Effect of inversion symmetry on the incommensurate order in multiferroic RMn₂O₅
\(R=\text{rare earth}\)

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(Received 10 April 2008; published 3 July 2008)

Starting from the irreducible representations of the group of the wave vector, we construct the spin-wave functions consistent with inversion symmetry, neglected in the usual representation analysis. We obtain the relation between the basis functions of different members of the star of the wave vector. We introduce order parameters and determine their transformation properties under the operations of the space group of the paramagnetic crystal. The results are applied to construct terms in the magnetoelectric interaction, which are quadratic and quartic in the magnetic order parameters. The higher-order magnetoelectric interactions can in principle induce components of the spontaneous polarization, which are not allowed by the lowest-order magnetoelectric interaction. We also obtain the relation between the spin-wave functions of the incommensurate phase and those of the commensurate phase, which lead to analogous relations between the order parameters of these two phases.

DOI: 10.1103/PhysRevB.78.014407

I. INTRODUCTION

The problem of determining the symmetry of incommensurate (IC) magnetic order from diffraction experiments is an old one and is the subject of several well-known reviews.¹ ² The reviews are based on the idea that the spin structure that develops at a continuous transition must transform like an irreducible representation (irrep) of the group of operations, which leaves the IC wave vector \(\mathbf{q}\) invariant.³ However, perhaps surprisingly, these standard references do not exploit additional restrictions that are due to inversion symmetry when that operation is not a member of the group of the wave vector. Although the group theoretical formalism for doing this has been described⁴ ⁵ and these restrictions had previously been used to aid in structure determinations,⁶ ⁹ the effect of inversion symmetry is often not included in the classification of possible magnetic structures.

Here we perform the requisite analysis for the star of wave vectors of the IC phases¹⁰ ¹² of the “125” systems, \(\text{RMn}_2\text{O}_5\), where \(R\) is a rare earth ion, which may be magnetic or not (e.g., when \(R\) is yttrium). The interest in these materials stems from the fact that they exhibit ferroelectricity¹³ ¹⁶ whose onset coincides with a magnetic ordering transition.¹⁷ ²¹ We show that when inversion symmetry is taken into account, there are about half as many degrees of freedom that describe the basis functions of the irreducible representations compared to an analysis when inversion symmetry is overlooked. Even when an unrestricted fit (not taking account of any symmetry) is performed,²² it is useful to have the results of the present paper to see if the hypothesis of a single irrep²³ holds. Thus, it is clear that magnetic structure determination using an approach that includes inversion symmetry will lead to an increase in the accuracy of the structure determinations. Finally, this approach leads naturally to the introduction of order parameters, which have symmetry properties that we explicitly display and in terms of which a Landau expansion was developed for a number of systems⁶ ⁹ and which has led to a generic magnetoelectric (ME) phase diagram for the 125’s (Ref. 24). The purpose of the present paper is to (a) analyze the symmetry of the various IC phases, (b) show how the symmetry implies relations between order parameters of different symmetry magnetic phases, and (c) analyze the symmetry of the ME interactions, which explain the appearance of ferroelectric order at some of the magnetic phase transitions.

Briefly, this paper is organized as follows: In Sec. II we list the results obtained using the canned program MODY for the IC phase and we show how to modify this to take account of inversion symmetry. Here order parameters are introduced as the complex amplitudes of the spin-wave functions. In Sec. III we show how, having obtained the basis functions for one member of the star of \(\mathbf{q}\), one can determine the basis functions for all the other wave vectors in the star of \(\mathbf{q}\). Here we also determine how the order parameters transform under all the operations of the space group. Having determined the symmetry properties of the order parameters, we are able, in Sec. IV, to construct the lowest-order (trilinear) ME interaction, which explains the orientation of the observed magnetically induced spontaneous polarization. Here we show that higher-order and \textit{Umklapp} ME interactions can lead to small contributions to all components of the spontaneous polarization. In Sec. V we discuss how the basis functions in the IC phase with \(q_s \neq 1/2\) connect to those in the adjacent \(q_s=1/2\) phase. Here we also analyze the symmetry of the special multicritical point for which \(q_s=1/2\). In Sec. VI we briefly summarize the results of this paper.

II. CALCULATION

A. Results without inversion symmetry

The lattice structure of the 125’s was determined by Quezel-Abrunaz \textit{et al}.²⁵ to be that of the orthorhombic space

\(\text{PHYSICAL REVIEW B 78, 014407 (2008)}\)
group $\text{Pbam}$ (No. 55 in Ref. 26). In Table I we list the general positions in the primitive unit cell, which defines the symmetry operations of the space group $\text{Pbam}$, and in Table II (Refs. 27–29) we give the actual positions of the ions for the 125 systems.

The magnetic and dielectric phases occurring in the 125’s are more complicated and we give a brief overview of them here. In Figs. 1(a) and 1(b) we show the ME phase diagrams of $\text{ErMn}_2\text{O}_4$ (taken from Ref. 17) and $\text{HoMn}_2\text{O}_4$ (taken from Ref. 18), which exhibit the simultaneous ferroelectric and magnetic phase transitions. When cooled from the paramagnetic phase, the 125’s develop IC order at about 45 K in a paraelectric phase described by the wave vectors whose star consists of $q_z = |(1/2 - \delta, 0, \pm (1/4 + e)|$ and their negatives, where $\delta$ and $e$ are of order 0.05 or less in reciprocal lattice units (r.l.u.). Upon further cooling of some 125’s, such as $\text{ErMn}_2\text{O}_4$ [shown in Fig. 1(a)]$^{9,17,21}$ $\text{YMn}_2\text{O}_4$ (Refs. 12, 14, 16, and 30), and $\text{TMn}_2\text{O}_5$ (Refs. 11 and 34), exhibit a ferroelectric $(I, 0, I)$ phase in which $e=0$, before entering a $(C, 0, C)$ phase in which $\delta = e = 0$. Other 125’s, such as $\text{TbMn}_2\text{O}_4$ (Refs. 14, 19, and 35), $\text{HoMn}_2\text{O}_4$ [shown in Fig. 1(b)] (Refs. 18, 20, 21, and 36), and $\text{DyMn}_2\text{O}_4$ (Refs. 20, 31, 32, and 36), go directly from the $(I, 0, I)$ phase into the $(C, 0, C)$ phase without the appearance of the $(I, 0, C)$ phase. At lower temperature the 125’s follow various scenarios in which the magnetic structures may be either IC or commensurate (CM) with a long period and they may or may not be ferroelectric. For a review of the properties and Landau theory for 125’s see Ref. 37.

Here we give a symmetry analysis of the allowed magnetic structures in the $(I, 0, I)$ or $(I, 0, C)$ phases. A detailed symmetry analysis applicable to the phase with $q_z = 1/2$ (Refs. 5 and 9) indicated that this phase was described by a two dimensional (2D) irreps and therefore could be characterized by two complex-valued order parameters$^9$ we will call $\sigma_1$ and $\sigma_2$. The symmetry of the phase when $q_z \neq 1/2$ is different. The group of this wave vector contains unity $E$ and the glide $m_{ac}$, which leaves the $b$ component of the wave vector invariant. Thus we have two one dimensional (1D) irreps, which we label $I_\gamma$ and $I_\gamma^* (\gamma "n"$ for even and “$n$" for odd). In particular, since the star of the wave vector contains four vectors, ordering within each irrep is described by four complex-valued order parameters.$^{24}$ The allowable wave functions are the basis functions of the irreps, which transform appropriately. These basis functions are actually eigenvectors of $\mathbf{m}_{ac}$ with eigenvalues $+\lambda^*$ (for $I_\gamma$) and $-\lambda^*$ (for $I_\gamma^*$), where $\lambda = \exp(-i\mathbf{q}_I)$. Since each irrep is contained 18 times in the original reducible representation generated by the three spin components of the 12 magnetic sites in the unit cell (here we assume that $R$ is magnetic), each wave function contains 18 independent free complex-valued parameters. These wave functions are listed in Table III (Ref. 38) and they are in agreement with (i.e., a reparametrization of) the results of the MODY program.$^{39}$

To illustrate the transformation laws, we check that the vectors in Table III are indeed eigenfunctions of $m_{ac}$. Note that we use the so-called “unit-cell” Fourier transforms whereby,$^{40}$

$$S(R, n) = S(q, n)e^{2\pi i q \cdot R} + c.c.,$$

where $n$ labels the sublattice and $R$ locates the unit cell. A transformation $\mathcal{O}$ takes the “initial” basis function into a “final” basis function. If a prime indicates final, i.e., “after transformation,” then $S'(R_f, n_f)$ denotes the spin of sublattice $n_f$ in the unit cell at $R_f$ after transformation. This quantity is obtained by applying the transformation to the spin at the

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
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\end{tabular}
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TABLE III. Symmetry-adapted basis functions for wave vector (Ref. 38) $q_i = (q_x, q_y, q_z)$, which transform according to the irreps $\Gamma_e$ and $\Gamma_m$ where $\lambda = \exp(-\pi i q_i)$. We have not yet yielded the effect of inversion symmetry.

