momenta corresponding to $\vec{k}=\left[\frac{1}{4};0;0\right]$.[31] Also, in the cases of $\mathrm{TbMnO_3}$ and $\mathrm{DyMnO_3}$, a similar magnetic field, applied along the a axis, stabilizes a commensurate plateau with $\vec{k}=\left[\frac{1}{4};0;0\right]$ and induces a ferroelectric phase polar along the c axis.[12,24,34] An external magnetic field is therefore capable of altering the symmetry of the magnetic structure and rotating the spontaneous polarization by 90°.

The $R\mathrm{MnO_3}$ compounds also show, in addition to the magnetoelectric effects briefly described above, a strong lattice modulation originated from exchange striction. The modulate arrangement of the Mn spin moments with a wave vector $\vec{k}=[\delta;0;0]$ induces a lattice modulation with a wave vector $\vec{k}_{latt}=[2\delta;0;0]$.[12,35] The superlattice reflections therefore correspond to a second harmonic of the magnetic modulation and, together with the electrical polarization, must be considered as secondary effects of a primary order parameter.

III. DESCRIPTION OF THE METHOD

To some extent, the elusive interaction between electric and magnetic degrees of freedom results from the different symmetries of the electric polarization (P) and magnetization (M) that are expressed by their different behavior under spatial inversion (i) or time reversal (θ). This different behavior imposes, for example, that the coupling between static and homogeneous P and M must necessarily be nonlinear ($\propto \pm P^{2n}M^{2m}$, where n and m integers). As a result, a homogeneous polarization can never result from the onset of a homogeneous magnetization because this would require the existence of coupling terms linear in P (Ref. 28) that are, in this case, forbidden by symmetry. Therefore, if we restrict ourselves to time independent phenomena, a magnetically driven ferroelectricity may only eventually occur when the primary magnetic order parameter is spatially nonhomogeneous.

Let us then consider the case of a modulated order parameter that is characterized by a single wave vector $\vec{k}$ located in the interior of the Brillouin zone and directed along a line of fixed symmetry (which corresponds to a Σ or Λ line, in the case of the $R\mathrm{MnO_3}$ compounds or BCCD, respectively). This modulated order parameter can be written as

$$\vec{S}(\vec{x}) = \vec{S}e^{i\vec{k}\cdot\vec{x}} + \vec{S}^* e^{-i\vec{k}\cdot\vec{x}}, \tag{1}$$

where $\vec{S}=\vec{S}_0 e^{i\pi\Phi}$ and Φ is the phase defined with respect to the underlying discrete lattice. Note that, because $\vec{S}(\vec{x})$ is a real quantity, $\vec{S}^*_{\vec{k}}=\vec{S}_{-\vec{k}}$. Also, given its magnetic nature, $\theta\vec{S}(\vec{x})=-\vec{S}(\vec{x})$. Under which conditions does this general modulated order parameter allow for mixed invariants linear in P and, therefore, for improper ferroelectricity?

A general nomial constructed from the complex conjugated components of $\vec{S}(\vec{x})$ has the form $(S)^p(S^*)^q$. Naturally, if $p=q$, such a term is independent of the phase of the order parameter and gives rise to a homogeneous contribution to the free energy. Moreover, given its magnetic nature, it is necessarily even under inversion and does not allow for mixed invariants linear on P. We must therefore look for terms with $p\neq q$, that is, terms that depend on the phase Φ of the order parameter. Given that the polarization P is translational invariant, we must consider only those nomials that are themselves translationally invariants in order to obtain possible coupling terms of the form $(S)^p(S^*)^q P$. In general, these phase dependent terms can be written as (p and p' integers)

$$f^p(S,S^*) = S^{p'}S^{*(p-p')} = S_o^p e^{i\pi(2p-p')}. \tag{2}$$

Consider now the requirement of translational invariance of Eq. (2). Let $\hat{T}=m\vec{a}_i$ be a Bravais translation of the reference phase, directed parallel to the modulation wave vector $\vec{k}=\delta\vec{a}_i^*$. Under such operation, f^p is transformed as

$$\hat{T}f^p = f^p e^{-2\pi i\delta(p-2p')}. \tag{3}$$

Hence, for f^p invariant under this translation, $\delta(p-2p')$ must be an integer m. This is obviously not possible for $p\neq 2p'$ if $\vec{k}$ is incommensurate with respect to the reference lattice. An incommensurate order parameter does not allow for phase dependent translational invariants and, in consequence, cannot induce an electrical polarization. Incommensurate magnetic order and ferroelectricity are mutually incompatible.

On the other hand, if $\vec{k}$ is commensurate, the condition $\delta(p-2p')=m$ can be satisfied and nontrivial translational invariants do exist. If, under the symmetry operations of the reference phase, any of these invariants is transformed as a polar vector, then a mixed invariant linear in P can be constructed and improper ferroelectricity is allowed by symmetry. We can therefore verify if a given magnetic commensurate phase may or may not be polar by checking the transformation properties of the order parameter translational invariants.

