REVIEW ARTICLE

Order parameters and phase diagrams of multiferroics

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Abstract

The symmetry properties, order parameters, and magnetoelectric phase diagrams of multiferroics are discussed. After brief reviews of Ni\textsubscript{3}V\textsubscript{2}O\textsubscript{8}, TbMnO\textsubscript{3}, and RbFe(MoO\textsubscript{4})\textsubscript{2}, we present a detailed analysis of RMn\textsubscript{2}O\textsubscript{5} (with R = Y, Ho, Dy, Er, Tb, Tm). (Some figures in this article are in colour only in the electronic version)

1. Introduction

Here we review recent and new developments which elucidate the symmetry and the description of the magnetic and dielectric states of multiferroics using order parameters. After some examples where the magnetoelectric (ME) behavior is relatively simple, we discuss a proposed generic phase diagram for the so-called ‘125’ systems, RMn\textsubscript{2}O\textsubscript{5}, where R is a rare earth. The most important consequence of the phenomenological theories we develop is to provide a general framework for understanding the magnetic and dielectric properties of these materials and how these properties combine to produce the interesting ME phenomena.

Briefly, this article is organized as follows. In section 2 we discuss the characterization of the magnetic structure obtained from symmetry arguments. Here we discuss briefly a simplified version of the group theoretical approach (known as representation theory) which is supplemented by less well-known arguments involving the use of inversion symmetry. As examples we consider Ni\textsubscript{3}V\textsubscript{2}O\textsubscript{8} (NVO), TbMnO\textsubscript{3}, and RbFe(MoO\textsubscript{4})\textsubscript{2} (RFMO) and discuss the introduction of order parameters (OPs) to characterize the magnetic symmetry. We then give a brief review of how symmetry restricts the form of the ME interaction when it is written in terms of both magnetic and dielectric OPs to characterize the magnetic symmetry. We then give a brief review of how symmetry restricts the form of the ME interaction when it is written in terms of both magnetic and dielectric OPs. In section 3 we give a detailed discussion of how these concepts enable us to construct a generic phase diagram for the 125 family of multiferroics, which does not rely on a knowledge of the details of the microscopic interactions. Section 4 contains an application of the theory of critical phenomena to the 125’s, and the paper is briefly summarized in section 5.

2. Symmetry and magnetic structure

Here we give a simplified review of the role of symmetry in determining the structure of the magnetically ordered phase which develops \textit{at a continuous phase transition}. This subject is of ancient vintage, being discussed about 60 years ago by Landau (see [1]). However, some reviews which discuss the analysis of diffraction data [2, 3] overlook the importance of inversion symmetry in reducing the number of parameters needed to describe the ordered magnetic structures. For multiferroics this was first corrected quite recently by Lawes \textit{et al} [4], by Kenzelmann \textit{et al} [5] and in more detail by Harris [6], which we follow here. Formal treatments appeared some time ago [7]. Recent papers include Schweizer \textit{et al} [8] and Radaelli and Chapon [9].

We start by assuming that the paramagnetic phase is characterized by a primitive unit cell with \( n \) magnetic sites. The Landau expansion of \( F_2 \), the magnetic free energy at quadratic order in the spin components, is

\[
F_2 = \sum_{\textbf{q}} \sum_{\tau,\tau'=1}^{n} \sum_{\alpha,\beta} \left[ x^{-1}(\textbf{q}) \right]_{\tau,\tau';\beta} S_{\alpha}(\textbf{q}, \tau)^* S_{\beta}(\textbf{q}, \tau'),
\]
and translation of \( \text{TbMnO}_3 \) (space group \( \text{Pbnm} \)). The glide \( m_1 \) is indicated by the mirror plane at \( z = \frac{3}{4} \) and \( z = 3/4 \) are mirror planes. (c) RFMO, where large balls are Fe spins 5/2 on a stacked triangular lattice, small balls are oxygens, Mo ions are inside the oxygen tetrahedra, and the Rb ions are not shown.

Table 1. General positions [10] (given as fractions of lattice constants) within the primitive unit cell for NVO (space group \( \text{Cmca} \)) and \( \text{TbMnO}_3 \) (space group \( \text{Pbnm} \)). Here \( r^+ = r + 1/2, 2a \) is a two-fold rotation (or screw) axis, and \( m_y \) is a mirror (or glide).

| \( \text{Ni}_3\text{V}_2\text{O}_8 \) | \( \text{TbMnO}_3 \) |
|---|---|
| \( \text{Er} = (x, y, z) \) | \( \text{Er} = (x, y, z) \) |
| \( \frac{1}{2}x, r = (x, y, z) \) | \( 2r = (\pi, y, z+) \) |
| \( \frac{1}{2}x, r = (\pi, y, z) \) | \( 2r = (\pi, y, z) \) |
| \( \text{Er} = (x, y, z) \) | \( \text{Er} = (x, y, z) \) |
| \( m_x = (x, y, z) \) | \( m_y = (x, y, z) \) |
| \( m_x = (x, y, z) \) | \( m_y = (x, y, z) \) |
| \( m_z = (x, y, z) \) | \( m_z = (x, y, z) \) |
| \( m_z = (x, y, z) \) | \( m_z = (x, y, z) \) |

where \( \chi \) is the wavevector-dependent susceptibility matrix and

\[
S_{\tau}(\mathbf{R}, \tau) = \sum q S_{\tau}(q, \tau) e^{i\mathbf{q}\cdot\mathbf{R}},
\]

where \( S_{\tau}(\mathbf{R}, \tau) \) is the \( \alpha \)-component of spin of the \( \tau \) th magnetic site in the unit cell at \( \mathbf{R} \) and \( S_{\tau}(-\mathbf{q}, \tau) = S_{\tau}(\mathbf{q}, \tau)^* \). For each value of the wavevector, the inverse susceptibility has 3\( n \), eigenvalues (which may or may not be distinct from one another). At high temperature \( T \) all these eigenvalues are positive and the paramagnetic state is thermodynamically stable. As \( T \) is reduced through a critical value, \( T_c \), one eigenvalue, \( \lambda_c(q, \tau) \), at some wavevector \( \mathbf{q} \), (and wavevectors equivalent to it by symmetry which leave the star of \( \mathbf{q} \)) is determined by the microscopic interactions. Since these interactions are not well known, we regard the wavevector as an experimentally determined parameter. The degeneracy of this critical eigenvalue \( \lambda_c \) is \( n_qN \), where \( n_q \) is the number of wavevectors in the star of \( \mathbf{q} \) and \( N \) is the dimensionality of the irreducible representation (irrep) of the symmetry group (the so-called ‘little group’) which leaves the wavevector invariant. (For ferromagnetic Ising, \( x-, y-, \) and Heisenberg models \( N \) assumes the values 1, 2, and 3, respectively.) To avoid technicalities, in this section we consider the simplest case, \( N = 1 \). This case is simple because then we can use the familiar principle that the eigenvectors of a matrix (here the inverse susceptibility) are also simultaneously eigenvectors of operators (here the symmetry operations \( O \), of

the space group which leave the selected wavevector invariant) which commute with each other and with the matrix. In this way we avoid using the full apparatus of group theory and the reader need not know anything at all about ‘irreps’. We now illustrate this idea and show how inversion symmetry introduces further simplifications for three recently studied multiferroic magnetic materials, whose lattice structures are shown in figure 1 and whose positions (except for RFMO where the Fe ions form a Bravais lattice) are given in table 1.4

2.1. NVO

For NVO the incommensurate (IC) wavevector for magnetic
ordering is [11, 12] \( \mathbf{q} \equiv 0.28(2\pi/a)a \). Thus the space
group operations \( O \), which leave the wavevector invariant are
generated by \( 2\mathbf{a} \), a two-fold rotation about the \( a \)-axis which passes
through the origin and \( m_c \), a glide operation which
takes \( c \) into \( -c \) followed by a translation through \( (b/2)\mathbf{b} +
(c/2)\mathbf{c} \). Thus the critical eigenvector (which is the spatial
Fourier transform of the spin distribution) must not only be
an eigenvector of the inverse susceptibility matrix, but it must
also simultaneously be an eigenvector of both \( 2\mathbf{a} \) and \( m_c \). Since
\( |2\mathbf{a}|^2 = 1 \), the eigenvalues of \( 2\mathbf{a} \) must be \( \lambda(2\mathbf{a}) \equiv \lambda = \pm 1 \).
Since \( |m_c|^2 \) is a translation along the \( b \) axis, the eigenvalues of
\( m_c \) must be \( \lambda(m_c) \equiv \lambda' = \pm \exp(i\theta q_c/2) = \pm 1 \). Thus, if we
assume continuous transitions, there can only be four distinct
symmetries of ordered phases, corresponding to independently
selecting the eigenvalues of \( 2\mathbf{a} \) and \( m_c \). The corresponding

\[4\] We interchangeably denote the \( \mathbf{a} \), \( \mathbf{b} \), and \( \mathbf{c} \) axes as \( x \), \( y \), and \( z \), respectively.
eigenvectors must be of the form
\[ S(q, 1) = (\alpha_1, \alpha_2, \alpha_3)\xi, \]
\[ S(q, 2) = \lambda (\alpha_1, -\alpha_2, -\alpha_3)\xi, \]
\[ S(q, 3) = \lambda' (-\alpha_1, -\alpha_2, -\alpha_3)\xi^2, \]
\[ S(q, 4) = \lambda' (-\alpha_1, -\alpha_2, +\alpha_3)\xi^2, \]
\[ S(q, 5) = [(1 + \lambda)|a_4, [1 - \lambda)|a_5, [1 - \lambda)|a_6), \]
\[ S(q, 6) = -\lambda' [(1 + \lambda)|a_4, [1 - \lambda)|a_5, [1 - \lambda)|a_6]\xi^2, \]