| $S(q_i)$ | $\psi(\Gamma_e)$ | $\psi(\Gamma_m)$ |
|----------|------------------|------------------|
| $S(q,1)$ | $(s_1, s_1, s_1)$ | $(u_1, u_1, u_1)$ |
| $S(q,2)$ | $-\lambda (s_1, -s_1, s_2)$ | $\lambda (u_1, -u_2, u_2)$ |
| $S(q,3)$ | $-\lambda (s_1, -s_1, s_1)$ | $\lambda (u_1, -u_1, u_2)$ |
| $S(q,4)$ | $(t_1, t_1, t_1)$ | $(v_1, v_1, v_1)$ |
| $S(q,5)$ | $(s_2, s_2, s_2)$ | $(u_1, u_2, u_2)$ |
| $S(q,6)$ | $-\lambda (s_2, -s_1, s_2)$ | $\lambda (u_1, -u_1, u_2)$ |
| $S(q,7)$ | $-\lambda (s_2, -s_2, s_2)$ | $\lambda (u_1, -u_2, u_2)$ |
| $S(q,8)$ | $(t_2, t_2, t_2)$ | $(v_2, v_2, v_2)$ |
| $S(q,9)$ | $(s_3, s_3, s_3)$ | $(u_3, u_3, u_3)$ |
| $S(q,10)$ | $-\lambda (s_3, -s_3, s_3)$ | $\lambda (u_3, -u_3, u_3)$ |
| $S(q,11)$ | $-\lambda (s_3, -s_3, s_3)$ | $\lambda (u_3, -u_3, u_3)$ |
| $S(q,12)$ | $(t_3, t_3, t_3)$ | $(v_3, v_3, v_3)$ |

initial location $R_i + \tau_n$. Thus by transformation for $m_{ac}$, we write,

$$S'(q, n_f) = \xi_{a} S(a, q, n_f) e^{-2\pi i q [R_f - R]}$$

where $\xi_{a}$ is the appropriate factor for the mirror operation $m_{ac}$ on the components of a pseudovector: $\xi_{a} = \xi_{x} = \xi_{y} = 1$. We will check that the basis vector of irrep $\Gamma_e$ is an eigenfunction of $m_{ac}$. Note that under $m_{ac}$ when the initial sublattice index is $n_f = 2n - 1$, then the final sublattice index is $n_f = 2n$ and vice versa. Thus,

$$S'(q, 1) = \xi_{a} S(a, q, 2) e^{-2\pi i q [R_f - R]} = \xi_{a} \lambda \xi_{a} s_{a1} e^{-2\pi i q} = \lambda^{*} s_{a1} = \lambda^{*} S(a, q, 1)$$

$$S'(q, 2) = \xi_{a} S(a, q, 1) e^{-2\pi i q [R_f - R]} = \xi_{a} s_{a1} = \lambda^{*} [\lambda \xi_{a} s_{a1}] = \lambda^{*} S(a, q, 2)$$

$$S'(q, 3) = \xi_{a} S(a, q, 4) e^{-2\pi i q [R_f - R]} = \xi_{a} s_{a1} e^{-2\pi i q} = \lambda^{*} [\lambda^{*} s_{a1}] = \lambda^{*} S(a, q, 3)$$

$$S'(q, 4) = \xi_{a} S(a, q, 3) e^{-2\pi i q [R_f - R]} = \lambda^{*} s_{a1} = \lambda^{*} S(a, q, 4)$$

$$S'(q, 5) = \xi_{a} S(a, q, 6) e^{-2\pi i q [R_f - R]} = \lambda^{*} s_{a2} = \lambda^{*} S(a, q, 5)$$

$$S'(q, 6) = \xi_{a} S(a, q, 5) e^{-2\pi i q [R_f - R]} = \lambda^{*} s_{a2} e^{-2\pi i q} = \lambda^{*} [\lambda^{*} s_{a2}] = \lambda^{*} S(a, q, 6)$$

$$S'(q, 7) = \xi_{a} S(a, q, 8) e^{-2\pi i q [R_f - R]} = \xi_{a} s_{a2} e^{-2\pi i q} = \lambda^{*} [\lambda s_{a2}] = \lambda^{*} S(a, q, 7)$$

$$S'(q, 8) = \xi_{a} S(a, q, 7) e^{-2\pi i q [R_f - R]} = \xi_{a} \lambda^{*} s_{a2} = \lambda^{*} s_{a2} = \lambda^{*} S(a, q, 8)$$

$$S'(q, 9) = \xi_{a} S(a, q, 10) e^{-2\pi i q [R_f - R]} = \xi_{a} \lambda s_{a3} e^{-2\pi i q} = \lambda^{*} [\xi_{a} s_{a3}] = \lambda^{*} S(a, q, 9)$$

$$S'(q, 10) = \xi_{a} S(a, q, 9) e^{-2\pi i q [R_f - R]} = \xi_{a} s_{a3} = \lambda^{*} [\lambda^{*} \xi_{a} s_{a3}] = \lambda^{*} S(a, q, 10)$$

$$S'(q, 11) = \xi_{a} S(a, q, 12) e^{-2\pi i q [R_f - R]} = \xi_{a} s_{a3} e^{-2\pi i q} = \lambda^{*} [\lambda^{*} \xi_{a} s_{a3}] = \lambda^{*} S(a, q, 11)$$

$$S'(q, 12) = \xi_{a} S(a, q, 11) e^{-2\pi i q [R_f - R]} = \lambda^{*} \xi_{a} s_{a3} = \lambda^{*} S(a, q, 12)$$.

Thus $\psi(\Gamma_m)$ is an eigenvector of $m_{ac}$ with eigenvalue $\lambda^{*}$. In the other irrep, the fact that $\lambda$ is everywhere replaced by $-\lambda$ ensures that $\psi(\Gamma_m)$ is an eigenvector of $m_{ac}$ with eigenvalue $-\lambda^{*}$.

### B. Effect of inversion symmetry

Now we modify the above results to take account of inversion symmetry. A straightforward, if clumsy, way to do this is to use the fact that the inverse susceptibility matrix becomes singular at a continuous phase transition, which implies that one of its eigenvalues passes through zero. We wish to see what restrictions symmetry places on the associated critical eigenvector. We write the quadratic terms in the free energy $F_2$ in the form,

$$F_2 = \frac{1}{2} \Psi^{\dagger} F \Psi$$

where $F$ is the inverse susceptibility matrix. Instead of considering the quadratic form in the original spin variables, we consider the quadratic form in terms of the variables of Table III. So the matrix $F$ is an 18 dimensional Hermitian matrix operating on an 18-component vector $\Psi(\Gamma)$, which we write as $(s_1, t_1, s_2, t_2, s_3, t_3)$, where the $s$'s and $t$'s are three component subvectors taken from Table III. Thus

$$s_n = (s_{n1}, s_{n2}, s_{n3})$$

Because the paramagnetic phase has symmetry under spatial inversion $I$, we must have:

$$F_2 = \frac{1}{2} \Psi^{\dagger} F \Psi$$

for all values of the spin coordinates.

To implement this, we note that for transformation under $I$, the result follows a logic similar to that leading to Eq. (2), namely:

$$S'_a(q, \tau) = S_a(q, \tau) e^{2\pi i [q_f - q]}$$

where again the prime indicates the value after transformation by $I$. Note that inversion relates sites (1, 4), (2, 3), (5, 8), (6, 7), (9, 12), and (10, 11). Now use Eq. (7) to get

$$s'_{a1} = s_{a1} e^{-2\pi i (q_x + q_y)}$$

$$s'_{a2} = t_{a2} e^{-2\pi i (q_x + q_y)}$$

$$s'_{a3} = t_{a3} e^{-2\pi i (q_x + q_y)}$$

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These simple results arise because we reparametrized with an eye to avoid complexity.

The eigenvalue equation for the $18 \times 18$ matrix $F$ can be represented as

$$
\begin{bmatrix}
A & B & C & D & E & J' \Lambda^* \\
B^* & A^* & D^* & C^* & J & E' \Lambda^* \\
\tilde{C}^* & \tilde{D} & L & M & N & Q' \Lambda^* \\
\tilde{D}^* & \tilde{C} & M^* & L^* & Q & N' \Lambda^* \\
E^* & \tilde{J}^* & N^* & \tilde{Q}^* & S & T \\
\tilde{I} & \tilde{E} & \tilde{Q} & \tilde{A} & \tilde{N} & T^* & S^*
\end{bmatrix}
$$

where $\Lambda = \exp(2\pi i q_z)$. Now consider this matrix operating on a vector of the form,

$$
\Psi = [\rho, \rho^*, \psi, \psi^*, \chi, \Lambda \chi^*].
$$

One can show that $F \Psi$ is a vector of the same form as $\Psi$. This means that any eigenvector can be taken to be of this form and the eigenvalue equations are

$$
E' \rho + J' \rho^* + N' \psi + Q' \psi^* + S \chi + T \Lambda \chi^* = \lambda \chi,
$$

$$
C' \rho + \tilde{D} \rho^* + L \psi + M \psi^* + N \chi + Q' \chi^* = \lambda \psi,
$$

$$
A \rho + B' \rho^* + C' \psi + D \psi^* + E' \chi + J' \chi^* = \lambda \chi.
$$

(The other three equations are the complex conjugates of these.) These give rise to 18 simultaneous equations for the real and imaginary parts of the three component vectors $\rho$, $\psi$, and $\chi$.