Since we have established for an irreducible order parameter that improper ferroelectricity can only occur in the case of a commensurate phase, we may use an alternative method to investigate whether P is a possible secondary order parameter. Given the symmetry of the order parameter by specifying the irreducible representation according to which it is transformed, we can directly calculate the possible magnetic space groups of the ordered phase and check if any of these groups is compatible with ferroelectricity. Let G denote the unitary space group and $M=G\otimes\{E,\theta\}$ the magnetic space group of the paramagnetic reference phase, with E and θ representing the identity and the time reversal operation, respectively. Let $\{g;\vec{t}\}$ and $\{\theta g;\vec{t}\}$ be elements of G and $M-G$, respectively. By definition of order parameter, the symmetry of the ordered magnetic commensurate phase will be described by a magnetic space group M' formed by the unitary and antiunitary operators that leave the order parameter invariant up to a Bravais translation. That is, if $\hat{D}(g)$ and $\hat{D}(\theta g)$ are matrices that represent the operations $\{g;\vec{t}\}$ and $\{\theta g;\vec{t}\}$ in the (irreducible) space of the components of the order parameter and if the conditions

$$\hat{T}\times\hat{D}(g)\times\vec{S}=\vec{S}, \tag{4a}$$

$$\hat{T}\times\hat{D}(\theta g)\times\vec{S}^*=\vec{S} \tag{4b}$$

are verified, then $\{g;\vec{t}+\vec{T}\}$ and $\{\theta g;\vec{t}+\vec{T}\}$ will belong to M'. The set of symmetry operations that verify Eqs. (4a) and (4b) and form the symmetry group of the ordered phase will, in general, depend on the symmetry of the order parameter, the commensurate value of δ [that is, on the odd (even) value of the integers in the fraction δ], and the particular phase of the order parameter with respect to the underlying lattice.

We therefore have systematic methods for determining if a given commensurate magnetic order parameter can induce a ferroelectric polarization. They require the knowledge of the way the different elements of the symmetry group of the reference phase act on the linear space generated by the components of the order parameter. If we assume that the order parameter is irreducible, this amounts to knowing the complete irreducible corepresentations (CICR) of the paramagnetic space group for a given commensurate vector $\vec{k}_c$ in the interior of the Brillouin zone. In the case pertaining to $R\mathrm{MnO}_3$, the paramagnetic space group of the reference phase is $(Pnma)'$ and the modulation wave vector of the order parameter is $\vec{k}=(\delta(T),0,0)$. This vector corresponds to the wave vector k_7 in Kovalev's tables.[37] Following the standard methods,[37–40] we can readily obtain the CICR matrices that are given in Table I for the generators of the magnetic space group (C_{2x}, σ_y, i, and $i\theta$). The matrices corresponding to the other symmetry elements can then be obtained from the multiplication table of the group and by taking into account that the antiunitary operators conjugate the coefficients of the matrices upon which they act.

In the following sections, we will apply these methods to characterize the potential polar properties of a magnetic commensurate phase and to deduce symmetry based free energy functionals that are adequate to describe the magnetoelectric effect in orthorhombic rare-earth manganites.

IV. POSSIBLE MAGNETIC SPACE GROUPS FOR THE COMMENSURATE PHASES IN $R\mathrm{MnO}_3$

As seen above, the magnetic space groups of the possible commensurate modulated phases, originating from the condensation of a given irreducible magnetic order parameter, can be directly obtained from the inspection of the set of

TABLE I. Matrices representing the generators of the group $(Pnma)'$ in the four of its complete irreducible corepresentations at $\vec{k}=\delta\vec{a}_1^*$.

	C_{2x}	σ_z	$i\theta$	i
$\Gamma(A_1)$	$\begin{bmatrix}\varepsilon & 0\\ 0 & \varepsilon^*\end{bmatrix}$	$\begin{bmatrix}\varepsilon & 0\\ 0 & \varepsilon^*\end{bmatrix}$	$\begin{bmatrix}-1 & 0\\ 0 & -1\end{bmatrix}$	$\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}$
$\Gamma(B_2)$	$\begin{bmatrix}-\varepsilon & 0\\ 0 & -\varepsilon^*\end{bmatrix}$	$\begin{bmatrix}-\varepsilon & 0\\ 0 & -\varepsilon^*\end{bmatrix}$	$\begin{bmatrix}-1 & 0\\ 0 & -1\end{bmatrix}$	$\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}$
$\Gamma(A_2)$	$\begin{bmatrix}\varepsilon & 0\\ 0 & \varepsilon^*\end{bmatrix}$	$\begin{bmatrix}-\varepsilon & 0\\ 0 & -\varepsilon^*\end{bmatrix}$	$\begin{bmatrix}-1 & 0\\ 0 & -1\end{bmatrix}$	$\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}$
$\Gamma(B_1)$	$\begin{bmatrix}-\varepsilon & 0\\ 0 & -\varepsilon^*\end{bmatrix}$	$\begin{bmatrix}\varepsilon & 0\\ 0 & \varepsilon^*\end{bmatrix}$	$\begin{bmatrix}-1 & 0\\ 0 & -1\end{bmatrix}$	$\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}$

unitary (R) and antiunitary (B) symmetry operations that leave a given irreducible order parameter invariant up to a Bravais translation of the reference lattice. That is, if the equations

$$\begin{bmatrix}e^{-2\pi jn\delta} & 0\\ 0 & e^{2\pi jn\delta}\end{bmatrix}\times\begin{bmatrix}D_{11}(R) & D_{12}(R)\\ D_{21}(R) & D_{22}(R)\end{bmatrix}\times\begin{bmatrix}e^{j2\pi\Phi}\\ e^{-j2\pi\Phi}\end{bmatrix}=\begin{bmatrix}e^{j2\pi\Phi}\\ e^{-j2\pi\Phi}\end{bmatrix}, \tag{5a}$$