where \( \xi = \exp(iq_x a/4) \) and the \( \alpha_n \) assume arbitrary complex values. To check this note that under \( 2_a \) sublattices \#1 and \#2 are interchanged as are \#3 and \#4, whereas under \( m_c \) sublattices \#1 and \#4 are interchanged as are \#2 and \#3. Note that \( 2_a \) changes the signs of the \( b \) and \( c \)-components of spin, while \( m_c \) changes the signs of the \( a \) and \( b \) components of spin since spin is a pseudovector. This type of analysis, known as representation theory, is well known and widely used. However, less well known and often overlooked (as documented in [6]) is the fact that in these multiferroic systems the free energy must be invariant under the inversion symmetry \( T \) possessed by the lattice [7]. One can then show [4, 13, 12, 6] that this symmetry fixes the phases of the \( \alpha_n \): for \( \lambda = \lambda' = 1 \), apart from an overall complex phase factor, \( \alpha_1 \) and \( \alpha_3 \) must be pure imaginary and \( \alpha_2 \) and \( \alpha_4 \) must be pure real. For other irreps (i.e. for the three other choices of the eigenvalues \( \lambda(\xi) \)) one has analogous results. If (1) is generalized to include terms of fourth order in the spin variables, then a mean field analysis for \( T \) near \( T_c \) shows that the overall amplitude of the spin wavefunction varies (proportionally to \( (T_c - T)^{1/2} \)), but the ratios among the \( \alpha_n \)'s are nearly temperature independent. Therefore we replace \( \alpha_n \) by \( \sigma(\mathbf{q})\alpha_n \) and require the normalization \( \sum |\alpha_n|^2 = 1 \). Thus the temperature dependence is incorporated in the order parameter \( \sigma \). If we require that \( \alpha_1 \), say, be real, then the freedom to fix the overall phase is taken into account by allowing the order parameter to be complex, as one would expect, since the origin of the IC ordering is not fixed, at least within \( F_2 \). It should be noted that the order parameter inherits the symmetry of the spin functions, so that
\[ 2_0 \sigma = \lambda(2_0)\sigma = \lambda\sigma, \]
\[ m_c \sigma = \lambda(m_c)\sigma = \lambda'\sigma, \]
\[ T \sigma = \sigma^*. \]

In the analysis of diffraction experiments one tries to fit the structure assuming in turn each of the four symmetries. In so doing one has not \( 3n_c = 18 \) complex-valued fitting parameters, but rather the 4 or 5 \( \alpha \)'s of (3) (depending on which symmetry one is considering). However, the use of inversion further reduces the number of fitting parameters by half since their phases are fixed [12].

The left phase diagram in figure 2 shows the experimentally observed sequence of magnetic phases of NVO. As \( T \) is lowered, the first ordered phase to appear (at \( T_c \approx 9 \) K) is the HTI phase, which has a single eigenvector associated with predominantly collinear sinusoidally modulated order. Analysis of experimental data indicates that the eigenvalues of this phase are [12] \( \lambda(2_a) = 1 \) and \( \lambda(m_c) = +1 \). At a lower temperature \( T_c \approx 6 \) K the LTI phase appears with an additional order parameter associated with dominantly transverse spin order and with \( \lambda(m_c) = +1 \) and \( \lambda(m_c) = -1 \). The magnetic free energy which describes the development of these two successive ordering transitions is of the form [12, 6, 21]
\[ F_M = a(T - T_c) (\sigma_{HTI})^2 + b(T - T_c) (\sigma_{LTI})^2 + O(\sigma^4), \]

where \( a \) and \( b \) are constants and \( T_c \) and \( T \) are the respective temperatures (when nonquadratic terms are ignored) at which \( \sigma_{HTI} \) and \( \sigma_{LTI} \) become nonzero. The unwritten terms in \( F_M \) which are quartic in \( \sigma \), favor fixed spin length. Thus \( \sigma_{LTI} \) is out of phase relative to \( \sigma_{HTI} \) and the spins thereby order in a spiral structure [12, 15, 16].

2.2. \( \text{TbMnO}_3 \)

The case of \( \text{TbMnO}_3 \) is almost identical to that for NVO. Here the IC wavevector is of the form \( (0, q_y, 0) \) [19, 5], so that the symmetry operations which leave it invariant are generated by the glide \( m_a \) and the mirror \( m_c \). The eigenvalues of \( m_c \) \( (m_a) \) are \( \pm 1 \) \( (\pm \lambda) \), where \( \lambda = \exp(i\pi q_y) \). For \( \lambda(m_c) = 1 \) and \( \lambda(m_a) = \Lambda \) one has
\[ S(q, 1) = \alpha_1 \hat{i} - \alpha_2 \hat{j} - \alpha_3 \hat{k}, \]
\[ S(q, 2) = \alpha_1 \hat{i} + \alpha_2 \hat{j} + \alpha_3 \hat{k}, \]
\[ S(q, 3) = -\alpha_1 \hat{i} + \alpha_2 \hat{j} - \alpha_3 \hat{k}, \]
\[ S(q, 4) = -\alpha_1 \hat{i} - \alpha_2 \hat{j} + \alpha_3 \hat{k}, \]
\[ S(q, 5) = \alpha_4 \hat{k}, \]
\[ S(q, 6) = -\alpha_5 \hat{k}, \]
\[ S(q, 7) = \alpha_6 \hat{k}, \]
\[ S(q, 8) = -\alpha_7 \hat{k}, \]

where the \( \alpha_n \) are arbitrary complex numbers. As for NVO one can now require that \( F_2 \) be invariant under \( T \). In this case the result is that apart from an overall phase factor, \( \alpha_n \) for \( n = 1, 2, 3 \) are real, \( \alpha_4 \) is an arbitrary complex number, and
\(\alpha_s = \alpha_s^* \) [5, 13, 6]. When inversion symmetry relates sites within the same Wyckoff orbit of the operators of the group of the wavevector (as it does for NVO), the complex phases get fixed, whereas when inversion relates sites in different Wyckoff orbits (as for the Tb sites here), the previously independent amplitudes of the two orbits are now related. Again, we replace \(\alpha_s\) by \(\sigma(q)\alpha_s\), so that the temperature dependence of the spin function is essentially contained in the order parameter \(\sigma(q)\) and the complex phase of the IC ordering is incorporated in the arbitrary complex phase of \(\sigma(q)\) which transforms as

\[
m_n \sigma(q) = \lambda(m_n) \sigma(q), \quad m_n \sigma(q) = \lambda(m_n) \sigma(q),
\]

\[I \sigma(q) = \sigma(q^*)^*.
\]

The center phase diagram in figure 2 shows the sequence of magnetic phases of TbMnO\(_3\). As the temperature is lowered (through \(T_\gamma = 40\) K) the first ordered phase to appear is the HTI phase in which the single eigenvector associated with predominantly collinear order appears with \(\lambda(m_\gamma) = -\exp(i\pi q) = -\Lambda\) and \(\lambda(m_\gamma) = 1\). At a lower temperature \((T_L < 30\) K) the LTI phase appears with an additional order parameter associated with transverse spin order and with \(\lambda(m_L) = -\Lambda\) and \(\lambda(m_L) = -1\). The phenomenology of the magnetic phase diagram of TbMnO\(_3\) is very similar to that of NVO.

2.3. RFMO

The magnetic Fe ions in RFMO form triangular lattice planes which are stacked directly over one another, as shown in figure 1(c) [17]. Below \(T = 180\) K but above the magnetic ordering temperature (at \(T_c = 4\) K) the lattice has \(P\bar{3}\) symmetry [20], so that the only symmetry operation (apart from \(I\)) is a three-fold rotation \(R\) about the \(c\)-axis, which is perpendicular to the triangular lattice plane. At low fields, the spins within a single triangular lattice plane form a \(120^\circ\) structure and as one moves from one plane to the next the spins are all rotated through an angle \(\delta \phi = q \cdot c\), so that the component of the IC wavevector along \(\hat{c}\) is \(q_c\) [18]. To generate the \(120^\circ\) structure, the in-plane component of the wavevector must be chosen to be at the corner, \(X\), of the Brillouin zone of the triangular lattice, i.e. \(q = X + \hat{c}q_c\). Then the symmetry operations \(O\), which leave the wavevector invariant are \(R\) and \(R^{-1}\). \(R\) takes \(X\) into a vector equivalent to \(X\). We thus end up with a one-dimensional irrep \(\Gamma^s\) and its complex conjugate \(\Gamma^s\). The spin distribution is given by [18, 6]

\[
S(r) = [\sigma_1(q_c)(\hat{t} + \hat{j}) + \sigma_2(q_c)(\hat{t} - \hat{j})]e^{iqr} + c.c.,
\]

where \(u = \exp(2\pi i/3)\). The order parameters transform as

\[
R \sigma_n(q_c) = \mu \sigma_n(q_c), \quad I \sigma_n(q_c) = \sigma_{3-\mu}(q_c)^*.
\]

The magnetic free energy up to order \(\sigma^4\) is

\[
F = (T - T_c) \sigma^2 + u \sigma^4 + v |\sigma_1(q_c)\sigma_2(q_c)|^2,
\]

where \(\sigma^2 = |\sigma_1(q_c)|^2 + |\sigma_2(q_c)|^2\), and \(u\) and \(v\) are constants (with \(u\) positive). It is found [18] that only one of the two order parameters is nonzero in a single domain, from which we deduce that \(v\) must be positive. (This conclusion is confirmed by the appearance of ferroelectricity, as we will see in a moment.)