The point is that the permissible form for an 18-component eigenvector is restricted by inversion symmetry. The critical eigenvector is the one whose eigenvalue first passes through zero as the temperature is lowered. As the temperature is further lowered, we may have a small amount of admixing of noncritical eigenvectors into the critical eigenvector due to higher-than-quadratic terms in the free energy. However, these admixtures will only be within the same irrep unless one crosses a phase boundary.

Since the eigenvalue problem is in a complex vector space, we write critical eigenvector as

$$
\Psi = e^{i\phi} [\rho, \rho^*, \psi, \psi^*, \chi, \Lambda \chi^*],
$$

where the phase $\phi$ is arbitrary (as far as the quadratic terms are concerned) and the other Greek letters are three component vectors. In Tables IV and V we tabulate the results. In so doing we have introduced the complex-valued order parameters $\sigma(\Gamma)$, such that

$$
\sigma(\Gamma) = |\sigma(\Gamma)| e^{i\phi(\Gamma)}.
$$

To avoid overparametrizing, we specify the normalization,

$$
\sum_{a=x,y,z} \sum_{n=1,2,3} \left| s_{an} \right|^2 = 1.
$$

Including inversion symmetry, we have nine complex-valued $s$ parameters and one complex-valued order parameter $\sigma(q_z)$, so that we have 19 real valued parameters (taking account of the normalization of the $s$’s), whereas without taking account of inversion symmetry, we would have had 36 real valued parameters to determine from a fit to diffraction data.
TABLE IV. Symmetry-adapted spin-wave functions for wave vector \( \mathbf{q}_1 = (q_x, 0, q_z) \), which transform according to the irrep \( \Gamma_6 \), where \( \lambda = \exp(-\pi q_z) \), \( \Lambda = \exp(2\pi i q_x) \), and \( \sigma_r \) is the complex-valued order parameter. We require the normalization of Eq. (22). Otherwise, all constants assume arbitrary complex values. Here we include the effect of inversion symmetry.

\[
\psi(\Gamma_6) = \begin{cases} 
\sigma_r(q_x)(s_{x1}, s_{y1}, s_{z1}) \\
-\sigma_r(q_x)(s_{x1}, -s_{y1}, -s_{z1}) \\
-\sigma_r(q_x)\lambda^*(s_{x1}, -s_{y1}, s_{z1}) \\
\sigma_r(q_x)(s_{x1}, -s_{y1}, s_{z1}) \\
\sigma_r(q_x)(s_{x2}, s_{y2}, s_{z2}) \\
-\sigma_r(q_x)\lambda^*(s_{x2}, -s_{y2}, s_{z2}) \\
\sigma_r(q_x)(s_{x2}, s_{y2}, s_{z2}) \\
\sigma_r(q_x)(s_{x3}, s_{y3}, s_{z3}) \\
-\sigma_r(q_x)\lambda^*(s_{x3}, -s_{y3}, s_{z3}) \\
\sigma_r(q_x)(s_{x3}, s_{y3}, s_{z3}) \\
\end{cases}
\]

One may notice that we could have said that the 18-component eigenvector of \( s \)'s was of the form,

\[
\Phi = e^{i\Phi}[\pi, -\pi^*, \tau, -\tau^*, \xi, -\Lambda \xi^*], \tag{23}
\]

and indeed the eigenvector is equivalent to this form because if you multiply the previous eigenvector \( \Psi \) by \( i \), it will be exactly of the form of \( \Phi \).

The comparison with NiV\(_2\)O\(_8\) (Refs. 6, 8, and 9) (NVO) and TbMnO\(_3\) (Refs. 7 and 9) (TMO) is significant. In the case of NVO the magnetic Ni sites are of two types, spine and cross tie.8 All sites of the same type are related to one another by a symmetry operation which leaves the wave vector invariant. It happens that the Wyckoff orbit of this set of operators generates the entire set of spine sites and also separately the entire set of cross-tie sites. In that case inversion (which does not leave the wave vector invariant) fixes all the relative phases.6,8,9 (The phases are not necessarily the same, but they are fixed.) In the case of TMO the Mn sites form a Wyckoff orbit of the symmetry operations that leave the wave vector invariant, but the Tb sites break into two orbits. In this case inversion fixes the relative phases within the Mn orbit and within a single Tb orbit. Inversion connects the two Tb orbits. As a result the amplitudes of the two Tb orbits are fixed to be the same and they have phases, which are the negatives of one another, but the magnitude of this phase is arbitrary.7,9 Here the Mn\(^{3+}\), Mn\(^{4+}\), and RE sites each break up into two orbits, which are interconnected by inversion. So it is not surprising that this situation is like that of the Tb sites in TMO: the magnitudes of the two related orbits, which according to Mody were unrelated, are now, by virtue of inversion symmetry, fixed to be the same.

III. DISCUSSION

A. Order parameters

It is natural to introduce order parameters because as the temperature is reduced into the ordered phase, the critical eigenvector is nearly temperature-independent except for a change in its normalization, governed by the magnitude of the order parameter. Furthermore, the phase of the complex order parameter is either a free variable or, if it is fixed, it is only fixed by subtle effects of higher-than-quadratic terms in the free energy. So the order parameter describes properly the low-energy sector of the free energy.

Note that our definition of the order parameter is such that if one is given the spin-wave function over all the sublattices it is possible to uniquely determine both the phase and the magnitude of the order parameter, except that it could be multiplied by \( -1 \). (But that indeterminacy is inherent for this order-parameter symmetry.) To make this unique identification from a knowledge of the wave functions, the wave functions must be first put into the canonical form of Tables IV and V. In so doing, the normalization condition has to be obeyed. Then the prefactor will be the desired order parameter. Note that the phase is fixed by having the first and fourth components written in terms of complex conjugates. This type of identification would not be possible for a one-component complex variable.

It should be noted that the order parameter inherits the symmetry of the full wave function. Having the basis functions for \( q \) replaced by \( \Lambda^* \) and \( \lambda \), we obtain the basis functions for the other wave vectors in the star of \( q \). We first obtain the basis functions for \( -q \) and \( -q^* \), i.e., with \( \Lambda \) replaced by \( \lambda^* \) and, for notational convenience, \( s_{u,n} \) replaced by \( t_{u,n} \). However, this is not the basis function we want. We want the particular basis function, which is obtained from that of \( q \) by a symmetry operation—which takes \( q \) into \( q^* \) (Ref. 41) because it is this basis function that results from the actual interaction between spins. In other words, we want to relate \( t_{u,n} \) to \( s_{u,n} \). To do this, we now study the transformation of the spin Fourier transforms.