$$\begin{bmatrix}e^{-2\pi jn\delta} & 0\\ 0 & e^{2\pi jn\delta}\end{bmatrix}\times\begin{bmatrix}D_{11}(B) & D_{12}(B)\\ D_{21}(B) & D_{22}(B)\end{bmatrix}\times\begin{bmatrix}e^{j2\pi\Phi}\\ e^{-j2\pi\Phi}\end{bmatrix}^*=\begin{bmatrix}e^{j2\pi\Phi}\\ e^{-j2\pi\Phi}\end{bmatrix} \tag{5b}$$

are satisfied for a given R or B, then this element will belong to the magnetic group of the ordered phase. These groups will depend, in general, on the irreducible representation considered for the order parameter, on its phase, and on the type of the modulation wave number, that is, on the odd (even) value of the integers defining the fraction δ. The results obtained for the case pertaining to the $R\mathrm{MnO}_3$ compounds are listed in the Table II. Here, the magnetic space groups are denoted as $M(G)$ if θ is not a symmetry element or $(G)'=G\otimes\{E,\theta\}$ if θ is a symmetry element of the group.

It is interesting to consider the particular case of time reversal and spatial inversion because these operations directly provide us with two necessary conditions for the existence of ferroelectricity. Moreover, in the particular case under analysis, the matrices corresponding to these two operations are found to be independent of the particular irreducible corepresentation considered for the order parameter. Let us see first the case of time reversal. From the matrix representing this operation, one finds from Eq. (5b) that θ is a symmetry of the ordered phase if and only if δ_c =odd/even. Therefore, in the case under analysis, only this type of irreducible magnetic order parameter can induce improper ferroelectricity.

TABLE II. The possible magnetic space groups of the commensurate phases for the different symmetries of the order parameter.

$\delta=\frac{2k+1}{2m+1}$	$\Phi=0$	$\Phi=\frac{\pi}{2}$
$\Gamma(A_1)$	$Pnma\left(P1\frac{2_1}{m}1\right)$	$Pnma(Pnm2_1)$
$\Gamma(B_2)$	$Pnma(Pnma)$	$Pnma(P2_1ma)$
$\Gamma(A_2)$	$Pnma\left(P11\frac{2_1}{a}\right)$	$Pnma(Pn2_1a)$
$\Gamma(B_1)$	$Pnma\left(P\frac{2_1}{n}11\right)$	$Pnma(P2_12_12_1)$
$\delta=\frac{2k}{2m+1}$	$\Phi=0$	$\Phi=\frac{\pi}{2}$
$\Gamma(A_1)$	$Pnma(Pnma)$	$Pnma(P2_1ma)$
$\Gamma(B_2)$	$Pnma\left(P1\frac{2_1}{m}1\right)$	$Pnma(Pnm2_1)$
$\Gamma(A_2)$	$Pnma\left(P\frac{2_1}{n}11\right)$	$Pnma(P2_12_12_1)$
$\Gamma(B_1)$	$Pnma\left(P11\frac{2_1}{a}\right)$	$Pnma(Pn2_1a)$
$\delta=\frac{2k+1}{2m}$	$\Phi=0$	$\Phi=\frac{2k+1}{4m}\pi$
$\Gamma(A_1)$	$\left(P1\frac{2_1}{a}1\right)'$	$(Pna2_1)'$
$\Gamma(B_2)$	$\left(P1\frac{2_1}{a}1\right)'$	$(Pna2_1)'$
$\Gamma(A_2)$	$\left(P1\frac{2_1}{a}1\right)'$	$(Pna2_1)'$
$\Gamma(B_1)$	$\left(P1\frac{2_1}{a}1\right)'$	$(Pna2_1)'$

For spatial inversion, one finds that, independent of the modulation wave number type, the operation is always a symmetry element of the commensurate phase if $\Phi=0$. In this case, a ferroelectric polarization is obviously not allowed but an improper magnetization M_i may possibly occur. In fact, for δ=odd/odd, M_x, M_y, or M_z is allowed if $\Phi=0$, and the irreducible order parameter has a symmetry $\Gamma(B_1)$, $\Gamma(A_1)$, or $\Gamma(A_2)$, respectively, while for δ=even/odd, M_x, M_y, or M_z is allowed if $\Phi=0$ and the irreducible order parameter has a symmetry $\Gamma(A_2)$, $\Gamma(B_1)$, or $\Gamma(A_1)$. For δ=odd/even, no homogeneous magnetization is allowed because of the existence of time reversal symmetry. From these results, it may be possible to identify the symmetry of the irreducible order parameter related to a given commensurate phase from the knowledge of the modulation wave number and magnetization of that phase.

Also, in the case of δ=odd/odd, or δ=even/odd, time reversal symmetry is broken and ferroelectricity is not allowed even if the unitary subgroup is compatible with the onset of a spontaneous polarization. In fact, as we will see in the next section, the symmetry of the order parameter does not allow, in these cases, coupling terms linear in P. Interestingly, the symmetry of a commensurate phase with $\delta=(2k+1)/2m$ is independent of the irreducible representation of the order parameter and allows for a ferroelectric polarization directed along the c axis if $\Phi=[(2k+1)/4m]\pi$.