2.4. Magnetoelectric interaction

Here we describe the ME interaction which leads to a spontaneous polarization induced by magnetic ordering which breaks inversion symmetry. For this purpose we show the dielectric phase diagrams of the three systems under consideration in figure 2.

We write the free energy as

\[
F = F_M + F_E + V_{\text{int}},
\]

where \(F_M\) (\(F_E\)) is the magnetic (dielectric) free energy and \(V_{\text{int}}\) is the ME interaction which is responsible for the magnetically induced ferroelectricity.

We first consider NVO [4, 12] and TbMnO\(_3\) [5, 6]. Both have two magnetic ordered phases, the high-temperature incommensurate (HTI) phase at higher temperature \((T_\gamma > T > T_c)\), described by a single order parameter \(\sigma_{\text{HTI}}\) for which spins are predominantly confined to the easiest direction, and the low-temperature incommensurate (LTI) phase (for \(T < T_L\)) in which a new order parameter \(\sigma_{\text{LTI}}\) appears, describing ordering transverse to that of \(\sigma_{\text{HTI}}\). The order parameters are out of phase (to minimize the fourth order terms in the magnetic free energy) [12], and thus give rise to a magnetic spiral. These order parameters transform as specified by (4) and (7), respectively.

We have \(F_E = (1/2)\chi \cdot \mathbf{P}^2\), where \(\chi\) is the dielectric susceptibility and \(\mathbf{P}\) is the polarization vector. Because there is no tendency for ferroelectricity to form in the absence of magnetic ordering, \(\chi\) never gets large. In the absence of ME coupling, the equilibrium value of \(\mathbf{P}\) is zero. The ME interaction has to conserve wavevector and be invariant under time reversal. At lowest (quadratic) order in \(\sigma\), it therefore must be of the form \(V_{\text{int}} \sim \sigma(q)\sigma(-q)P = \sigma\sigma^*P\). In the present situation, the two \(\sigma\)'s cannot both be HTI or LTI, because then \(V_{\text{int}}\) would not be invariant under spatial inversion. So

\[
V_{\text{int}} = \sum_Y [c_y \sigma_{\text{HTI}}(q)\sigma_{\text{LTI}}(q)^* + c_y^* \sigma_{\text{HTI}}(q)^*\sigma_{\text{LTI}}(q)]P_y, \tag{12}
\]

and to be invariant under inversion we must have \(c_y = i r_y\), where \(r_y\) is real, so that (4)

\[
V_{\text{int}} = \sum_Y r_y \sigma_{\text{HTI}}(q)\sigma_{\text{LTI}}(q)^* - \sigma_{\text{HTI}}(q)^*\sigma_{\text{LTI}}(q)]P_y \tag{13}
\]

\[
= 2 \sin(\phi_{\text{HTI}} - \phi_{\text{LTI}})\sigma_{\text{HTI}}\sigma_{\text{LTI}}(\sum Y r_y P_y), \tag{14}
\]

where \(\sigma_{\text{HTI}} = |\sigma_{\text{HTI}}| \exp(i\phi_{\text{HTI}})\) and similarly for \(\sigma_{\text{LTI}}\). The transformation properties given in (4) and (7) for the order parameters under the mirror and glide operations then imply that \(r_y\) in (14) is only nonzero for \(y = b\) for NVO [4, 12, 13, 6] and \(y = c\) for TbMnO\(_3\) [5, 13, 6]. The fact that \(P\) is proportional to \(|\sigma_{\text{HTI}}\sigma_{\text{LTI}}|\) has been experimentally verified for NVO [22].

For RFMO the argument is slightly different. There (9) indicates that \(\sigma_1(q_c)\sigma_2(q_c)^*\) is invariant under inversion (which changes the sign of \(\mathbf{P}\)). Thus (9) implies that the ME interaction quadratic in \(\sigma\), which conserves wavevector, is [18, 6]

\[
V_{\text{int}} = \sum_Y r_y |\sigma_1(q_c)|^2 - |\sigma_2(q_c)|^2 P_y, \tag{15}
\]
where \( r_p \) is real valued. Since the square bracket is invariant under the three-fold rotation \( R \), \( P_p \) must also be invariant under \( R \). So at this order \( r_p \) can only be nonzero for \( \gamma = c \), as is observed [18]. At higher order [23] a transverse polarization is in principle possible. Note that \( R(P_x - i P_y) = \mu(P_x - i P_y) \) and \( R \sigma_i \sigma_j^z = \mu \sigma_i \sigma_j^z \). Then one can have an ME interaction of the form

\[
V_{\text{int}}^{(4)} = c (|\sigma_1(q_x)|^2 - |\sigma_2(q_x)|^2) |\sigma_i(q_x)\sigma_j(q_x)|^2 (P_x - i P_y) + c.c.
\]  

(16)

However, the fourth order terms written in (10) select \( |\sigma_1(q_x)| = |\sigma_2(q_x)| \) if \( v \) is negative and \( |\sigma_1(q_x)\sigma_2(q_x)| = 0 \) if \( v \) is positive. In either case \( V_{\text{int}}^{(4)} \) does not come into play. Since the ordered phase is ferroelectric, we deduce that \( v \) is positive and that only \( P_2 \) is nonzero. Then, within mean field theory, \( P_2 \) is proportional to \( \langle |\sigma|^2 \rangle \), as is the intensity of the magnetic Bragg peaks. This is experimentally confirmed [18] \(^5\).

3. 125’s

We now consider the ‘125’ orthorhombic (space group Pbam) family RMn_2O_5 (RMO), where R = Y, Ho, Er, Dy, Tb, Tm. Their lattice structure and the corresponding space group operations are shown in figure 3. The paramagnetic unit cell of the RMO’s contains 12 potentially magnetic ions: 4 Mn\(^{2+}\), 4 Mn\(^{4+}\) and 4 R\(^{3+}\). Experiments show that all the RMO’s exhibit magnetic spin density wave ordering, with a wavevector \( q \) which undergoes a sequence of phase transitions [24–29]. To discuss these phases we introduce the notation \( q = (U, V)_n \), which we abbreviate as \( (U, V)_n \) (in figure 5 these are denoted by \( U/V_n \)). If \( U = C \) \( (U = I) \), then \( q_x = 1/2 \) \( (q_x = 1/2 - \delta) \) and if \( V = C \) \( (V = I) \), then \( q_z = 1/4 \) \( (q_z = 1/4 + \epsilon) \), where the wavevector is in reciprocal lattice units and \( \delta \) and \( \epsilon \) are of order 0.01 and depend on temperature. \( V = X \) includes the cases when \( \epsilon \neq 0 \) and when \( \epsilon = 0 \). The subscript \( n \) is used, if it is given, indicates the number (1 or 2) of OPs, see below. As the temperature \( T \) decreases, all the RMO’s (with the possible exception of \( R = Dy \)) first order below \( T_c \) (\( \approx 45 \) K), into an incommensurate \( (I, I) \) phase with no ferroelectric (FE) order. For YMO (at \( T_F = 41 \) K) [30, 31], ErMO (at \( T_F = 39 \) K) [32] and TmMO (at \( T_F = 39 \) K) [33], this paraelectric incommensurate state gives way to an \( (I, C) \) phase and this phase displays a weak FE moment \( P \) along the \( b \)-axis. Below \( T_c \approx 37–39 \) K, \( q \) locks into a commensurate (CM) value (\( C, C \)) and \( P_b \) increases significantly [31]. TbMO [30, 36], HoMO [37, 38], and probably DyMO [37] go directly from the \( (I, I) \) phase into the ferroelectric \( (C, C) \) phase. At lower temperature (about 10–20 K) most of the RMO’s return to having some kind of incommensurate order \(^6\). We will not be concerned here with these low-temperature phases, since their existence probably depends sensitively on the details of the spin–spin interactions. As we shall see, the behavior of the higher temperature phases can be described by a generic Landau free energy. The magneto-dielectric phase diagrams of various 125’s are shown in figure 4.

Based on the symmetry of the OPs we construct a Landau theory for the various RMO’s, which yields a generic phase diagram, shown in figure 5, which is independent of the detailed microscopic interactions [21]. Each RMO has particular coupling constants which determine the wavevector \( q \). Varying these parameters, \( J_q \) for \( q_x \), \( J_q \) for \( q_z \), changes the value of the optimal \( q \) at which magnetic ordering occurs. The rest of this section is devoted to an explanation of this phase diagram (including the definitions of the various phases) and to a discussion of its consequences. This analysis is particularly relevant for the RMO’s, because the microscopic theory of their multiferroicity is somewhat controversial. Our theory provides a unified explanation for the various sequences of phase transitions of the magnetic wavevector, and explains why ferroelectricity does or does not occur in the various magnetic phases. It also explains the occurrence of two distinct spin structures from neutron diffraction studies of the CM phase [35, 25]. This phenomenological theory suggests several new experiments and makes a number of predictions, which can be tested experimentally.

3.1. Magnetic structure of the \((I, I)_1\) and \((I, C)_1\) phases of the 125’s

Given the experimental information, we now analyze the various phases in the order in which they arise upon cooling from the P phase. The first phase which is encountered is the \((I, I)\) type. Since \( q_z = 1/4 \) plays no special symmetry role, it is convenient to discuss the \((I, I)\) and the \((I, C)\) phases together. Here, the star of \( q \) consists of four wavevectors, namely, \( q_x = (\pm(1/2 - \delta), 0, 1/4 + \beta) \) and their negatives. Each wavevector is invariant under unity and \( m_r \). This symmetry group has two one-dimensional (1D) irreps, \( \Gamma_0 \) and \( \Gamma_1 \), with complex OPs as amplitudes. By symmetry, all

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\(^5\) However, critical fluctuations may imply different exponents for \( P_1 \) and \( |\sigma|^2 \), see section 4 below.