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We first consider transformation by \(2_\nu\), which takes \(q \rightarrow (q_x, 0, q_z)\) into \(q' = (-q_x, 0, q_z) = -q\), where here and below we use a prime to indicate a quantity after transformation. We have that
\[
S'_\nu(R_\nu, 1) = \rho_{a} S_{\nu}(R_\nu, 4),
\]
(24)
where \(\rho_{a} = \rho_{a} = -1\). We now write this in terms of Fourier components using Eq. (1). The initial position is \(r_i = (X, Y, Z) + \tau_i\) and the final position is \(r_f = (\bar{X}, \bar{Y}, -1, Z) + \tau_i\), which gives \([\eta = \sigma_x(-q) = \sigma_x(q_x)]\) and \(\sigma = \sigma_x(q)\)
\[
\eta' t_{a1} e^{-2\pi i (q_x, 0, q_z) \cdot (X - 1, -Y, -1, Z)} = \rho_{a} \sigma_{a}^{-1} e^{-2\pi i (q_x, 0, q_z) \cdot (X, Y, Z)}.
\]
(25)
So with \(\exp(-2\pi i q_x) = \lambda^2\), we have
\[
\eta' \lambda^2 t_{a1} = \rho_{a} \sigma_{a}^{-1}.
\]
(26)
Similarly,
\[
S'_\nu(R_\nu, 4) = \rho_{a} S_{\nu}(R_\nu, 1),
\]
(27)
with \(r_i = (X, Y, Z) + \tau_i\) and \(r_f = (\bar{X}, \bar{Y}, -1, Z) + \tau_i\), which gives
\[
\eta' t_{a1} e^{-2\pi i (q_x, 0, q_z) \cdot (X - 1, -Y, -1, Z)} = \rho_{a} \sigma_{a} e^{-2\pi i (q_x, 0, q_z) \cdot (X, Y, Z)}.
\]
(28)
so that
\[
\eta' \lambda^2 t_{a1} = \rho_{a} \sigma_{a}.
\]
(29)
Similarly,
\[
S'_\nu(R_\nu, 5) = \rho_{a} S_{\nu}(R_\nu, 5),
\]
(30)
with \(r_i = (X, Y, Z) + \tau_5\) and \(r_f = (\bar{X}, \bar{Y}, Z) + \tau_5\), which is
\[
\eta' t_{a2} e^{-2\pi i (q_x, 0, q_z) \cdot (X - 1, -Y, Z)} = \rho_{a} \sigma_{a} e^{-2\pi i (q_x, 0, q_z) \cdot (X, Y, Z)}.
\]
(31)
so that
\[
\eta' \lambda^2 t_{a2} = \rho_{a} \sigma_{a}.
\]
(32)
Similarly,
\[
S'_\nu(R_\nu, 7) = \rho_{a} S_{\nu}(R_\nu, 7),
\]
(33)
with \(r_i = (X, Y, Z) + \tau_7\) and \(r_f = (\bar{X}, \bar{Y}, -1, Z) + \tau_7\). In using Table IV we must replace \(\lambda\) by \(\lambda^2\) to convert the table for the wave vector \(q'\). Thus Eq. (33) yields
\[
\xi_{a2} \eta' \lambda^2 t_{a2} e^{-2\pi i (q_x, 0, q_z) \cdot (X - Y, -1, Z)} = \rho_{a} \sigma_{a} \lambda^2 \sigma_{a}^{-1} e^{-2\pi i (q_x, 0, q_z) \cdot (X, Y, Z)},
\]
(34)
so that
\[
\eta' \lambda^2 t_{a2} = \rho_{a} \sigma_{a}^{-1}.
\]
(35)
Similarly,
\[
S'_\nu(R_\nu, 9) = \rho_{a} S_{\nu}(R_\nu, 9),
\]
(36)
with \(r_i = (X, Y, Z) + \tau_{12}\), \(r_f = (\bar{X}, \bar{Y}, -1, Z) + \tau_{12}\), which gives
\[
\eta' t_{a3} e^{-2\pi i (q_x, 0, q_z) \cdot (X - 1, -Y, -1, Z)} = \rho_{a} \sigma_{a} \lambda^2 \sigma_{a}^{-1} e^{-2\pi i (q_x, 0, q_z) \cdot (X, Y, Z)},
\]
(37)
so that
\[
\eta' \lambda^2 t_{a3} = \rho_{a} \lambda \sigma_{a}.
\]
(38)
Similarly,
\[
S'_\nu(R_\nu, 12) = \rho_{a} S_{\nu}(R_\nu, 12),
\]
(39)
with \(r_i = (X, Y, Z) + \tau_{12}\), \(r_f = (\bar{X}, \bar{Y}, -1, Z) + \tau_{12}\), which gives
\[
\eta' t_{a2} e^{-2\pi i (q_x, 0, q_z) \cdot (X - 1, -Y, Z)} = \rho_{a} \sigma_{a} \lambda^2 \sigma_{a}^{-1} e^{-2\pi i (q_x, 0, q_z) \cdot (X, Y, Z)},
\]
(40)
so that
\[
\eta' \lambda^2 t_{a2} = \rho_{a} \lambda \sigma_{a}.
\]
(41)
Equations (26), (29), (32), (35), (38), and (41) yield
\[
t_{a1} = \rho_{a} \sigma_{a}^{-1}, \quad t_{a2} = \rho_{a} \sigma_{a}^{-1}, \quad t_{a3} = \Lambda \rho_{a} \sigma_{a}^{-1},
\]
(42)
and
\[
\eta' = \lambda^2 \sigma.
\]
(43)
There is an equivalent solution in which all the transformed quantities are multiplied by \(-1\). This ambiguity is unavoidable because it is inherent in the symmetry of the order parameter. Using Eq. (42) and the fact that the basis functions for \(-q\) are the complex conjugates of those for \(q\), we obtain the results of Table VI. The relations for the basis functions of irrep \(\Gamma_o\) are the same as for \(\Gamma_v\), so Table VI also applies for \(\Gamma_o\).

We now obtain the transformation properties of the order parameter under all the symmetry operations of the space group (except translations). For this discussion it is convenient to introduce an order-parameter vector \(v\) whose components are the various order parameters:
\[
v_1 = \sigma_x(q_x), \quad v_2 = \sigma_x(-q_x), \quad v_3 = \sigma_x(q_z),
\]
\[
v_4 = \sigma_y(q_y), \quad v_5 = \sigma_y(-q_y), \quad v_6 = \sigma_y(-q_z),
\]
\[
v_7 = \sigma_z(-q_z), \quad v_8 = \sigma_z(-q_z).
\]
(44)
The transformation properties of the vector \(v\) are given in Table VII whose construction we now discuss. The row of

| \(q^* = (q_x, 0, q_z)\) | \(s_{a1}\) | \(s_{a2}\) | \(s_{a3}\) |
|--------------------------|---------|---------|---------|
| \(-q^* = (-q_x, 0, q_z)\) | \(\rho_a s_{a1}\) | \(\rho_a s_{a2}\) | \(\Lambda \rho_a s_{a3}\) |
| \(q = (q_x, 0, -q_z)\) | \(\rho_a s_{a1}\) | \(\rho_a s_{a2}\) | \(\Lambda \rho_a s_{a3}\) |
| \(-q^* = (-q_x, 0, -q_z)\) | \(s_{a1}\) | \(s_{a2}\) | \(s_{a3}\) |

TABLE VI. Amplitudes of the basis functions for the irrep \(\Gamma_o\) for the star of \(q\), where \(\rho_o = (-1, -1, 1)\). Here we give the basis functions for sublattices 1, 5, and 9. The remaining amplitudes are found by the appropriate modification of Table IV for the wave vector in question. For the irrep \(\Gamma_o\), replace all the \(s\) by \(us\) and the remaining amplitudes are found by the appropriate modification of Table V for the wave vector in question.
m_{ac} is obtained by using the fact that the basis vector of irrep \( \Gamma_c \) for wave vector \( \mathbf{q} = (q_x, 0, q_z) \) is an eigenvector of \( m_{ac} \) with eigenvalue \( \lambda \). The eigenvalue for irreps \( \Gamma_e \) and \( \Gamma_o \) have opposite signs and changing the sign of the wave vector leads to complex conjugation of the eigenvalue.

We consider next the effect of 2 on the order parameters. In Eq. (43) we found that under 2, the new value of \( v_5 \) is \( \lambda^2 v_1 \). Since the prefactor \( \lambda^2 \) does not depend on \( q_z \) and it was obtained without specifying the irrep, we see that the prefactors in the last four columns of the second row are the same. The prefactors of the first four entries of this row are obtained from the last four entries by complex conjugation.

Next we consider the effect of inversion on the order parameters. This discussion is simplified by having in hand the results of Table VI. Note that \( I \) does not change the orientation of the spin, because spin is a pseudovector. So under \( I \) we have

\[
S'_d(R,1) = S_d(R,4),
\]

where \( r_1 = (X, Y, Z) + \tau_1 \) and \( r_2 = (X-1, Y-1, Z-1) + \tau_1 \), which gives [with \( \gamma = \sigma_c(-\mathbf{q}) \) and \( \sigma' = \sigma_c(\mathbf{q}) \)]

\[
\eta' \sigma'_a e^{\pm i\pi p(x,y,z)} = \eta \sigma_a e^{\pm i\pi p(x,y,z)}
\]

This has to be an equality for all integer \( X, Y, \) and \( Z \). Also \( S'_{a1} = S'_{a1} \) (from Table VI), so we find that

\[
\eta' \lambda^2 \Lambda' = \sigma.
\]

Thus \( \lambda^2 \Lambda v_1 \) is the entry under \( v_5 \) in the third row. Having this result, one can construct the other entries in this row by noting the dependence on \( q_z \) and \( q_x \).

The other rows of Table VII are found by using the multiplicative properties,

\[
m_{ab} = 2, \quad m_a = m_{ab} m_{ab},
\]

\[
m_{bc} = 2, \quad m_b = m_{bc} I.
\]

IV. MAGNETOELECTRIC INTERACTION

Now we discuss the form of the ME coupling in the phases with \( q_y \neq 1/2 \), i.e., in the \( (1,0,1) \) and \( (1,0,c) \) phases. In the first subsection we will discuss the trilinear ME interaction which involves the lowest number (two) of magnetic order parameters. In succeeding subsections we will discuss higher-order ME interactions which involve a product of four magnetic order parameters. These higher-order terms yield components of the spontaneous polarization, which are allowed by symmetry but are not present in the trilinear interaction. However, these higher-order terms are probably small for two reasons. First, in the IC phases, which occur at high temperatures near the paramagnetic phase, the order parameters are small. Second, most microscopic models of the ME interaction treat (within lowest-order perturbation theory) a trilinear Hamiltonian involving two spin variables and one displacement variable. However, to obtain higher-order phenomenological interactions probably involves processes of higher order in some small parameter such as \( t/U \) or \( \lambda/k_B \), where \( t \) is a hopping matrix element, \( \lambda \) is the spin-orbit constant, and \( U \) is a Coulomb interaction.