V. LANDAU FREE ENERGY DENSITY AND MAGNETOELECTRIC COUPLING FOR AN IRREDUCIBLE ORDER PARAMETER: THE CASE OF $GdMnO_3$

The potential polar properties of a magnetic commensurate phase induced by a given irreducible order parameter can also be investigated by analyzing the transformation properties of the translational invariants. This alternative method is adequate if one wants to discuss the thermodynamics of the phase transition within the scope of the Landau-Devonshire theory. In this section, we will briefly discuss this approach in order to characterize the type of magnetoelectric coupling that may be at the origin of a ferroelectricity induced by a magnetic irreducible order parameter.

As seen in Sec. III, for a commensurate phase with $\delta=n/m$, the nontrivial translational invariants that depend on the phase of the order parameter are nomials of the form $(S)^p(S^*)^q$ $(p\neq q)$. In this case, given that S and S^* are complex numbers, the analytical form of these translational invariants is determined by the image induced in the complex plane by the translational subgroup of the reference phase. For a wave number $\delta=n/m$, this image is isomorphic to the group Cm.[41] Then, as shown in Refs. 27 and 41, any homogeneous polynomial defined in the space of the complex numbers that is invariant under Cm may be expressed as linear combinations of terms of the type $S_0^m\cos(m\Phi)$ and $S_0^m\sin(m\Phi)$. Because of the different parity of these terms under spatial inversion, a coupling term linear in P must necessarily be of the form $PS_0^m\sin(m\Phi)$. Consider now the restrictions imposed by the requirement that the mixed term be invariant under time reversal. Because $\theta P=P$ and $\theta S_0=-S_0$, the mixed term will be invariant only if m is even. That is, in agreement with the analysis of the preceding section, only magnetic commensurate phases of the type δ=odd/even can support a ferroelectric polarization. Conversely, the translational invariants of the form $S_0^m\cos(m\Phi)$, being even under spatial inversion and odd under time reversal if m is odd, allow for mixed invariants linear on a magnetization. In this case, an improper magnetization may occur.

With the inclusion of terms of the form $S_0^{2m}\cos(2m\Phi)$, which are globally invariant and give rise to umklapp terms in the free energy density whenever δ is commensurate, the trivial invariants of the type S_0^{2n}, and additional magnetic or electric terms, one finds the following Landau free energy densities:

$$f_1=\frac{\alpha}{2}S_0^2+\frac{\beta}{4}S_0^4+\cdots+\xi MS_0^m\cos(m\Phi)+\gamma S_0^{2m}\cos(2m\Phi)+\Omega_M S_0^2M^2+\frac{M^2}{2\chi_M}-MH \quad \text{if } \delta\neq\frac{\text{odd}}{\text{even}} \tag{6}$$

and

$$f_2=\frac{\alpha'}{2}S_0'^2+\frac{\beta'}{4}S_0'^4+\cdots+\gamma' S_0^{2m}\cos(2m\Phi)+\Omega'_M S_0'^2M^2+\frac{M^2}{2\chi_M}-MH+\cdots+\upsilon PS_0'^m\sin(m\Phi)+\Omega_P S_0'^2P^2+\frac{P^2}{2\chi_P} \quad \text{if } \delta\neq\frac{\text{odd}}{\text{even}}. \tag{7}$$

In order to discuss the thermodynamics of the lock-in transition, we need to include the analysis of the possible stability of an incommensurate phase (although these phases are necessarily nonpolar). For this purpose, the incommensurate phase can be described as a distorted commensurate phase. Consequently, we must include in the free energy expansion terms that depend on the spatial derivatives of the order parameter. If we assume that the spatial variations of the order parameter are slow, we can consider only the contributions of its first order derivatives and limit ourselves to lower order terms. In such a case, we find the following four possibilities: $(\partial\vec{S}/\partial x),(\partial\vec{S}^*/\partial x),(\vec{S}\partial\vec{S}^*/\partial x\pm\vec{S}^*\partial\vec{S}/\partial x)$, and $(\partial\vec{S}/\partial x)\times(\partial\vec{S}^*/\partial x)$. The first two of these terms are naturally forbidden by symmetry because they are not invariant under spatial inversion, a symmetry operation of the space group of the paramagnetic phase. The third term with the sign "+" can be written as $(1/2)[d(\vec{S}\cdot\vec{S}^*)/dx]$ and gives rise to a contribution to the free energy that is, in fact, homogeneous $(\Delta F\propto\int[d(\vec{S}\cdot\vec{S}^*)/dx]dx\propto S_0^2)$. The fourth term $(\partial\vec{S}/\partial x)\times(\partial\vec{S}^*/\partial x)=[S_0^2(\partial\Phi/\partial x)^2+(\partial S_0/\partial x)^2]$ does not depend on the phase of the order parameter and is always allowed by symmetry. In particular, it is invariant under time reversal and spatial inversion. The third term with the sign "−", the Lifshitz term, may or may not be allowed depending on the symmetry of the system. In the case of the rare-earth manganites $R\mathrm{MnO}_3$, because the prototype space group contains inversion and the wave vector $\vec{k}$ space is located inside the Brillouin zone, such an invariant is allowed.[27] In fact, under the spatial symmetry operations of the space group of the reference phase, $\vec{S}\partial\vec{S}^*-\vec{S}^*\partial\vec{S}$ transforms exactly as $\vec{x}$ if $\vec{k}\|\vec{x}$. However, under time reversal, $\vec{S}\partial\vec{S}^*-\vec{S}^*\partial\vec{S}$ changes sign. Therefore, the Lifshitz invariant must be explicitly written as $j(\vec{S}\partial\vec{S}^*/\partial x-\vec{S}^*\partial\vec{S}/\partial x)=S_0^2(\partial\Phi/\partial x)$, where $j=\sqrt{-1}$. (Obviously, the two relevant terms $[(\partial\vec{S}/\partial x)\times(\partial\vec{S}^*/\partial x)$ and $j(\vec{S}\partial\vec{S}^*/\partial x\pm\vec{S}^*\partial\vec{S}/\partial x)]$ are invariant under the unitary or nonunitary symmetry operations of the magnetic space group of the reference phase and cannot be linearly coupled to the electric polarization. For example, a term of the type $P(S\partial S^*/\partial x-S^*\partial S/\partial x)$ is not possible if P is itself not invariant under all the spatial operations of the reference group.)