\(^6\) This order may be commensurate but with a large unit cell.
the wavevectors of the star must have degenerate eigenvalues of (1). Therefore, we introduce complex OPs, \( \sigma_a^+ = \sigma_a(q_{(a)}^{(o)}) \) and \( \sigma_a^- = \sigma_a(q_{(a)}^{-}) \) associated with irreps \( \Gamma_a \) at its wavevectors \( q_{(a)}^{(o)} \), and similarly for \( \Gamma_b \). Here \( q_{(a)}^{(o)} \) and \( q_{(a)}^{-} \) \( q_{(b)}^{(o)} \) and \( q_{(b)}^{-} \) are defined to be the wavevectors at which the \( \langle \sigma_a(q)\sigma_a(q') \rangle \) \( \langle \sigma_b(q)\sigma_b(q') \rangle \) susceptibility is maximal as \( T \to T_{ca} \). Specific basis functions are given elsewhere [41], where it is also shown that they transform as

\[
m_j \sigma_a(q_{(a)}^{(o)}) = \lambda_a \sigma_a(q_{(a)}^{(o)}), \quad \mathcal{I} \sigma_a(q_{(a)}^-) = \kappa_+ \sigma_a(q_{(a)}^+) \times \sigma_a(q_{(a)}^+) \times \n^2 \sigma_a(-q_{(a)}^-),
\]

\[
2 \lambda_a^2 \sigma_a(q_{(a)}^+) = \n^2 \sigma_a(-q_{(a)}^-),
\]

where \( \lambda_a = -\lambda_b = \exp(\i \pi q_{(a)}) = \n^2 \kappa_+ = \n^2 \exp(\pm 2 \i \pi q_{(a)}) \).

As one cools from the P phase, one must enter a phase described by a single irrep because we do not accept an accidental degeneracy of ordering temperatures of OPs having different symmetry. Arbitrarily choosing this irrep as \( \Gamma_a \), the corresponding free energy is

\[
F^{(o)} = (T - T_{ca})[|\sigma_a^+|^2 + |\sigma_a^-|^2] + c_1[|\sigma_a^+|^2 + |\sigma_a^-|^2]^2 + c_2|\sigma_a^+|^2 \sigma_a^-|^2 + c_3[\sigma_a^+ \sigma_a^-]^2 + \text{c.c.} \delta_{q_{(a)},1},
\]

and analogously for \( \Gamma_b \). The coefficients \( c_1 \) and \( c_2 \) may differ for \( F^{(b)} \), and we assume that \( T_{cb} < T_{ca} \), which is the case as the order parameter becomes larger than the critical temperature. If \( T_{cb} \) is larger than the critical temperature, the system becomes a weakly first order transition. Clearly, this term arises only when both \( \sigma_a^+ \) and \( \sigma_a^- \) order, which would now happen only if \( c_2 - 2|c_1| < 0 \). In this case, one again has \( |\sigma_a^+| = |\sigma_a^-| \) and \( F^{(o)} = -r(q_0)^2/\n^2 \), with \( w = 4c_1 + 2c_2 - 2|c_1| \). One would then have a first order transition from \( (I, I) \) into \( (I, C, 1) \) when \( F^{(o)} = F^{(c)} \). Since \( r(q) \) has a minimum at \( q_0 \), we have \( r(1/4) \approx r(q_0) + \alpha(1/4 - q_0) \). Thus, the transition would occur when \( r(q_0) + \alpha(1/4 - q_0) = r(q_0)^2 \), \( r(q_0) \). Remembering that \( r(q_0) = T - T_{ca} \), we have \( q_z \approx 1/4 \approx (T_{ca} - T)^{1/2} \).

Figure 4. ME phase diagrams of ErMO [26], TmMO [28], YMO [34, 35], HoMO [32, 29], TbMO [27], and DyMO [39, 40, 38, 37]. We do not indicate possible phase changes which have a dielectric signature but only a weak magnetic signature and hence may represent a minor spin reorientation. In section 3.4 we argue that for \( 40 < T < 44 \) DyMO is in an \( (I, I) \) phase.

Figure 5. Left: schematic 3D phase diagram for \( q \) near \( 1/2, 0, 1/4 \). The top (red) surface represents the phase boundary between the P and \( (I, I) \), phases (where both \( q_x \) and \( q_y \) are incommensurate). Below the blue surface, which is a parabola in \( J_x \), one has \( q_x = 1/4, \) in phases \( (I, C) \) and \( (I, C)_2 \). The green surface represents \( (I, I)_1 \to (I, I)_2 \) and \( (I, C)_1 \to (I, C)_2 \); (the subscripts 1 and 2 denote the number of irreps which order). Below the orange surface, which is a parabola in \( J_x \) (depending only weakly on \( J_y \)), one has \( q_x = 1/2 \). Right: a cut at constant \( T_{cb} \). The \( (I, I)_2 \) and \( (I, C)_2 \) phases disappear below the orange surface (as \( q_x \to 1/2 \), where one has a 2D irrep. The dashed and dotted lines are possible trajectories followed by specific RMO’s as the temperature is varied.
with \( q_z = 1/4 \). Thus, the transition from \((I, I)_1\) into \((I, C)_1\) occurs at \( T = T_{c_a} \), with

\[
T_{c_a} - T_{c_b} \propto (J_z - J_{zc})^2,
\]

as shown in figure 6(a). This parabolic relation is a mean field result.

Now consider the implications of having \( q_z \) locked to the value 1/4 in the \((I, C)\) phases. From (18) we see that for this locking to occur, both wavevectors \( q_x \) and \( q_z \) must appear (in the same domain). Then, since we do not allow a direct transition from the \( P \) phase to the \((I, C)_1\) phase (we ignore the unlikely case of a multicritical point, at which \( J_z = J_{zc} \)), the question is whether or not a single domain of the neighboring \((I, I)_1\) phase has two wavevectors. From (18), the condition to have two wavevectors is that \( c_2 < 0 \). An alternate scenario would be that \( c_2 > 0 \) and the two wavevectors do not order simultaneously (in the same domain) in the \((I, I)_1\) phase. In that case, barring the existence of an as-yet-undetected phase boundary, the two wavevectors would have to appear in conjunction with the phase transition between the \((I, I)_1\) and \((I, C)_1\) phases. For the two wavevectors not to be present in the \((I, I)_1\) phase would imply that \( c_2 > 0 \). Then if \( c_2 - 2|c_3| < 0 \), the two wavevectors would appear at the \((I, I)_1 \rightarrow (I, C)_1\) phase transition. It would be interesting to experimentally determine (following the logic of [42]) which scenario actually occurs, i.e. whether or not the \((I, I)_1\) phase has simultaneous condensation at both wavevectors. For this purpose, it would be interesting to perform an experiment analogous to that of [42]. Here, since the ME interaction is present, one could use an electric field parallel to one of the wavevectors to manipulate the domains.

### 3.2. Magnetoelastic structure of the \((I, I)_2\) and \((I, C)_2\) phases of the 125's

Similarly to NVO and TbMnO₃, the second 1D irrep \( \Gamma_5 \) may order upon further cooling. In addition to the ‘decoupled’ free energies \( F^{(a)} \) and \( F^{(b)} \), the total free energy now contains many terms which couple the OPs \( \sigma_a^\pm \) and \( \sigma_b^\pm \). We start by discussing the \((I, I)_2\) phase, where all the wavevector components remain incommensurate. Then the quartic terms which couple the two sets of OPs are given by

\[
F_4^{(x)} = c_d[(\sigma_a^+ \sigma_b^-)^2 + (\sigma_a^- \sigma_b^+)^2] + c_s[(\sigma_a^+ \sigma_b^-)^2 + (\sigma_a^- \sigma_b^+)^2] + \Delta,
\]

where \( \Delta \) contains the locking terms,

\[
\Delta = c_4[\sigma_a^\pm \sigma_b^\pm]^2 + (\sigma_a^- \sigma_b^-)^2 + (\sigma_a^+ \sigma_b^+)^2] + c_7[(\sigma_a^\pm \sigma_b^\pm)^2 + (\sigma_a^\pm \sigma_b^\pm)^2] \delta_{q_{4}}^{(a)} \delta_{q_{4}}^{(b)} + c_8[(\sigma_a^\pm \sigma_b^\pm)^2 + (\sigma_a^\pm \sigma_b^\pm)^2] \delta_{q_{4}}^{(a)} \delta_{q_{4}}^{(b)}. \tag{21}
\]