A. Trilinear ME coupling

Initially we will consider the lowest-order (trilinear) ME coupling. We start by considering the case when only the wave vectors \( \pm \mathbf{q}_y = \pm (1/2 - \delta, 0, 1/4 + \epsilon) \), where \( \epsilon \) may or may not be zero, are involved. The interaction of lowest order in the magnetic order parameters, which conserves wave vector and is time-reversal invariant is of the form

\[
V_{int} = \sum_{\gamma \in \Gamma} c_{\gamma a} \sigma_a(\mathbf{q}_y) \sigma_b(-\mathbf{q}_y) P_{\gamma y},
\]

where \( a \) and \( b \) assume the values \( e \) and \( o \), \( \mathbf{P} \) is the spontaneous electric polarization and \( \gamma \) labels the component. Using Table VII, one sees that terms in \( V_{int} \) with \( a=b \) are not allowed by inversion invariance. If one has only a single irrep present, then one can always redefine the location of the origin so as to have inversion symmetry with respect to that new origin and hence such a phase cannot exhibit magnetically induced ferroelectricity. If both irreps are present, then we write,
\[ V_{\text{int}} = \sum_{\gamma} \left[ c_{\gamma} \sigma_{\gamma}(q_{\gamma}) \sigma_{\gamma}(-q_{\gamma}) + c_{\gamma}^* \sigma_{\gamma}(-q_{\gamma}) \sigma_{\gamma}(q_{\gamma}) \right] P_{\gamma}, \]

(50)

and inversion invariance forces \( c_{\gamma} \) to be pure imaginary: \( c_{\gamma} = i r_\gamma \), where \( r_\gamma \) is real. Then,

\[ V_{\text{int}} = i \sum_{\gamma} r_\gamma \left[ \sigma_{\gamma}(q_{\gamma}) \sigma_{\gamma}(q_{\gamma})^* - \sigma_{\gamma}(q_{\gamma})^* \sigma_{\gamma}(q_{\gamma}) \right] P_{\gamma}. \]

(51)

From Table VII one sees that the square bracket in this equation changes sign under \( m_{\text{ac}} \), so \( P_{\gamma} \) must also change sign under \( m_{\text{ac}} \) in order for \( V_{\text{int}} \) to be invariant under \( m_{\text{ac}} \). Thus \( c_{\gamma} \) can be nonzero only for \( \gamma = b \), as is observed. If we set \( \sigma_{\gamma}(q_{\gamma}) = |\sigma_{\gamma}(q_{\gamma})| \exp(i \theta_{\gamma}) \), then we have the result,

\[ V_{\text{int}} = 2 r \sin(\phi_{b} - \phi_{c}) P_{c} \sigma_{b}(q_{c}) \sigma_{b}(q_{c}). \]

(52)

However, this is not the whole story because we must include the terms involving the other wave vectors in the star of \( q_{\gamma} \). Indeed it is possible that in the highest temperature paraelectric IC phase there is a simultaneous condensation of the order parameters of all wave vectors \( q_{\gamma} \) (Ref. 24.).

Since we have already incorporated the effect of \( \mathcal{I} \) and \( m_{\text{ac}} \), it only remains to use \( \gamma \) to obtain the other terms which make up the invariant interaction. To do that we use the results given in Table VII, which give \( 2 \alpha_{\gamma}(q_{\gamma}) = \lambda^{2} \sigma_{\gamma}(q_{\gamma})^{*} \), for \( n = 0 \) or \( e \), and, of course, \( 2 \sigma_{b} = -P_{b} \). Therefore we obtain the complete result for \( V_{\text{int}} \),

\[ V_{\text{int}} = i r \sum_{q, p = \pm} \left[ \sigma_{p}(q_{p}) \sigma_{p}(q_{p})^* \sigma_{n}(q_{n})^* - \sigma_{p}(q_{p})^* \sigma_{p}(q_{p}) \sigma_{n}(q_{n})^* \right] P_{b}. \]

(53)

At this order one needs the simultaneous presence of both the \( e \) and \( o \) irreps to have ferroelectricity. (However, below we find that a polarization along \( e \) can be induced by Umklapp ME interactions by a single irrep. But this scenario is unlikely.\textsuperscript{24}) Note that from this interaction the spontaneous polarization \( P \) is aligned along the \( b \) axis irrespective of which wave vector condenses. However, the \( \gamma \) of \( P \) depends on how the signs of the order parameters are chosen (i.e. how symmetry is broken) when \( \sigma_{e} \) and/or \( \sigma_{o} \) order. Furthermore, within the trilinear ME interaction, even if both irreps are present, if they are in phase \([i.e. \text{if} \ (\phi_{e} - \phi_{o})/\pi \text{ is an integer}]\), then a spontaneous polarization does not arise.\textsuperscript{6,9}

When cooling from the paramagnetic phase into the (\( I, I, 0 \)) phase, one expects only a single irrep.\textsuperscript{23} Upon further cooling, systems that follow the scenario of Fig. 1(a) condense a second irrep and thereby\textsuperscript{24} induce ferroelectricity. When we have both irreps of the wave vector present, their relative phase \([\phi(\Gamma_{\alpha}) - \phi(\Gamma_{\alpha})]/\pi \) is usually fixed by fourth-order terms in the magnetic free energy to be nonintegral,\textsuperscript{9,24} in which case no choice of origin will simultaneously make both irreps inversion invariant. This situation is reminiscent of TMO (Ref. 7) or NVO (Ref. 6) and was previously noted in connection with second harmonic generation.\textsuperscript{47} Finally, from Eq. (53) one sees that even when irreps are present, if the order parameters of the two wave vectors \( q_{e} \) and \( q_{o} \) have the same magnitude, the spontaneous polarization could vanish. (This probably corresponds to the spirals of the two wave vectors having opposite helicity.\textsuperscript{48})

### B. Higher-order ME coupling

Sergienko et al.\textsuperscript{49} have pointed out the existence of higher-order terms in the ME coupling, in particular terms quartic in the order parameters. As they indicate, these terms have the potential to induce a spontaneous polarization in direction(s) different from those of the trilinear ME coupling. For the so-called 113 compounds (such as HoMnO\textsubscript{3}, which they consider), these terms usually do not come into play in view of the anisotropy of the terms in the purely magnetic free energy, which are quartic in the order parameters. (See citation 28 of Ref. 24.) Here the situation is different: the quartic order-parameter anisotropy is much more complicated for the 125’s, so that these higher-order ME terms may come into play, although, as mentioned, their effect may be small. We start by first considering terms, which strictly conserve wave vector. Later, we will investigate the corresponding Umklapp terms, which only conserve wave vector to within a nonzero reciprocal lattice vector.

To construct this ME interaction, we need to construct quartic terms in the order parameters, which transform like a vector. To avoid complications, it is simplest to use the following approach suggested by Mukamel.\textsuperscript{50} The idea is to first find the number of such vector representations by using the character tables to determine how many times each vector irrep is contained in the reducible representation formed by the basis functions of all fourth-order terms. The 34 fourth-order terms are the nine distinct terms of the form,

\[ \sigma_{k}(q_{k}) \sigma_{l}(q_{l}) \sigma_{m}(q_{m}) \sigma_{n}(q_{n})^{*}, \]

(54)

the nine distinct terms of the form,

\[ \sigma_{k}(q_{k}) \sigma_{l}(q_{l}) \sigma_{m}(q_{m})^{*} \sigma_{n}(q_{n})^{*}, \]

(55)

and the 16 terms of the form,

\[ \sigma_{k}(q_{k}) \sigma_{l}(q_{l}) \sigma_{m}(q_{m})^{*} \sigma_{n}(q_{n})^{*}, \]

(56)

where \( k, l, m, \) and \( n \) assume the values \( o \) and \( e \). The character table for the irreps of the point group of Pbam and that for the representation \( \Gamma \) generated by the quartic terms are given in Table VIII. The characters of the representation \( \Gamma \) for each operator are obtained by taking the trace of the operator in the 34 dimensional vector space under consideration.

Then, we find the number of times \( n(\Gamma_{\alpha}) \) that \( \Gamma_{\alpha} \) is contained in \( \Gamma \) is given by the scalar products of the character vectors given in Table VIII as\textsuperscript{51}

\[ n(\Gamma_{s}) = (34 - 4 + 2 + 4 - 10 + 4 - 10 - 4)/8 = 2, \]

\[ n(\Gamma_{s}) = (34 + 4 - 2 + 4 - 10 - 4 + 10 - 4)/8 = 4, \]

\[ n(\Gamma_{s}) = (34 + 4 - 2 - 4 - 10 - 4 + 10 + 4)/8 = 2. \]

(57)

We find the two \( x \)-like functions to be

\[ \phi_{s, 1} = v_{x}^{2} v_{z}^{2} + v_{y}^{2} v_{z}^{2} - v_{x}^{2} v_{y}^{2} - v_{y}^{2} v_{y}^{2} \]

\[ = [\sigma_{o}(q_{o}) \sigma_{o}(q_{o})^{*}]^{2} + [\sigma_{o}(q_{o}) \sigma_{o}(q_{o})^{*}]^{2} \]

\[ - [\sigma_{e}(q_{e}) \sigma_{e}(q_{e})^{*}]^{2} - [\sigma_{e}(q_{e}) \sigma_{e}(q_{e})^{*}]^{2}, \]

(58)
TABLE VIII. Character table for the point group for the 125’s. \( \Gamma_{1,2} \) where \( \alpha=x, y, z \) are vector irreps. The next to last row gives the characters of the 34-dimensional reducible representation \( \Gamma \) and the last row gives those of the 18-dimensional reducible representation, \( \Gamma_U \).