With these terms allowing for incommensurate distortions of the commensurate phases, the free energy densities [Eqs. (6) and (7)] become

$$f_1' = f_1 - \eta S_0^2 \left(\frac{\partial \Phi}{\partial x}\right) + \frac{k}{2}\left[S_0^2 \left(\frac{\partial \Phi}{\partial x}\right)^2 + \left(\frac{\partial S_0}{\partial x}\right)^2\right], \quad (8)$$

$$f_2' = f_2 - \eta S_0'^2 \left(\frac{\partial \Phi}{\partial x}\right) + \frac{k}{2}\left[S_0'^2 \left(\frac{\partial \Phi'}{\partial x}\right)^2 + \left(\frac{\partial S'_0}{\partial x}\right)^2\right], \quad (9)$$

for $\delta \neq$ odd/even and $\delta =$ odd/even, respectively.

Let us now see the case of $GdMnO_3$. The magnetic modulation observed in this compound below T_i corresponds to a simple collinear modulation of the magnetic momenta of the Mn ions. If we assume that this structure results from the condensation of a irreducible magnetic order parameter, then the previous results show that a magnetically driven ferroelectricity is only possible in the case of a magnetic modulated commensurate phase of the type $\delta =$ odd/even. Consistently, the polar phase induced in this compound by an external field corresponds precisely to the stabilization of the lowest possible order of this type of modulation $\left(\delta = \frac{1}{4}\vec{a}_1^*\right)$. However, at zero field, the system remains paraelectric. Let us now analyze how the free energy densities given above may allow us to describe the stabilization of the ferroelectric phase by an external magnetic field.

In Eqs. (8) and (9), the magnetization M and the polarization P are secondary order parameters that can be eliminated by imposing the conditions $\partial f_1'/\partial M = 0$ and $\partial f_2'/\partial M = \partial f_2'/\partial P = 0$, corresponding to thermal equilibrium. These equations lead to

$$\frac{\partial f_1'}{\partial M} = 0 \Rightarrow M = \bar{\chi}_M [H - \xi S_0^m \cos(m\Phi)],$$

$$\frac{\partial f_2'}{\partial M} = 0 \Rightarrow M = \bar{\chi}'_M H,$$

$$\frac{\partial f_2'}{\partial P} = 0 \Rightarrow P = -\nu \bar{\chi}_P S'^m_0 \sin(m\Phi'), \quad (10)$$

where, $\bar{\chi}_M = \chi_M/(1+2\Omega_M \chi S_0^2)$, $\bar{\chi}'_M = \chi'_M/(1+2\Omega'_M \chi S_0'^2)$, and $\bar{\chi}_P = \chi_P/(1+2\Omega_P \chi_P S_0'^2)$ represent renormalized magnetic and electric susceptibilities. The substitution of Eq. (10) into Eqs. (8) and (9) gives

$$f_1' = \frac{\alpha}{2} S_0^2 + \frac{\beta}{4} S_0^4 - \eta S_0^2 \left(\frac{\partial \Phi}{\partial x}\right) + \frac{k}{2}\left[S_0^2 \left(\frac{\partial \Phi}{\partial x}\right)^2 + \left(\frac{\partial S_0}{\partial x}\right)^2\right] + \left(\gamma - \frac{\xi^2 \bar{\chi}_M}{2}\right) S_0^{2m} \cos^2(m\Phi) - \gamma \sin^2(m\Phi) - \frac{1}{2}\bar{\chi}_M H^2 + \xi S_0^m \bar{\chi}_M H \cos(m\Phi), \quad (11)$$

$$f_2' = \frac{\alpha'}{2} S'^2_0 + \frac{\beta'}{4} S'^4_0 + - \eta S'^2_0 \left(\frac{\partial \Phi'}{\partial x}\right) + \frac{k}{2}\left[S_0^2 \left(\frac{\partial \Phi'}{\partial x}\right)^2 + \left(\frac{\partial S'_0}{\partial x}\right)^2\right] + \gamma' S'^{2m}_0 \cos^2(m\Phi') - \left(\gamma' + \frac{\bar{\chi}_P \nu^2}{2}\right) S'^{2m}_0 \sin^2(m\Phi') - \frac{1}{2}\bar{\chi}'_M H^2. \quad (12)$$

In the case of f_1', which expresses the free energy density for a commensurate phase with $\delta \neq$ odd/even, one can directly see that the phase of the order parameter $\Phi = 0$ is favored if $\gamma < 0$. In such a case, a spontaneous magnetization proportional to S_0^m may occur. In addition, the application of an external magnetic field gives rise to a magnetostatic term that is linear in H. The effect of such a term in the relative stability of the phase is determined by the sign of the coefficient ξ. If ξ is positive, the field increases the energy and tends to destabilize the phase. On the other hand, in the case of a commensurate phase $\delta =$ odd/even, such a term is forbidden by symmetry. Here, the coupling between the external magnetic field and the order parameter is simply expressed in f_2 by a renormalization of the magnetic susceptibility and, consequently, only the usual magnetostatic term $\propto H^2$ is allowed.