Notice that so far we have not assumed that \( q_{4(1)}^{(a)} \) and \( q_{4(1)}^{(b)} \) are identical. If the exchange interactions were isotropic, then the inverse susceptibility would be invariant under a global rotation of all spin directions. Here, in the generic case, we have small anisotropic interactions which break this degeneracy and, in principle, would cause these critical wavevectors to be slightly different. In this case, the quartic terms \( \Delta \) can lock the wavevectors of the two modes into equality, as happens for NVO [12]. The mechanism for this locking is as follows. Assume that, say, \( \sigma_a \) orders first at \( T = T_{c_a} \), and for simplicity we first treat the case with only a single wavevector, so that, say, \( \sigma_a \), but not \( \sigma_b \), is nonzero. In analogy with what happens for NVO [12], we assume that \( q_{4(1)}^{(a)} \) is almost equal to \( q_{4(1)}^{(b)} \), at which the inverse susceptibility \( \chi_b^{-1}(q) \) of \( \sigma_b \) has its minimum. For \( T_{c_a} > T > T_{c_b} \) this minimum in \( \chi_b^{-1}(q) \) is positive since \( \sigma_b \) has not yet ordered. Now, the quartic terms \( \Delta \) give rise to an effective quadratic term, \( V_{2, eff} \). Since only \( \sigma_a^\pm \) is nonzero, we have

\[
V_{2, eff} = c_6[(\sigma_a^+ \sigma_b^-)^2 + (\sigma_a^- \sigma_b^+)^2] \delta_{q_{4}}^{(a)} \delta_{q_{4}}^{(b)} \tag{22}
\]

where \( (X) \) indicates the thermal average of \( X \). Even before \( \sigma_b^\pm \) orders, this term gives an additional contribution (beyond \( T - T_{c_b} \)) to the inverse susceptibility of \( \sigma_a^\pm \), but only when \( q_{4(1)}^{(a)} = q_{4(1)}^{(b)} \). Since this additional term depends on the relative phase of the \( \sigma_a^\pm \)’s and \( \sigma_b^\pm \)’s, the minimization of this term fixes the phase of \( \sigma_a^\pm \), reducing its symmetry from that of the XY model (two components of a complex number) to that of an Ising model. The minimization always leads to a negative contribution to the inverse susceptibility of \( \sigma_a^\pm \). If \( |(\sigma_a^\pm)|^2 \) is sufficiently large, this term can thereby shift the minimum in the \( \sigma_a^\pm \) inverse susceptibility from the wavevector \( q_{4(1)}^{(b)} \) (which it would have had when \( \Delta = 0 \)) into equality with \( q_{4(1)}^{(a)} \). Also, the star of the wavevector associated with \( \sigma_a^\pm \) now contains only the two vectors \( q_{4(1)}^{(a)} \) and \( -q_{4(1)}^{(a)} \). This scenario applies if the wavevectors for \( \sigma_a \) and \( \sigma_b \) are close enough to be locked.

---

**Figure 6**: Phase diagrams (a) for \( q_z \approx 1/4 \), based on (19) and (b) for \( q_z \approx 1/2 \), based on (31) and (32), when the \((I, I)_1 - (I, I)_1\) phase boundary (dashed line) is preempted by locking \( q_z \) to \( q_z = 1/2 \). Parabolas shown as a function of \( J_x (J_z) \) are weak functions of \( J_x (J_z) \). (c) \( r_{4}(q_z) \) for nonzero \( \Delta F \), based on (30). The OP associated with each point is given in the box along with the parameters which characterize the wavefunction, as explained in [41]. In (a) and (b) the points M and M' are multicritical points that can only be reached by adjusting both the temperature and some additional control parameter.
to $q^{(b)}$ by the term $V_{2,ab}$ before reaching the temperature $T_{cb}$ at which $\sigma_b$ condenses. This, in turn, relies on the smallness of the anisotropic terms which cause $q^{(b)}$ to differ from $q^{(a)}$.

If both $\sigma_a(q^{(a)})$ and $\sigma_b(q^{(a)})$ condense at $T = T_{cb}$, then we need to consider all the terms in (21). In the $(I, I)_1$ phase, both $\langle \sigma^+_a \rangle = e^{i\delta_b}$ and $\langle \sigma^-_{a} \rangle = e^{i\delta_f}$ break the symmetry and have well defined phases $\phi$ and $\chi$ (in real number). Substituting these values into (21) the yields a quadratic form in the four real and imaginary parts of $e^{i\phi}$ and $e^{i\delta_f}$, with eigenvalues $2x^2[c_b \pm (c_7 + c_8)]$ and $2x^2[c_b \pm (c_7 - c_8)]$. Since only one of these eigenvalues is lowest, only one combination of the four OP components of $\sigma_b^{\pm}$ orders, and thus we still have an Ising-like ordering into $(I, C)_2$. In any case, we henceforth assume that both OPs have the same critical wavevectors.

Experimentally, it seems that the phase $(I, I)_2$ has never been observed. Instead, the phase with two OPs below $T_{cb}$ to $1/4$, which would correspond to the appearance of the $(I, C)_2$ phase, that is, both $q_x$ close to $1/4$, (20) must include additional Umklapp terms, which are also consistent with the symmetry of (17) and which lock $q_x$ to $1/4$. For $q_x \neq 1/2$, these are

$$U_{ab} = \{c_9 \sigma_a^+ \sigma_a^- + c_{10} [\langle \sigma^+_a \rangle \langle \sigma^-_a \rangle] + c_{11} [\langle \sigma^+_a \rangle \langle \sigma^-_a \rangle] + c_{12} \} \delta_{ab}$$

where $c_9$ and $c_{10}$ are real. The locking is stronger when two irreps, rather than a single irrep as in (18), are present, because then the additional terms of (23) come into play. However, in either case, note that this locking requires the presence of both wavevectors $q_a$ and $q_b$.

Finally, we discuss the ME interactions in the $(I, I)$ and $(I, C)$ phases. In analogy with (14), the lowest order ME interaction which is invariant under the operations of (17) is

$$V_{\text{int}} = i P \sum_k \{ \sigma_a(q_k) \sigma_b(q_{-k}) \} \sigma_a(q_k) \sigma_b(q_{-k}) \}$$

Thus, in the $(I, I)$ and in the $(I, C)$ phases, at this order, ferroelectricity requires the presence of two order parameters which are not in phase with one another. At fourth order in the magnetic order parameters, the ME interaction can lead to small spontaneous polarizations in the other coordinate directions, but due to space limitations we refer the reader to (21). We should also point out that when $\langle \sigma_a \rangle \neq 0$, one has a linear coupling between $P_y$ and $\sigma_b$, which gives rise to electromagnons [44–46].

3.3. Magnetoelastic structure of the $(C, X)$ phases

This case includes both $X = C$ ($q_x = 1/4 + \epsilon$) and $X = C$ ($q_x = 1/4$). Because $q$ is on the Brillouin zone boundary ($q_x = 1/2$), the wavevector is invariant under $m_a$ and $m_b$, and the star of $q$ consists of $q$ and $-q$. These operations lead to a two-dimensional irrep [43, 6] and we choose the basis functions as in table XVI of [6]. The actual wavefunction is a linear combination of the two basis functions with complex amplitudes $\sigma_1(q)$ and $\sigma_2(q)$. These are the OPs which characterize the magnetic structure and they transform as [6]

$$m_x \sigma_a(q) = \zeta_a \sigma_a(q), \quad m_y \sigma_a(q) = \zeta_a \sigma_{3-n}(q),$$

$$\langle \sigma_a(q) \rangle = \sigma_{3-n}(q)^*,$$

where $\zeta_a \equiv (-1)^{n+1}$. Consistent with these symmetries the magnetic free energy up to quartic order in $\sigma$ is

$$F_M = (T - T_C)[\langle \sigma_1(q) \rangle^2 + \langle \sigma_2(q) \rangle^2] + \mu \left[ \langle \sigma_1(q) \rangle^2 + \langle \sigma_2(q) \rangle^2 \right]$$

$$+ \nu \left[ \langle \sigma_1(q) \rangle^2 \langle \sigma_2(q) \rangle^2 + \langle \sigma_1(q) \rangle^2 \langle \sigma_2(q) \rangle^2 + \langle \sigma_1(q) \rangle^2 \langle \sigma_2(q) \rangle^2 \right]$$

$$+ \kappa_1 \left[ \langle \sigma_1(q) \rangle^2 + \langle \sigma_2(q) \rangle^2 \right] + \kappa_2 \left[ \langle \sigma_1(q) \rangle^2 \langle \sigma_2(q) \rangle^2 + \langle \sigma_1(q) \rangle^2 \langle \sigma_2(q) \rangle^2 + \langle \sigma_1(q) \rangle^2 \langle \sigma_2(q) \rangle^2 \right]$$

where $\mu, \nu, \kappa_1, \kappa_2$ are real. Under the terms quadratic in $\sigma$ and those scaled by $\mu$, all directions in the four-dimensional space of $\sigma_1 \equiv \sigma_1(q)$ and $\sigma_2 \equiv \sigma_2(q)$ are equally unstable relative to ordering. However, for $q_x \neq 1/4$, the fourth order terms select $\sigma_1 = \sigma_2$ for $w + 4v < 0$ if $v$ is negative, $\sigma_1 = \pm i \sigma_2$ for $w < 0$ if $v$ is positive, and $\sigma_1 = 0$ otherwise. For $q_x = 1/4$ in the terms in $x$ and $y$ are difficult to analyze analytically, but in many cases we find that the phases of $\sigma_1$ and of $\sigma_2$ can be chosen so that $F_M$ still has minima when either $\langle \sigma_1 \rangle = \langle \sigma_2 \rangle$ or $\sigma_1 \sigma_2 = 0$.