| \( \Gamma \) | \( E \) | \( m_{bc} \) | \( m_{ac} \) | \( m_{ab} \) | \( I \) | \( 2_a \) | \( 2_b \) | \( 2_c \) |
|---|---|---|---|---|---|---|---|---|
| \( \Gamma_1 \) | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| \( \Gamma_4 \) | 1 | -1 | 1 | 1 | -1 | 1 | -1 | -1 |
| \( \Gamma_y \) | 1 | 1 | -1 | 1 | -1 | 1 | -1 | 1 |
| \( \Gamma_z \) | 1 | 1 | -1 | -1 | -1 | 1 | 1 | 1 |
| \( \Gamma_{yz} \) | 1 | 1 | -1 | -1 | -1 | 1 | 1 | 1 |
| \( \Gamma_{xy} \) | 1 | -1 | 1 | -1 | 1 | -1 | -1 | 1 |
| \( \Gamma_U \) | 18 | 6 | 2 | 0 | 0 | 0 | 0 | 6 |

\[
\phi_{x,2} = v_3v_2y_6 - v_1v_2y_5 = \sigma_5(q_4)\sigma_5(q_4)\sigma_5(q_4)^* \sigma_5(q_4)^* \\
- \sigma_5(q_4)\sigma_5(q_4)\sigma_5(q_4)^* \sigma_5(q_4)^*.
\]

The above are easy to check, at least apart from the complex phase factors, which always combine to give unity. To be invariant under \( m_{ac} \), we must have an even number of \( o \)'s and an even number of \( e \)'s. Note that to be odd under \( I \), the form must be odd under complex conjugation. To be even under \( m_{ab} \), the form must be even under interchange of \( q_e \) and \( q_o \).

We find the four \( y \)-like functions to be

\[
\phi_{x,1} = v_1v_2y_3 + v_2y_3v_7 - v_1v_2v_5 - v_1v_2v_7 \\
= \left[ \sigma_5(q_4)^2[\sigma_5(q_4)\sigma_5(q_4)^* - \sigma_5(q_4)\sigma_5(q_4)^*] \right] \\
+ \left[ \sigma_5(q_4)^2[\sigma_5(q_4)\sigma_5(q_4)^* - \sigma_5(q_4)\sigma_5(q_4)^*] \right] \\
\phi_{x,2} = v_2v_3v_7 + v_3v_7v_8 - v_2v_3v_8 - v_2v_3v_7 \\
= \left[ \sigma_5(q_4)^2[\sigma_5(q_4)\sigma_5(q_4)^* - \sigma_5(q_4)\sigma_5(q_4)^*] \right] \\
+ \left[ \sigma_5(q_4)^2[\sigma_5(q_4)\sigma_5(q_4)^* - \sigma_5(q_4)\sigma_5(q_4)^*] \right] \\
\phi_{x,3} = v_1v_2[v_3y_5 - v_3y_7] \\
= \left[ \sigma_5(q_4)^2[\sigma_5(q_4)\sigma_5(q_4)^* - \sigma_5(q_4)\sigma_5(q_4)^*] \right] \\
+ \left[ \sigma_5(q_4)^2[\sigma_5(q_4)\sigma_5(q_4)^* - \sigma_5(q_4)\sigma_5(q_4)^*] \right] \\
\phi_{x,4} = v_1v_2[v_3y_5 - v_3y_7] + v_2v_3[v_3y_5 - v_3y_7] \\
= \left[ \sigma_5(q_4)^2[\sigma_5(q_4)\sigma_5(q_4)^* - \sigma_5(q_4)\sigma_5(q_4)^*] \right] \\
+ \left[ \sigma_5(q_4)^2[\sigma_5(q_4)\sigma_5(q_4)^* - \sigma_5(q_4)\sigma_5(q_4)^*] \right].
\]

These can be checked similarly. To be odd under \( m_{ac} \), the \( e \)'s and the \( o \)'s must both appear an odd number of times.

We find the two \( z \)-like functions to be

\[
\phi_{z,1} = v_3v_2v_6 - v_1v_2v_5 = \sigma_5(q_4)\sigma_5(q_4)\sigma_5(q_4)^* \sigma_5(q_4)^* \\
- \sigma_5(q_4)\sigma_5(q_4)\sigma_5(q_4)^* \sigma_5(q_4)^*.
\]

The ME interaction of order \( \sigma^2 \) is written as

\[
V_{ME}^{(4)} = \sum_{n, \gamma} c_{n, \gamma} \phi_{n, \gamma} P_{\gamma},
\]

where the \( c_{n, \gamma} \) are unknown coefficients. Now we discuss how \( V_{ME}^{(4)} \) affects the ME phase diagrams. First of all, if there is only a single irrep, either an \( e \) or an \( o \), then this interaction vanishes. So in the \((I, 0, I)\) phase, which has only a single irrep,\(^{23}\) we still have no spontaneous polarization. As mentioned in the introduction to this section, this higher-order ME interaction may be small and difficult to observe.

C. Umklapp ME interactions

Now we consider Umklapp terms relevant to the phase, in which \( q_z = 1/4 \) but \( q_y \neq 1/2 \). Here the reducible representation \( \Gamma_U \) is generated by the nine terms of the form,

\[
\sigma_5(q_4)\sigma_5(q_4)\sigma_5(q_4)^* \sigma_5(q_4)^* \delta_{qz,1},
\]

and the nine terms of the form,

\[
\sigma_5(q_4)\sigma_5(q_4)\sigma_5(q_4)^* \sigma_5(q_4)^* \delta_{qz,1}.
\]

The characters for \( \Gamma_U \) are given in Table VIII. Then, we find the number of times \( n(\Gamma_0) \) where \( \Gamma_0 \) is contained in \( \Gamma_U \) to be\(^{31}\)

\[
n(\Gamma_0) = (18 + 6 + 2 + 0 - 0 - 0 - 0 - 6)/8 = 1,
\]

\[
n(\Gamma_0) = (18 + 6 - 2 + 0 - 0 - 0 - 0 - 6)/8 = 2,
\]

\[
n(\Gamma_0) = (18 + 6 + 2 - 0 - 0 - 0 + 0 + 6)/8 = 4.
\]

We find the \( x \)-like function to be

\[
\phi_{x,2} = v_3v_2y_6v_8 - v_1v_2y_5v_7 = \sigma_5(q_4)\sigma_5(q_4)\sigma_5(q_4)^* \sigma_5(q_4)^* \\
- \sigma_5(q_4)^* \sigma_5(q_4)^* \sigma_5(q_4)^* \sigma_5(q_4)^*.
\]
the two y-like functions to be

$$\psi_{y,1} = v_1 v_5 v_6^2 + v_2 v_7 v_8 - v_2 v_6 v_7 - v_1 v_6 v_8 = \sigma_y(q_1)\sigma_y(q_2)^* - \sigma_y(q_1)\sigma_y(q_2) + \sigma_y(q_1)\sigma_y(q_2)^* - \sigma_y(q_1)\sigma_y(q_2)^*,$$

$$\psi_{y,2} = v_2 v_4 v_5 - v_2 v_7 v_8 = \sigma_y(q_1)\sigma_y(q_2)^* - \sigma_y(q_1)\sigma_y(q_2)^* + \sigma_y(q_1)\sigma_y(q_2)^* - \sigma_y(q_1)\sigma_y(q_2),$$

and the four z-like functions to be

$$\psi_{z,1} = v_1 v_5 v_6^2 - v_2 v_7 v_8 = \sigma_z(q_1)\sigma_z(q_2)^* - \sigma_z(q_1)\sigma_z(q_2) + \sigma_z(q_1)\sigma_z(q_2)^* - \sigma_z(q_1)\sigma_z(q_2)^*,$$

$$\psi_{z,2} = v_2 v_4 v_5 - v_2 v_7 v_8 = \sigma_z(q_1)\sigma_z(q_2)^* - \sigma_z(q_1)\sigma_z(q_2)^* + \sigma_z(q_1)\sigma_z(q_2)^* - \sigma_z(q_1)\sigma_z(q_2),$$

The transformation properties of the $\psi_{n,n}$ can be checked just as we did for the $\phi_{n,n}$. The Umklapp ME interaction of order $\sigma^3$ is written as

$$V_{\text{ME,U}}^{(4)} = \delta_{q_1,1} \sum_{n,y} c_{n,y}^r \psi_{n,n} P_y,$$

where the $c_{n,y}^r$ are unknown coefficients.

Clearly this interaction is only operative when $q_z$ is locked to the CM value $q_z = 1/2$. This is therefore a generalization of the term introduced by Betouras et al.\cite{24} but here we give the first analysis of the symmetry of this interaction. It is interesting to note that this interaction can induce a spontaneous polarization along the z axis even when only a single irrep is present. (Inspection of $\psi_{z,1}$ and $\psi_{z,2}$ indicates that this requires simultaneous condensation of order at wave vectors $q_z$. However, as mentioned in the introduction to this section, this higher-order ME interactions may be small and difficult to observe.