The above functionals therefore suggest a simple mechanism for the stabilization of a ferroelectric phase by an external magnetic field in the case of $GdMnO_3$. Consider, for example, a set of modulated phases of a common symmetry except for the different wavelengths of the magnetic modulation. Below a certain temperature, several modulations may correspond to relative minima of the free energy and compete for absolute stability. If, at a given temperature and zero magnetic field, the free energy density of the stable commensurate phase corresponds to Eq. (6) with $\xi > 0$, then an external field increases the energy of the phase and may give rise to a first order transition to another commensurate phase with a different modulation wavelength, provided this other phase is less affected by the field. As seen, this can only occur if the modulation wave is of the type $\delta =$ odd/even, for which a linear coupling in the field is not allowed by symmetry. In other words, above a certain threshold, the cost in energy required to change the wavelength of the modulation wave to a value compatible with ferroelectricity is smaller than that necessary to maintain the low field stable magnetic modulation. Magnetization and polarization are secondary order parameters that are not directly coupled but compete with each other via their coupling with competing primary modulated order parameters.

VI. CASE OF A REDUCIBLE ORDER PARAMETER: $TbMnO_3$ AND $DyMnO_3$

The analysis given above can also be applied to the case of the similar systems $(Tb,Dy)MnO_3$. Let us consider first the situation at zero magnetic field in which the ferroelectric phase, observed in these compounds below $T_c \approx 28$ K, corresponds to a cycloidal magnetic structure. For 28 K $< T <$ 41 K there exists an incommensurate collinear modulation

TABLE III. Transformation properties of the lowest order mixed translational invariants in the case of a reducible order parameter of symmetry $\Gamma=\Gamma_i\otimes\Gamma_j$.

		Γ_1	Γ_2	Γ_3	Γ_4
(a) $S_iS_j^*-S_jS_i^*$	Γ_1		B_{1u}	A_u	B_{2u}
	Γ_2	B_{1u}		B_{2u}	A_u
	Γ_3	A_u	B_{2u}		B_{1u}
	Γ_4	B_{2u}	A_u	B_{1u}	
(b) $S_iS_j^*+S_jS_i^*$	Γ_1	A_g	B_{2g}	B_{3g}	B_{1g}
	Γ_2	B_{2g}	A_g	B_{1g}	B_{3g}
	Γ_3	B_{3g}	B_{1g}	A_g	B_{2g}
	Γ_4	B_{1g}	B_{3g}	B_{2g}	A_g

that is nonpolar, as expected given the incommensurate nature of the magnetic order.

The cycloidal ferroelectric structure can be seen as resulting from the simultaneous condensation of two irreducible order parameters S_i and S_j of symmetry Γ_i and Γ_j, respectively. This phase is often referred to as incommensurate[25,42] because $\delta(T)$ shows a quasiplateau and slightly depends on temperature.[25] However, this phase may also be seen as a disordered commensurate phase in which the C domains are separated by discommensurations, that is, regions where the phase of the order parameter varies rapidly. The spontaneous polarization is originated from the modulated regions that are characterized by a reducible order parameter that is transformed as the Krönecker product of its components ($\Gamma=\Gamma_i\otimes\Gamma_j$). Then, the onset of an electric polarization along a given crystallographic direction ($\vec{P}_k$) is allowed only if $\Gamma_i\otimes\Gamma_j\otimes\Gamma^*(\vec{P}_k)$ contains the totally symmetric representation of the space group.[43–46] As shown in Ref. 43, this requires, as a necessary condition, that the sum over the wave vectors characterizing the three order parameters vanishes ($\vec{k}_i+\vec{k}_j+\vec{k}_{P_k}=0$). Given that $\vec{k}_{P_k}=0$, this selection rule imposes that we must consider all pairs of vectors of the stars of $\vec{k}_i$ and $\vec{k}_j$ such that $\vec{k}_i+\vec{k}_j=0$. In terms of the transformation properties of possible mixed invariants involving the components of S_i, S_j, and P_k, this condition imposes that the lowest order coupling between the reducible order parameter and an electric polarization must necessarily involve combinations of mixed forms of the type $S_i^*S_jP_k$ and $S_iS_j^*P_k$. We can therefore investigate the possible onset of a ferroelectric polarization by analyzing if the translational invariants of the type $S_iS_j^*\pm S_jS_i^*$ transforms as components of a polar vector. This can be easily done with the help of the matrices of Table I and the results are given in Table III. Note that the transformation properties of these invariants are similar to those of the symmetric (+) or antisymmetric (−) Dzyaloshinskii-Moriya interaction $\vec{D}\cdot\vec{S}_n\times\vec{S}_{n+1}$.[47,48] In particular, they are always even under time reversal because they correspond to the product of two components that are odd under this operation. Therefore, we need only to consider in Table III the unitary symmetry operations of the paramagnetic space group.