Now we consider the dielectric properties. At quadratic order in $\sigma$, since $\mathcal{I} \sigma^2 \equiv \sigma_1 \sigma_2$, (15) also applies to the 125’s when $q_x = 1/2$, 0, $q_x$ and then (25) indicates that $r_j$ is only nonzero for $\nu^2 = b$. Including terms of higher order in $\sigma$ in [23] the ME interaction for the 125’s is of the form

$$V_{\text{int}} = r_x [\langle \sigma_1 \rangle^2 - \langle \sigma_2 \rangle^2] P_b$$

$$+ i \sum_{f, g} \left[ \langle \sigma_1 \rangle^2 - \langle \sigma_2 \rangle^2 \right] P_{ab}$$

where, according to (25), the real coefficient $r_j$ is only nonzero for $\nu^2 = b$. However, as mentioned above, (26) probably allows only either $\langle \sigma_1 \rangle = \langle \sigma_2 \rangle$ or $\sigma_1 \sigma_2 = 0$, in which case the last term in (27) is inoperative. On the other hand, if $\sigma_1 \sigma_2 = 0$ (so that, say, $\sigma_1 = 0$) and if one applies an electric field, $E_{av}$, in the $a$ direction, which induces a nonzero value of $P_{ab}$, the second term in (27) will induce a nonzero out-of-phase value in the order parameter, $\sigma_1$, that was zero for $E_{av} = 0$. Thus one sees that applying an electric field $E_{av}$ modifies the spin structure.

The ME coupling can induce lattice displacements at wavevectors which are even integer multiples of the magnetic wavevector [47, 48]. Since the results are particularly simple for the $(C, C)$ phase, where $q = (1/2, 0, 1/4)$, we now discuss the lowest order interaction in that case. So far we considered a trilinear spin–phonon coupling involving $\sigma(q) \sigma(q)$, which conserves wavevector and therefore couples to a uniform polarization. We now generalize this analysis, and consider terms of the form $\sigma(q)^2 \sigma(q)^2 \sigma(q)$, which couple to phonon modes with wavevector $\pm 2q$. Within a reciprocal lattice vector, this phonon wavevector is equal to the antiferroelectric wavevector (0, 0, 1/2). To construct this interaction we need the site symmetry analysis for this wavevector, which is the same as for the wavevector (0, 0, 0) as given in table I of [49]. There it is indicated that there are 15 $B_{2u}$ ($x$-like) modes, 15 $B_{2u}$ ($x$-like) modes, and 9 $B_{2u}$ ($x$-like) phonon modes. An $x$-like mode, for instance, need not involve displacements along the $x$-axis; rather such a mode need only transform like $x$ under the space group operations. Accordingly, let $u_{AB}(\nu, \tau)$
denote such a phonon, where \( \gamma \) labels the symmetry \((x, y \text{ or } z)\), since we are only interested in vector-like modes which carry a polarization) and the index \( r \) labels the occurrence. We use the transformation properties of (25) with \( m_z = I m_{\sigma_r m} \), so that \( m_{r \sigma_r} = \sigma_r^2 \). Thus the combination \((\sigma_r^2 + \sigma_r^2)\) is even under \( m_z \) and \( m_y \), so that the spin–phonon interaction contains the term

\[
V_{\text{sp-ph},z} = \sum_r [\epsilon_1 (\sigma_r^2 + \sigma_r^2) + \text{c.c.}] J_{\text{AF}}(z, r),
\]

where \( r \) is real, so that the square bracket is odd under \( m_z \). Similarly \( \sigma_2 \sigma_2 \) is odd under \( m_z \) and \( m_y \), so it cannot couple to a vector. Finally \((\sigma_r^2 - \sigma_r^2)\) is even under \( m_z \) and odd under \( m_y \), and it gives rise to an ME interaction of the form

\[
V_{\text{sp-ph},y} = \sum_r [\epsilon_2 (\sigma_r^2 - \sigma_r^2) + \text{c.c.}] J_{\text{AF}}(y, r),
\]

where \( r' \) is real and we noted that the square bracket is even under \( m_z \). In summary, at this order one can have antiferroelectricity with polarization along either \( y \) or \( z \).

We next analyze the tongue associated with \( q_x = 1/2 \). Note that for a critical value, \( J_x \), of the control parameter \( J_x \), the two branches (denoted \( r_{\pm}(q_x, J_x) \)) of the quadratic coefficients \( r(q_x) \) of the inverse susceptibility are degenerate and are minimal at \( q_x = 1/2 \), so that \( r_{\pm}(q_x, J_x) = r(0) + a(q_x - 1/2)^2 + O(q_x - 1/2)^4 \), where \( a \) is a positive constant. As \( J_x \) is varied away from \( J_x \), a term in \( r_{\pm}(q_x) \) which is linear in \( k_x = (1/2 - q_x) \) is allowed and generically is of order \( \Delta J_x \equiv J_x - J_{x-c} \) [41]. The symmetry operation \( m_x \) dictates that the spectrum of the two branches \( r_{\pm}(q_x) \) should be independent of the sign of \( k_x \), as shown in figure 6(c), so that

\[
r_{\pm}(k_x, J_x) = r(0) + ak_x^2 \pm bk_x(J_x - J_{x-c})
\]

and for concreteness we assume that the constant \( b \) is negative and that \( J_x > J_{x-c} \). Symmetry thus implies the existence of equivalent minima at \( k_x = \pm b(J_x - J_{x-c})/(2a) \equiv k_x^* \). Thus at its minimum \( r_{\pm}(k_x^*) \) assumes the value \( r(k_x^*) = 0 \) or \(-\alpha J_x - J_{x-c}^2\), where \( \alpha \) is a constant. Accordingly, we can adopt the argument leading to (19), to the present case and obtain

\[
T_{ca} - T_c \propto (J_x - J_{x-c})^2,
\]

where \( T_c \) is the phase boundary between the \((I, X)\) and \((C, X)\) phases. (This phase boundary is the solid line in figure 6(b).)

The structure of (30) also allows us to discuss the phase boundary \( T_{ca} \) between the \((I, I_1)\) and \((I, I_2)\) phases. For that purpose we compare (30) with (18) (and with its analog for \( F(\sigma) \)) and identify \( r_{\pm} \) with \( T - T_{ca} \) and \( r_{-} \) with \( T - T_{cb} \). We thereby find that

\[
T_{ca} - T_{cb} = 2bk^* (J_x - J_{x-c}) \sim c(J_x - J_{x-c})^2,
\]

where \( c \) is a constant. Thus \( T_{I-x} \) is proportional to \((J_x - J_{x-c})^2\). Depending on the parameters, this parabolic tongue can be either narrower or wider than that considered above for locking \( q_z \) to \( q_x = 1/2 \). In the figure we show the former case, since the \((I, I)\) phase has not been observed for any of the 125’s.

3.4. Generic phase diagram for \( \text{RMn}_2\text{O}_3 \)

We now explain how the generic phase diagram of figure 5 describes the various RMO’s. Since \( q_z = 1/4 \) is not a high symmetry point, we can not condense from the \( P \) phase into \( q_x = 1/4 \) unless we adjust the \( J \)'s appropriately to reach this higher order multicritical point. Since we reject this accidental possibility, the first ordered phase we encounter has \( q_x \neq 1/4 \). Although \( q_x = 1/2 \) is a special value (characteristic of antiferromagnetically doubling the size of the unit cell), the result shown in figure 6(b) indicates that a continuous transition from the \( P \) phase into a \((C, I)\) phase is not allowed because it would also involve a multicritical point. For the RMO’s (except \( \text{R} = \text{Dy} \) which we discuss separately), experiment shows that the first ordered phase is \((I, I)\) and this case is shown in figure 5. From now on we arbitrarily set \( T_{ca} > T_{cb} \) (since we reject the possibility of accidental equality). Consequently we identify that the transition from the \( P \) phase is into an ordered phase \((I, I)\), with a single \( \sigma \) \( \sigma \) (except for the star of \( q \)). For a single \( \sigma \), (24) provides a phenomenological explanation for why this phase is not ferroelectric. As discussed above, we assume that in the \((I, I)\) the phases \( I_{a}^{(a)} \) and \( I_{a}^{(b)} \) become locked into equality without crossing a phase boundary. For the phases with \( q_x \neq 1/4 \), experiments have not yet indicated whether the two wavevectors \( \sigma_{b} \) occur in separate domains, or whether the true state is the superposition, within a single domain, of the two wavevectors. As \( T \) is further reduced through the \((I, I)\) phase, a second continuous transition could occur, producing a phase \((I, I)2\) in which both \( \sigma \) \( \sigma \) and \( \sigma_b \) are nonzero (as in \( \text{NVO} \) [4, 6] or \( \text{TbMnO}_3 \) [5]).

The above description applies for \( J_x \) relatively far away from \( J_{x-c} \), i.e. \( q_x \) relatively far away from 1/4. If \( q_x = 1/4 \), one goes directly from the \( P \) phase into the \((I, C_1)\) phase, which is similar to the \((I, I)\) phase. Upon cooling, the \( \sigma \) related to the other 1D irrep tends to order, and one has a transition into the \((I, C_2)\) phase. This transition happens at a higher temperature than that for \((I, I_1) \rightarrow (I, I_2)\), due to \( \text{Umklapp} \) terms like (23), which enhance the tendency of \( \sigma_b(q_x, 0, \pm 1/4) \) to order (compared to \( \sigma(q_x, 0, q_z) \) with an IC \( q_z \). If \( q_z \) is close to 1/4, one first goes from the \( P \) phase into the \((I, I)\) phase, but then \( \text{Umklapp} \) terms cause a transition into the \((I, C_1)\) phase, and one ends up with the phase diagram shown on the RHS of figure 5.