V. COMPATIBILITY RELATIONS

A first step to constructing a generic phase diagram for the 125’s (Ref. 24) is to understand how the wave functions behave near the phase transition between the phase with $q_z \neq 1/2$ and that for which $q_z = 1/2$. In Fig. 2 we show a simplified version of this phase diagram for fixed $q_z$. (However, to compare with experiment, the diagram for fixed $q_z$ is more relevant.)\cite{24} To avoid confusion, we introduce a control parameter $P$ such that when $P = P_c$ the wave vector, which minimizes the inverse susceptibility near the ordering transition, has $q_z = 1/2$, but when $P$ deviates slightly from this critical value the $x$ component of the selected wave vector is not exactly equal to $1/2$. (We refer to the point $P = P_c$ as “the multicritical point” because to reach this point requires not only fixing the temperature to be at the ordering transition, but also, as shown in Fig. 2, one must fix $P = P_c$ by varying some other parameter, such as the pressure.) As we have seen, as the temperature is lowered into the ordered phase when $P \neq P_c$, one of the 1D irreps $\Gamma_1$ or $\Gamma_2$ at $q_z = 1/2$ condenses, whereas exactly at $P = P_c$ one condenses into a phase with $q_z = 1/2$, which has only a single 2D irrep.\cite{33} Accordingly, we now study the compatibility relation, which must relate the wave functions of these two phases in the limit as we approach the multicritical point $M$ for which $P = P_c$. Experimentally, the phase transition between the phase with $q_z = 1/2$ and that having $q_z \neq 1/2$ has only been observed for $q_z = 1/4$. However, since the symmetry of the phases for $q_z = 1/4$ is not different from that for $q_z = 1/2$, we will leave $q_z$ as a free parameter, which we consider to be incommensurate. Although the actual phase transition between the $q_z = 1/2$ phase and the phase with $q_z \neq 1/2$ must be discontinuous, the discontinuity vanishes in the limit when the multicritical point $M$ in Fig. 2 is approached. In this limit, one may consider the transition to be continuous, and therefore it must be possible to express each basis function of the two irreps of the $q_z \neq 1/2$ phase as a linear combination of the basis functions of the 2D irrep of the phase having $q_z = 1/2$. We do this explicitly in order to find the relation between the order parameters of the two phases. This relation will be perturbatively modified as one goes deeper into the ordered phase.

A. Wave functions near the multicritical point

In Table IX we record the wave functions allowed by symmetry for the $q_z = 1/2$ state, based on Table XVI of Ref. 9, which are modified in several ways. First of all, one has to include the corrections to the wave functions on sublattices 9–12, as described in an erratum.\cite{9} Second, we translate all sites by $0, 0, 1/2$. (This operation has no effect because the induced change of phase can be absorbed into the order parameters.) Third, we renumber the sublattices to make their
TABLE IX. Normalized spin functions (i.e., Fourier coefficients) within the unit cell of, e.g., TbMn$_2$O$_4$ for wave vector $(\frac{1}{2}, 0, q)$. Here the $r_{x_1}$, $r_{y_1}$, and $r_{z_1}$ are real, the $s$ are complex, and $A = \exp(2\pi i q)$ where $q_x$ is in rlu’s. The $x$, $y$, and $z$ components of each Fourier vector are listed in the corresponding entry. The actual spin structure is a linear combination, $\sigma_1$ times the first column plus $\sigma_2$ times the second column, where the $\sigma$ are complex order parameters and the entries in each column are normalized so that the sum of their absolute squares is unity.

| Spin | $\sigma_1$ | $\sigma_2$ | Spin | $\sigma_1$ | $\sigma_2$ |
|------|------------|------------|------|------------|------------|
| $S(q, 1)$ | $r_{1x}$ | $r_{2y}$ | $r_{1y}$ | $r_{2y}$ | $r_{1z}$ | $r_{2z}$ |
| $S(q, 2)$ | $r_{2x}$ | $-r_{1x}$ | $-r_{2y}$ | $r_{1y}$ | $-r_{1z}$ | $r_{2z}$ |
| $S(q, 3)$ | $r_{1x}$ | $-r_{2x}$ | $-r_{1y}$ | $r_{2y}$ | $-r_{1z}$ | $r_{2z}$ |
| $S(q, 4)$ | $-r_{2y}$ | $r_{1y}$ | $-r_{2y}$ | $r_{1y}$ | $-r_{1z}$ | $r_{2z}$ |
| $S(q, 5)$ | $z_x$ | $-z_x$ | $z_y$ | $z_y$ | $z_z$ | $-z_z$ |
| $S(q, 6)$ | $z_x$ | $z_x$ | $z_y$ | $z_y$ | $z_z$ | $z_z$ |
| $S(q, 7)$ | $z_x$ | $z_x$ | $z_y$ | $z_y$ | $z_z$ | $z_z$ |
| $S(q, 8)$ | $z_x$ | $z_x$ | $z_y$ | $z_y$ | $z_z$ | $z_z$ |
| $S(q, 9)$ | $r_{5x}A^{1/2}$ | $r_{6x}A^{1/2}$ | $r_{5y}A^{1/2}$ | $r_{6y}A^{1/2}$ | $r_{5z}A^{1/2}$ | $r_{6z}A^{1/2}$ |
| $S(q, 10)$ | $r_{6x}A^{1/2}$ | $-r_{5x}A^{1/2}$ | $r_{6y}A^{1/2}$ | $-r_{5y}A^{1/2}$ | $r_{6z}A^{1/2}$ | $-r_{5z}A^{1/2}$ |
| $S(q, 11)$ | $r_{5x}A^{1/2}$ | $-r_{5x}A^{1/2}$ | $r_{5y}A^{1/2}$ | $-r_{5y}A^{1/2}$ | $r_{5z}A^{1/2}$ | $-r_{5z}A^{1/2}$ |
| $S(q, 12)$ | $-r_{5x}A^{1/2}$ | $-r_{5x}A^{1/2}$ | $-r_{5y}A^{1/2}$ | $-r_{5y}A^{1/2}$ | $-r_{5z}A^{1/2}$ | $-r_{5z}A^{1/2}$ |

Near the multicritical point $M$ the critical spin-wave function $\Psi_{q_1=1/2}$ (for a fixed value of $q_z$ and $q_x=1/2$) is a linear combination of $\sigma_1$ times the basis functions of the first column of Table IX plus $\sigma_2$ times the basis function of the second column of Table IX. Alternatively, near the multicritical point $M$ for $q_z \neq 1/2$ phase, this spin-wave function can be formed within the space in which the two 1D irreps, $\Gamma_e$ and $\Gamma_o$, are considered degenerate for the fixed value of $q_z$. In this limit the wave function $\Psi_{q_1=1/2}$ of the 1D irrep is given by a linear combination of the basis functions associated with the four-order parameters $\sigma^z_e = \lim_{\delta \to 0} \sigma^z_e(\pm 1/2 - \delta, 0, q_z)$, where $s$ is $e$ or $o$. These basis functions are given in Tables IV and V. Equating $\Psi_{q_1=1/2}$ and $\Psi_{q_1=1/2}$ gives, with, as before, $\xi_o=(-1, 1, -1)$ and $\rho_o=(-1, -1, 1),$
The sign of $k_x$ (in view of the existence of the symmetry element $m_h$). Thus the two lowest branches in the eigenvalue spectrum of the inverse susceptibility as a function of $Q_x$ are as shown in Fig. 3.

Next consider allowed terms, which are linear in $y$ but have an unspecified dependence on $k_x$. These will give

$$\chi^{-1} = \begin{bmatrix} \tau + bk_x^2 & c(k_x)y & d(k_x)y \\ d(k_x)y & \tau + bk_x^2 + e(k_x)y \end{bmatrix},$$

where $c(k_x)$ and $e(k_x)$ are real and $\tau=a(T-T_c)$. For the spectrum to be the same for both signs of $k_x$, $c(k_x)+e(k_x)$ must be an even function of $k_x$. The term in $[c(k_x)+e(k_x)]$ independent of $k_x$ leads to an allowed dependence of $T_c$ on $y$ and the term of order $k_x^2$ leads to an allowed dependence of the coefficient $b$ on $y$, so, in effect, up to order $k_x^2$, we have

$$\chi^{-1} = \begin{bmatrix} \tau + bk_x^2 + c'yk_x & d(k_x)y \\ d(k_x)y & \tau + bk_x^2 - c'yk_x \end{bmatrix},$$

where now $\tau$ and $b$ have an allowed, but unimportant, dependence on $y$. Now consider the dependence of $d(k_x)$ on $k_x$. Suppose that $d(k_x)$ were nonzero for $k_x=0$. This would imply that the minimum in the inverse susceptibility occurred for $k_x=0$, but that the eigenvalues were not degenerate. This contradicts group theory. So the generic case is that $d(k_x)=\beta k_x + O(k_x^3)$. Then the two eigenvalues are

$$\lambda_\pm = \tau + bk_x^2 \pm yk_x\sqrt{c'^2 + \beta^2}.$$  

This leads to two parabolic branches of the inverse susceptibility with minima symmetrically displaced away from $Q_x=1/2$ by an amount linear in $P-P_c$, as shown in Fig. 4. As shown there, the left parabola at $Q_x=q^+$ is associated with $\Gamma_e$ and is parametrized by the $s$‘s and the right parabola at $Q_x=q^+$ is associated with $\Gamma_o$ and is parametrized by the $u$‘s. The corresponding basis functions are given explicitly in Tables IV and V. However the basis functions for $\Gamma_o$ and $\Gamma_e$ at $q^+$ are related, respectively, to $\Gamma_o$ and $\Gamma_e$ at $q^-$ according to Table VI and this is indicated in Fig. 4. These eigenfunctions of the inverse susceptibility depend on wave vector, of course. But as $P\to P_c$, the two parabolas come into coincidence with their minimum at $Q_x=1/2$, and the points governed by $\sigma_x$ and $\sigma_o$ on the same parabola approach one another. Then in this limit, by continuity on the same parabola we obtain

$$u_{a,1} = \rho_o \sigma_{a,1}, \quad u_{a,2} = \rho_o \sigma_{a,2}, \quad u_{a,3} = \rho_o \Lambda \sigma_{a,3}.$$  