As seen in Table III(b), the translational invariants of the form $S_iS_j^*+S_jS_i^*$ are always even under inversion. They give rise to a coupling of the type $(S_iS_j^*+S_jS_i^*)\eta_{kl}(\vec{q}=0)$ between the magnetic order parameter and homogeneous lattice strains $\eta_{kl}(\vec{q}=0)$, the symmetry of which depends on the symmetry of the primary order parameter. Note that the transformation properties of terms of the type $S_iS_j+S_j^*S_i^*$, to which a wave number $|\vec{q}|=|2\vec{k}|$ corresponds, are similar to those given in Table III(b). These terms are of the form $[S_iS_j\eta_{kl}(-2\vec{k})+S_j^*S_i^*\eta_{kl}(2\vec{k})]$ and are responsible for the onset of a lattice modulation with one-half of the wavelength of the magnetic modulation. The symmetry of the primary order parameter determines the nature of the secondary modulated lattice strain.

For example, for an order parameter of symmetry $\Gamma_2\otimes\Gamma_3$, the modulated strain corresponds to the component η_{xy} of the strain tensor (symmetry B_{1g}). This shear strain reflects the breaking of the orthorhombic symmetry that necessarily occurs in the case of a reducible order parameter. Also, in the case of a single irreducible order parameter, terms of the type $[S_iS_i\eta_{jj}(-2\vec{k})+S_i^*S_i^*\eta_{jj}(2\vec{k})]$ are allowed. Because $S_iS_i+S_i^*S_i^*$ is transformed according to the totally symmetric representation A_g of the group D_{2h}, only the diagonal elements of the strain tensor are, in this case, possible secondary order parameters.

On the other hand, the mixed translational invariants $S_iS_j^*-S_jS_i^*$ are odd under inversion and, with the exceptions of the symmetries $\Gamma_1\otimes\Gamma_3$ and $\Gamma_2\otimes\Gamma_4$, are transformed as components of a polar vector (symmetry B_{1u} or B_{2u}). This means that polarizations oriented along the b or the c axis, depending on the symmetry of the magnetic order parameter, are allowed by symmetry but a polarization oriented along the a axis (that is, parallel to the modulation wave vector) is forbidden. The particular case of an induced polarization along the b axis (symmetry B_{2u}), as it is experimentally observed in $TbMnO_3$ and $DyMnO_3$ at zero field, can be obtained for a primary order parameter with a symmetry $\Gamma_2\otimes\Gamma_3$ or $\Gamma_1\otimes\Gamma_4$. Note that neutron diffraction data[25] suggest that is the first possibility ($\Gamma_2\otimes\Gamma_3$) that occurs in $TbMnO_3$. If, for example, we assume that this is the case, we can immediately write the Landau free energy density corresponding to a given modulation wave number.

Let us consider, as one illustrative example, the magnetoelectric effects in the case of homogeneous commensurate phases (that is, assume that $\partial S_i/\partial x=\partial\Phi_i/\partial x=0$) for a magnetic order parameter of symmetry $\Gamma_2\otimes\Gamma_3$. In such a case, we must consider the magnetization and the electrical polarization as the relevant secondary order parameters. The other possible secondary effects, such as the magnetoelastic effects and the magnetically induced lattice modulation, can be ignored. Accordingly, and for the sake of simplicity, we will not consider the magnetoelastic terms of the type $(S_iS_j^*+S_jS_i^*)\eta_{kl}(\vec{q}=0)$ or $[S_iS_j\eta_{kl}(-2\vec{k})+S_j^*S_i^*\eta_{kl}(2\vec{k})]$ in the free energy functionals. As seen, we must analyze separately the different types of modulation wave number δ. We can therefore write for the cases of $\delta=(2k+1)/(2m+1)$ or $\delta=2k/(2m+1)$ the free energy densities f_3 and f_4 given by Eqs. (13a) and (13b), respectively,

$$f_3 = \frac{\alpha}{2}S_2^2 + \frac{\beta}{4}S_2^4 + \cdots + \gamma S_2^{2m}\cos(2m\Phi_2) + \cdots + \frac{\alpha'}{2}S_3^2 + \frac{\beta'}{4}S_3^4 + \gamma' S_3^{2m}\cos(2m\Phi_3) + M^2(\Omega_M S_2^2 + \Omega'_M S_3^2) + \sum_i \frac{M_i^2}{2\chi_{iiM}} - \vec{M}\cdot\vec{H} + \xi M_z S_3^m \cos(m\Phi_3) + \sigma P_y(S_2 S_3^* - S_3 S_2^*) + P_y^2(\Omega_P S_2^2 + \Omega'_P S_3^2) + \frac{P_y^2}{2\chi_P}, \quad (13a)$$

$$f_4 = \frac{\alpha}{2}S_2^2 + \frac{\beta}{4}S_2^4 + \cdots + \gamma S_2^{2m}\cos(2m\Phi_2) + \cdots + \frac{\alpha'}{2}S_3^2 + \frac{\beta'}{4}S_3^4 + \gamma' S_3^{2m}\cos(2m\Phi_3) + M^2(\Omega_M S_2^2 + \Omega'_M S_3^2) + \sum_i \frac{M_i^2}{2\chi_{iiM}} - \vec{M}\cdot\vec{H} + \xi M_y S_2^m \cos(m\Phi_2) + \xi' M_x S_3^m \cos(m\Phi_3) + \sigma P_y(S_2 S_3^* - S_3 S_2^*) + (\Omega_P S_2^2 + \Omega'_P S_3^2)P_y^2 + \frac{P_y^2}{2\chi_P}. \quad (13b)$$