As the temperature is lowered, each individual RMO follows some trajectory in the parameter space. The RHS plot in figure 5 shows possible projections of such trajectories. The trajectories, as well as the optimal wavevectors, are assumed to have some temperature dependence, which can originate from the elimination of secondary degrees of freedom, which generate effective temperature-dependent exchange coefficients. Note that the whole diagram corresponds to the close vicinity of \( q = (1/2, 0, 1/4) \), so that this temperature
dependency is relatively weak. As shown in figure 4, the real RMO’s go directly from the \((I, I_1)\) phase into either an \((I, C)\) (for \(R = Er, Tm, Y\)) or into the \((C, C)\) phase (for \(R = Ho, Dy, Tb\)). In the former case, we now argue that this phase must be the \((I, C)_2\) phase: since the experimentally observed phase is ferroelectric, it follows that there must exist two OPs, \(\sigma_i\) and \(\sigma_0\). Once both order parameters exist, this phase could be either \((I, I_2)\) or \((I, C)_2\). Since the experiments find that \(q_x = 1/4\), this must be \((I, C)_2\). Indeed, we conclude that the trajectories for \(R = Er, Tm, Y\) are represented by the dashed lines with long dashes in the phase diagram. As the same lines indicate, one would then go into the \((C, C)\) phase, as indeed observed. At lower temperatures, the trajectories could leave the \((C, C)\) phase to the other side of the parabolic ‘tongue’, and enter a less commensurate phase, which could be paraelectric \([I, I_1]\) or ferroelectric \([I, I_2]\) or \([C, C]\).

As indicated by the dashed line with short dashes in the same figure, one can also go directly from \((I, I_1)\) into \((C, C)\). This trajectory thus describes the RMO’s with \(R = Ho, Dy, Tb\). In the \((C, C)\) phase, which is ferroelectric, (27) indicates that \(|\sigma_1| \neq |\sigma_2|\). The quartic term of (26) implies that either \(|\sigma_1| = |\sigma_2|\), or one of them is zero, so that \(\sigma_1\sigma_2 = 0\). Thus only the first term in (27) survives and it explains the observation [36, 37] that the spontaneous polarization lies along the \(b\) axis. Finally, we should mention that the fact that different \(R\)’s follow slightly different trajectories is reasonable from the following qualitative point of view. For \(Tm, Er, and Y\) the value of \(q_x\) (listed in table 2) is much closer to 1/4 and therefore is more likely to be locked to \(q_x = 1/4\) than is that of \(Ho and Tb\).

For DyMO, experiments have not definitively determined the sequence of phase transitions in the wavevector, because the large incoherent neutron cross section of the Dy nucleus causes experimental problems. A recent x-ray experiment [40] has confirmed the existence [39] of the \((C, C)\) state. The specific heat [37] provides evidence that there is a single intermediate phase between this state and the paramagnetic state. As argued in connection with figure 5, this intermediate phase has to be an \((I, I_1)\) phase, because we do not allow the possibility of accidentally hitting the multicritical point where the P phase meets the \((I, C)\) (in figure 5(a)) or \((C, I)\) phase (in figure 5(b)). This proposed phase exhibits a single OP, which is also consistent with the fact that DyMO is paraelectric for \(T > 40\) K (see figure 4).

We now return to the phase diagram of figure 5. All the RMO’s have \(q\) close to \((1/2, 0, 1/4)\) (see table 2), so they leave the P phase near the apex of the tongue of figures 6(a) or (b). The effects of a magnetic field are explained as follows: it generates magnetic moments on the R ions (even above their ordering temperature). Since these ions couple to the Mn ions, their moment changes the effective Mn–Mn interactions, thus changing the ‘control parameters’ and the optimal \(q\). This often moves the material towards the \((C, C)\) tongue, resulting in a transition from \((I, C) \rightarrow (I, I)\) when paraelectric back into the CM phase [32, 29]. Pressure [52] has similar effects.

### 3.5. Spin structures in the \((C, C)\) phase

The introduction of OPs leads to a natural interpretation of neutron scattering results for the \((C, C)\) phase in YMO. Figure 7 shows the Mn\[^{3+}\] a–b plane spin components in the CM phase of YMO, from the neutron diffraction results of [35] and [25]. These two structures are obviously similar, and one might ask what symmetry (if any) relates them. (This degeneracy was also found in the first-principles calculation of [53].) We now show that these two structures are indeed equivalent [21]. To identify the symmetry element that relates them note that the structure on the left is even under the glide operation \(m_x\), while that on the right is odd under \(m_x\). (Here one should note that spin, being a pseudovector, transforms with an additional minus sign under a mirror operation.) Then (25) indicates that the structure on the left has \(\sigma_2 = 0\), whereas that on the right has \(\sigma_1 = 0\). Going between these two structures corresponds to a rotation in OP space. This equivalence is easily understood when OPs are introduced, as done here. Since either \(\sigma_1 = 0\) or \(\sigma_2 = 0\), we conclude from the discussion below (26), that \(w + 2v - 2|v|\) is positive and both OPs can not order simultaneously [6, 21]. This conclusion supports that reached above, namely that since the CM phase is ferroelectric, the fourth order terms in (26) must select \(\sigma_1\sigma_2 = 0\).

To make this identification more quantitative, we consider the magnetic structure which Kimura et al [25] deduced from their neutron diffraction study, which we summarize in table 3. Their structure determination was based on an unrestricted fit, in which no particular symmetry was assumed. In contrast, our analysis based on representation theory assumes that the magnetic structure is characterized by the two complex-valued order parameters \(\sigma_1\) and \(\sigma_2\), with corresponding spin

| Table 2. Values of \(q_x, q_y, and \Pi = |1/2 - q_x| - |1/4 - q_y|\) for \(T\) near \(T_c\) for various RMO’s. Positive \(\Pi\) favors locking \(q_x\) to the value 1/4 in preference to locking \(q_y\) to the value 1/2. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| R               | q_x         | q_y         | \(\Pi\)         |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Tm [28] Er [26] Y [51, 34] Ho [29] Tb [27, 24] | 0.252 0.244 0.255 | 0.237 0.277 | 0.026 0.015 0.013 | -0.001 -0.010 |

Figure 7. Schematic diagram of the \(a\) and \(b\) components of the Mn\[^{3+}\] spins in a single \(a-b\) plane of YMO for the CM phase. The glide \(m_x\) consists of a mirror plane \(M\) at \(x = a/4\) followed by a translation \(b/2\) along \(y\). Left: the structure given in table III of [25] (with the \(c\)-components not shown). Right: the structure given in figure 2 of [35] (who reported zero \(c\)-components of spin).
We found the optimal structure constants to be magnetic structure in the seems unlikely that if such an additional order parameter would be related. To characterize the difference between these two structures, note that the magnetic sublattices are related in pairs, whereas in the sum of the squares of the spin amplitudes within the data from \[25\] on HoMn\textsubscript{2}O\textsubscript{5} exhibit the same symmetry: (This complex phase can not be explained by a low order anisotropy in the complex \(\sigma\).) Thus, if \(\sigma\) is represented by a single complex OP \(\sigma_1\). However, the phases \(\phi_i\) of the \(x\)-components of the Er magnetic moments (0.8\(\pi\) and \(-0.3\pi\)) do not agree with the values \((\pi\text{ or }0)\) corresponding to \(\sigma_1\). It would be interesting to check the sensitivity of the data to variation of these phases. It is interesting that the structures of all the 125's determined in \[25\] have \(\sigma_2 = 0\), even though the structure with \(\sigma_1 = 0\) represents an equivalent way that magnetic ordering can break symmetry. Apparently, the sample preparation (which might create some uniaxial strain) or some other experimental detail (stray electric fields?) chooses the structure with \(\sigma_2 = 0\) in these experiments. It would be interesting to study the cause for this apparent symmetry breaking.

The selection of which OP is nonzero in the \((C, C)\) phase is a result of broken symmetry. An electric field along \(b\) would order \(P_b\), and then \(15\) would select either \(\sigma_1\) or \(\sigma_2\), depending on the sign of the field. Therefore we suggest cooling the sample into the FE phase in the presence of a small electric field along \(b\). Depending on the sign of the electric field one should get either the left-or the right-hand panel of figure 7. This was indeed confirmed experimentally\(^{10}\). (A similar experiment was recently performed in TbMnO\textsubscript{3} \[56\].)

### 4. Critical phenomena

All the quantitative results presented above were based on the Landau expansion and on mean field theory. Although these theories usually give reasonable predictions far away from critical points, fluctuations must be included in the critical regimes. We start with NVO and TbMnO\textsubscript{3}. In these materials, one first goes from the P phase into the HTI phase, which is represented by a single complex OP \(\sigma_{\text{HTI}}\). Since the free energy only involves \(|\sigma_{\text{HTI}}|^2\), it does not depend on the phase of this complex number, and therefore this transition belongs to the universality class of the XY model, with the critical exponents of an isotropic \((n = 2)\)-component spin model. The transition from the HTI phase into the LTI phase, at \(T_{c},\) is also continuous. A priori, \(\sigma_{\text{HTI}}\) is also a complex number, which would be described by an XY model. However, as we discussed after (21), terms like \(|\sigma_{\text{HTI}}|^4 + c.c.| would

\(^{10}\) After we announced \[21\], we were informed about experiments by Radaelli \textit{et al} \[55\].
lock the wavevectors of the two order parameters to each other, even before one reaches \( T_c \). This lock-in is indeed observed experimentally in the LTI phases of NVO [12] and TbMnO\(_3\) [5].