Here, we have taken into account that, for the considered symmetry of the order parameter, only the magnetization M_z is allowed for $\delta=(2k+1)/(2m+1)$, while M_x and M_y can occur if $\delta=2k/(2m+1)$. Also, because $S_iS_j^*-S_jS_i^*$ is independent of $\vec{k}$, P_y is in both cases a possible secondary order parameter, whose value can be obtained from the condition $\partial f/\partial P_y=0$:

$$P_y = \frac{-\sigma(S_2 S_3^* - S_3 S_2^*)}{2(\Omega_P S_2^2 + \Omega'_P S_3^2) + \chi_P^{-1}}. \quad (14)$$

As seen, if $S_2=0$ or $S_3=0$, $P_y=0$, that is, this polarization vanishes in the case of an irreducible order parameter. Also, $P_y=0$ if the two order parameters S_2 and S_3 are in phase $(\Phi_2-\Phi_3=0)$ and P_y will be maximized if the two order parameters have a phase difference of $\Phi_2-\Phi_3=\pi/2$.

For the reasons clarified in the preceding sections, the case $\delta=(2k+1)/2m$ must be considered separately. Here, on one hand, a linear coupling of the primary order parameters with a magnetization is forbidden by symmetry. On the other hand, and as seen in Sec. IV, we have always P_z as a secondary order parameter. Hence, because $S_iS_j^*-S_jS_i^*$ does not depend on the wave number, we have here a potential competition between two polarizations P_y and P_z. For $\Gamma=\Gamma_2\otimes\Gamma_3$ and $\delta=(2k+1)/2m$, the free energy density must be written as

$$f_5 = \frac{\alpha}{2}S_2^2 + \frac{\beta}{4}S_2^4 + \cdots + \gamma S_2^{2m}\cos(2m\Phi_2) + \cdots + \frac{\alpha'}{2}S_3^2 + \frac{\beta'}{4}S_3^4 + \gamma' S_3^{2m}\cos(2m\Phi_3) + M^2(\Omega_M S_2^2 + \Omega'_M S_3^2) + \sum_i \frac{M_i^2}{2\chi_{iiM}} - \vec{M}\cdot\vec{H} + \sigma P_y(S_2 S_3^* - S_3 S_2^*) + P_z[\upsilon S_2^m \sin(m\Phi_2) + \upsilon' S_3^m \sin(m\Phi_3)] + (\Omega_P S_2^2 + \Omega'_P S_3^2)(P_y^2 + P_z^2) + \frac{P_y^2}{2\chi_{yyP}} + \frac{P_z^2}{2\chi_{zzP}}. \quad (15)$$

If $\gamma,\gamma'>0$, the phases $\Phi_2=\Phi_3=\pi/2$ will be favored. In this case, $P_y=0$ and

$$P_z = \frac{-[\upsilon S_2^m \sin(m\Phi_2) + \upsilon' S_3^m \sin(m\Phi_3)]}{2(\Omega_P S_2^2 + \Omega'_P S_3^2) + \frac{1}{\chi_{zzP}}}.$$

Let us finally consider the effect of an external magnetic field and the rotation of the polarization from P_y to P_z that is experimentally observed in $TbMnO_3$. The mechanism suggested by Eqs. (13)–(15) for the rotation of the polarization under a magnetic field is entirely similar to that described for the stabilization of the ferroelectric phase in $GdMnO_3$. Here again, due to the presence of coupling terms linear on M_z if $\delta=(2k+1)/(2m+1)$ or on M_x and M_y if $\delta=2k/(2m+1)$, the magnetostatic energy of the commensurate phase stable at zero field, polar along the b axis, can be strongly increased by an external field applied along the c axis [if $\delta=(2k+1)/(2m+1)$] or along the a or b axis [if $\delta=2k/(2m+1)$] if $\xi>0$ or $\xi'>0$. Consequently, above a certain threshold, it may become energetically favorable to diminish this magnetostatic energy by slightly adjusting the value of modulation wave number and the phase of S_2 and S_3 to the values $[\delta=(2k+1)/2m]$ and $\Phi_2=\Phi_3=\pi/2$, respectively, for which terms linear on M are forbidden. As a consequence of this discontinuous transition, the polarization rotates from the b axis to the c axis.

VII. CONCLUSION

The analysis made in the present work on the magnetoelectric coupling in the orthorhombic manganites $RMnO_3$ is purely phenomenological and based on general symmetry arguments. The method adopted allows us to draw several general conclusions about the compatibility between magnetic modulated order and ferroelectricity. We have seen that the lattice modulation observed in the rare-earth compounds is not an essential ingredient for the stabilization of the ferroelectric state. Being a secondary effect, it cannot determine the symmetry or the polar properties of the ordered phase. Note that although an incommensurate magnetic modulation, for example, may induce a lattice modulation with $\delta_{latt}=2\delta$, it is incompatible with the onset of a spontaneous polarization. This incompatibility is solely determined by the primary order parameter: symmetry forbids, in this case, a linear coupling between the order parameter and P. We have also shown that from the vantage point of symmetry, an irreducible commensurate order parameter (for example, a simple collinear magnetic modulation) may induce improper ferroelectricity. The fact that this possibility is not realized at zero field in $GdMnO_3$, for example, results from accidental reasons. Finally, we have also stressed that the symmetry and polar properties of the ordered magnetic phase critically depend on the parity of the modulation wave vector and on the phases of the order parameters.

In addition, the method provides us with well defined predictions about the possible space groups generated by the condensation of a given commensurate order parameter and gives us adequate and symmetry based free energy functionals that have the potential to describe the observed phenomenology.

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