Technically, near \( T_c \) we have a finite order parameter \( \langle \sigma_{\text{HTI}} \rangle \equiv a e^{i\theta} \). Writing also \( \sigma_{\text{LTI}} \equiv e^{-i\theta}(b + ic) \), the above locking term thus becomes \( \alpha^2(b^2 - c^2) \). Therefore, the real order parameters \( b \) and \( c \) now have different quadratic terms, and only one of them (depending on the sign of the overall coefficient) orders at a temperature slightly above the ‘bare’ \( T_c \). As stated above, the fixed length constraint prefers \( \sigma_{\text{HTI}} \) and \( \sigma_{\text{LTI}} \) to have different phases, which implies that \( c \) orders first, and the phases of the two order parameters differ by \( \pi/2 \). This then yields a helical structure in the LTI phase [15, 16, 12]. Furthermore, this phase relation is also confirmed by the existence of a ferroelectric moment in the LTI phase, which would not exist if \( \phi_{\text{HTI}} = \phi_{\text{LTI}} \) (namely if \( b \) were to order, rather than \( c \)) [14]. Thus, the transition from HTI to LTI belongs to the Ising \((n = 1)\) universality class. Further away from the critical point the critical exponents may approach their mean field values \( \gamma = 1 \) and \( \beta = 1/2 \).

We now consider the ME interaction, (12) and (14). Assuming that indeed only \( c \) orders, we find that near the HTI \( \rightarrow \) LTI transition one can replace (14) by

\[
V_{\text{int}} = 2\sigma_0ac P_b. \tag{35}
\]

This immediately implies that the actual order parameter at this transition is not just \( c \), but rather a linear combination of \( c \) and \( P_b \) [54, 6]. This implies that the dielectric constant should diverge near \( T_c \), as \( \varepsilon_b \sim |T - T_c|^{-\gamma} \), with the Ising susceptibility exponent \( \gamma \). However, as noted before (12), \( \varepsilon_b \) is much larger than \( |T - T_c| \), and therefore the amplitude of this divergent term (related to the amplitude of \( P_b \) in the mixed OP) can be quite small. It would be useful to search for this divergence experimentally. Similarly, we expect that both \( c \) and \( P_b \) grow below \( T_c \) as \( (T_c - T)^\beta \), with the Ising order parameter exponent \( \beta \).

We next turn to RFMO. As discussed in section 2.3, the ordered phase has two complex components of the magnetic OP, \( \sigma_1 \) and \( \sigma_2 \), and therefore altogether we have \( n = 4 \) OP components, as described by (10). In fact, this free energy can be written as

\[
F = (T - T_c)(|\sigma_1(q_c)|^2 + |\sigma_2(q_c)|^2) + u(\langle |\sigma_1(q_c)|^4 + |\sigma_2(q_c)|^4 \rangle + v|\sigma_1(q_c)|^2|\sigma_2(q_c)|^2). \tag{36}
\]

This can be viewed as the free energy of two XY models (with OPs \( \sigma_1 \) and \( \sigma_2 \)), which are coupled by the last term. In terms of the renormalization group (RG), this model has two competing fixed points: the isotropic \((n = 4)\) one with \( \tilde{v} = 2u \) and the decoupled one with \( \tilde{v} = 0 \) [57]. It turns out that \( v \) is slightly relevant near the isotropic fixed point, and \( \tilde{v} \) is slightly irrelevant near the decoupled fixed point, so that as \( T \) approaches \( T_c \) one could follow two scenarios. If \( v = \tilde{v} - 2u < 0 \), iteration would make it more negative, and one could end up with a crossover from the isotropic \((n = 4)\) critical behavior to the asymptotic behavior of two decoupled XY models. However, this crossover is very slow. Therefore, one might either observe effective exponents close to those of the isotropic \((n = 4)\) critical behavior, or one might encounter relatively large corrections to the decoupled critical behavior, due to the irrelevant parameter \( \tilde{v} \), which would be renormalized into \( \tilde{v}(T_c - T)^{-\alpha} \), where \( \alpha \) is the specific heat exponent of the XY model. Alternatively, if \( v > 0 \) then \( u \) would grow larger under iterations, and one would never reach the vicinity of the stable fixed point at \( \tilde{v} = 2u + v = 0 \). In this case, one probably ends up with a slow crossover to a weak first order transition.

The ME interaction in RFMO is given in (15). Thus, \( P_c \sim \langle |\sigma_1(q_c)|^2 - |\sigma_2(q_c)|^2 \rangle^2 \). The RHS of this relation represents an order parameter anisotropy. Near the isotropic fixed point, this average scales as

\[
P_c \sim \langle |\sigma_1(q_c)|^2 - |\sigma_2(q_c)|^2 \rangle^2 \sim \langle |\sigma_1|^2 \rangle^2, \tag{37}
\]

where the exponent \( \lambda > 1 \) is associated with the scaling of quadratic anisotropy terms near the isotropic \( n = 4 \) fixed point [58]. However, for this result to hold we must have \( \sigma_1 \sigma_2 = 0 \), which arises only if \( v > 0 \). As explained above, in this case we expect a crossover to a weak first order transition. Thus, as \( T \) is increased towards \( T_c \) we would expect a gradual variation from the mean field result, \( P_c \sim \langle |\sigma_1|^2 \rangle \), via the critical behavior of (37), to a weak first order transition. The mean field behavior, with \( \lambda = 1 \), implies that the FE moment is proportional to the intensity of Bragg peaks, as apparently found experimentally [18]. It would be interesting to check this relation close to \( T_c \).

Finally we turn to RMO. As stated, the ordering below the \( P \) phase is into the \((I, I)_1\) phase, which corresponds to a single irrep, say \( \Gamma_a \). As seen from (18), this ordering involves the two complex OPs \( \sigma_1^+ \) and \( \sigma_1^- \), and therefore belongs to some \( n = 4 \) universality class. In the \((I, I)_1\) phase, where \( q_c \neq 1/4 \), the quartic terms in the free energy include only those with the coefficients \( c_1 \) and \( c_2 \). Clearly, this free energy is equivalent to the one discussed above for RFMO, yielding only one wavevector if \( c_2 > 0 \) and two wavevectors if \( c_2 < 0 \). In the former case one probably flows under the RG towards a weak first order transition, while in the latter case one would flow towards the stable decoupled fixed point. Thus, the question whether one or two wavevectors order is directly related to the nature of the critical behavior.

The situation changes in the \((I, C)_1\) phase, where one also needs to include the Umklapp term with \( c_3 \). Near the decoupled fixed point, this term involves products of anisotropies in each of the XY models, and thus it can be shown to be relevant [57]. As far as we know, this free energy has no stable fixed point, and one would eventually end up with a weak first order transition. However, in the vicinity of the isotropic fixed point, where \( c_2 \) and \( c_3 \) are small, one could still observe the critical exponents of the isotropic \( n = 4 \) universality class. In any case, in the generic case the phase \((I, C)_1\) is reached from the phase \((I, I)_1\) via a first order transition, so that the critical behavior of the former can only be expected near the multicritical point where \( J_c = J_{zc} \).

We next discuss the transition into the (so far unobserved) \((I, I)_2\) phase. We start with the simple case, where only \( \sigma_1^+ \) orders in the \((I, I)_1\) phase. As explained after (22), the locking of the wavevectors of \( \sigma_1^+ \) and \( \sigma_1^- \) fixes the phase of \( \sigma_1^+ \), so that the transition into the \((I, I)_2\) phase now involves an Ising-like
order parameter. The situation now becomes exactly the same as in (35): the dielectric constant \( \epsilon_b \) would diverge with the Ising exponent \( \gamma \), and \( P_b \) would grow in the \((I, I)\) phase with the Ising exponent \( \beta \).

The transition from \((I, I)_1\) into \((I, C)\) is also weakly first order, since it involves a lock-in of \( q_1 \). However, if the discontinuity is small (as seems to be the case experimentally), we can still discuss criticality of the OPs associated with \( \Gamma_b \). As discussed after (22), this ordering should also belong to the Ising universality class: before one reaches this transition one should see \( \epsilon_b \sim |T - T_{cb}|^{-\gamma} \) and \( P_b \sim (T_{cb} - T)^\delta \), with Ising exponents. Since \( \Delta \) now introduces several additional quadratic terms in the \( \sigma_\epsilon \)'s, this transition is expected to occur at a temperature \( T_{cb}' \) higher than \( T_{cb} \), where one would have the \((I, I)_1 \rightarrow (I, I)_2\) continuous transition.

Near the \( P \rightarrow (I, I) \) transition (which occurs at \( T_{C1} \)), a leading fluctuation expansion yields \( \Delta \epsilon \propto \left| P_2^C \right|^{\frac{1}{\gamma}} \propto |\sigma_2^C|^{\frac{1}{\gamma}} |\sigma_2^C|^{\frac{1}{\gamma}} \). Since only \( \sigma_\epsilon \) becomes critical there, we expect singularities in \( \epsilon \) which behave as the energy \( (T - T_{C1})^{-\gamma} \) and as the square of the OP \((T_{C1} - T)^{\delta \beta} \), but with the appropriate effective \( n = 4 \) exponents. Indeed, experiments [52] show a break in slope at \( T_{C1} \), apparently confirming this prediction. This behavior is also expected for other multiferroics and indeed this may explain the anomaly seen in the dielectric constant of NVO shown in figure 4(b) of [22]. In addition, this anomaly in the zero frequency dielectric constant reflects the emergence of a resonance in the frequency-dependent dielectric constant due to electromagnons [44–46].

5. Summary

We have developed a phase diagram to explain the multiferroic behavior of the family of 125's systems and have proposed several experiments to explore the unusual symmetries of these systems. In view of our current understanding it seems unnecessary to invoke the alternate route to multiferroicity proposed in [59], particularly as a microscopic calculation [35] having exactly the symmetry we have invoked reproduces the experimental data for YMn2O5 quite well.

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