It should be remarked, that this multicritical point is not a Lifshitz point. At a Lifshitz point the coefficient of $k_x^2$ in the inverse susceptibility vanishes. Here, in the generic case, this

$$z_{a1}(-\rho_1 \sigma_1 + \sigma_2) = i \xi_{a1} \sigma_a \tau_{a,2} + (-i \xi_{a2}) \sigma_a \tau_{a,2} + (-i \xi_{a3}) \sigma_a \rho_a \tau_{a,2} + (i \xi_{a4}) \sigma_a \rho_a \tau_{a,2},$$

$$-\xi_{a1} \sigma_a (\sigma_1 + \rho_a \sigma_2) = \sigma_a \tau_{a,2} + \sigma_a \tau_{a,2} + \sigma_a \tau_{a,2} + \sigma_a \rho_a \tau_{a,2},$$

$$(\sigma_x \tau_{a,2} + \sigma_x \tau_{a,2}) \Lambda^{1/2} = \sigma_x \tau_{a,2} + \sigma_x \tau_{a,2} + \sigma_x \Lambda \rho_a \tau_{a,2} + \sigma_x \rho_a \tau_{a,2},$$

$$(\sigma_x \tau_{a,2} + \sigma_x \tau_{a,2}) \Lambda^{1/2} = \sigma_x \tau_{a,2} + \sigma_x \tau_{a,2} + \sigma_x \Lambda \rho_a \tau_{a,2} + \sigma_x \rho_a \tau_{a,2},$$

$$(\sigma_x \tau_{a,2} + \sigma_x \tau_{a,2}) \Lambda^{1/2} = \sigma_x \tau_{a,2} + \sigma_x \tau_{a,2} + \sigma_x \Lambda \rho_a \tau_{a,2} + \sigma_x \rho_a \tau_{a,2},$$

$$\xi_{a1} \rho_a (\sigma_x \tau_{a,2} + \sigma_x \tau_{a,2}) \Lambda^{1/2} = \Lambda (i \xi_{a1} \sigma_a \tau_{a,2} + \Lambda (-i \xi_{a2}) \sigma_a \tau_{a,2} + (i \xi_{a2}) \rho_a \sigma_a \tau_{a,2} + (i \xi_{a4}) \rho_a \sigma_a \tau_{a,2},$$

$$\rho_a (\sigma_x \tau_{a,2} + \sigma_x \tau_{a,2}) \Lambda^{1/2} = \Lambda \sigma_x \tau_{a,2} + \Lambda \sigma_x \tau_{a,2} + \sigma_x \rho_a \tau_{a,2} + \sigma_x \rho_a \tau_{a,2},$$

where $\sigma_a^x = \lim_{x \to a} \sigma_a^x \pm (1/2 - \delta, 0, q_a),$ where $s$ is $e$ or $o$. \n
B. Symmetry of the multicritical point

From the above equations we expect to obtain a relation between the order parameters of the phase with $q_x=1/2$ and that with $q_x \neq 1/2$ arbitrarily close to the multicritical point $M$. Presumably, giving the values of $\sigma_x^+$ and $\sigma_x^-$ will determine the values of $\sigma_1$ and $\sigma_2$, but having the values of $\sigma_1$ and $\sigma_2$ we cannot expect to determine the four parameters $\sigma_x^+$ and $\sigma_x^-$. Accordingly, we now study the basis functions for $\Gamma_e$ and $\Gamma_o$ and show that they are related in the limit when $q_x \to 1/2$. To see this, we will analyze the behavior of the inverse susceptibility as a function of $Q_x$, the $x$ component of the wave vector when the temperature is just above the temperature at which magnetic order appears, and for $P$ close to the critical value $P_c$ at which the minimum of the inverse susceptibility as a function of $Q_x$ occurs for $Q_x=1/2$. Note that the inverse susceptibility has 36 branches, each one corresponding to an eigenvalue of the inverse susceptibility matrix. Here we need to consider only the two lowest branches of the inverse susceptibility. These lowest two eigenvalues arise out of a $2 \times 2$ submatrix, which we now analyze for $Q_x=1/2 + k_x$ and $P=P_c+y$ for small $k_x$ and $y$. For $y=0$ this submatrix is of the form

$$\chi^{-1} = \begin{bmatrix} a(T-T_c) + bk_x^2 & 0 \\ 0 & a(T-T_c) + bk_x^2 \end{bmatrix},$$

where $k_x=Q_x-1/2$, $a$ and $b$ are constants, and $T_c$ is the temperature at which order first develops. Here and below we work only to order $k_x^2$. This form is dictated by the fact that the inverse susceptibility has to be twofold degenerate, have its minima at $k_x=0$, and the spectrum has to be independent
FIG. 4. (Color online) The two lowest branches of eigenvalues of $\chi^{-1}(q)$ with their wave functions indicated. Note that the labels $e$ and $o$ refer to the eigenvalues rather than the branch of the spectrum. We assume that the wave functions at $q^*$ for irreps $\Gamma_e$ and $\Gamma_o$ are given in terms of $s_n$ and $u_n$, respectively, as listed in Tables IV and V, respectively. Here $s_n = s_{n,r}$, $u_n = u_{n,o}$, and $\rho = \rho_o$. Then the wave functions at $q = q^*$ are obtained in terms of those at $q = q^*$ according to Table VI. In general, the $o$ and $e$ wave functions are unrelated. However, as $P \rightarrow P$ the $q^* \rightarrow 0$, and the two parabolas come into coincidence. In this situation the points corresponding to $\sigma_e$ and $\sigma_o$ come into coincidence. Therefore by continuity on either the right-hand or the left-hand parabola the $\sigma_e$ and $\sigma_o$ wave function on the same parabola become equal, leading to Eq. (85).

coefficient is nonzero, but the coefficient of $k_s$, which here is allowed because of the double degeneracy, vanishes. Furthermore, the Lifshitz point separates a regime of CM order from that of IC order. Here CM order (at the paramagnetic phase boundary) only occurs at a point (where the coefficient of $k_s$ changes sign thereby exchanging the instabilities of the two 1D irreps).

C. Compatibility equations

Using the relation between the $u$'s and the $s$'s, we see that Eqs. (69)–(80) become

$$\sigma_1^o r_{1,a} + \sigma_2^o r_{2,a} = \sigma^o s_{a,1} + \sigma^o \rho_o s_{a,1},$$
(86)

$$\sigma_1^o r_{2,a} - \sigma_2^o r_{1,a} = i \sigma^o s_{a,1} - i \rho_o \sigma^o s_{a,1},$$
(87)

$$\sigma_1^o r_{1,a} - \sigma_2^o r_{2,a} = i \rho_o \sigma^o s_{a,1} - i \sigma^o s_{a,1},$$
(88)

$$\sigma_1^o r_{2,a} + \sigma_2^o r_{1,a} = \rho_o \sigma^o s_{a,1} + \sigma^o s_{a,1},$$
(89)

$$\gamma_1'(\sigma_1^o + \rho_o \sigma_o^o) = (\rho_o \sigma^o + \sigma^o) s_{a,2},$$
(90)

$$\gamma_1'(\sigma_1^o - \rho_o \sigma_o^o) = (i \rho_o \sigma^o - i \sigma^o) s_{a,2},$$
(91)

$$\gamma_o^o(\sigma_1^o - \rho_o \sigma_o^o) = (-i \rho_o \sigma^o - i \sigma^o) s_{a,2},$$
(92)

$$\gamma_o^o(\sigma_1^o + \rho_o \sigma_o^o) = (-i \rho_o \sigma^o + i \sigma^o) s_{a,2},$$
(93)

$$\sigma_1^o r_{5,a} + \sigma_2^o r_{6,a} = \sigma^o s_{a,3} \Lambda^{1/2} + \sigma^o \Lambda^{1/2} \rho_o s_{a,3},$$
(94)

$$\sigma_1^o r_{6,a} - \sigma_2^o r_{5,a} = i \sigma^o s_{a,3} \Lambda^{1/2} - i \Lambda^{1/2} \rho_o \sigma^o s_{a,3},$$
(95)

$$\sigma_1^o r_{5,a} + \sigma_2^o r_{6,a} = \sigma^o s_{a,3} \Lambda^{1/2} + \sigma^o \Lambda^{1/2} \rho_o s_{a,3},$$
(96)

$$\sigma_1^o r_{6,a} - \sigma_2^o r_{5,a} = i \sigma^o s_{a,3} \Lambda^{1/2} - i \Lambda^{1/2} \rho_o \sigma^o s_{a,3},$$
(97)

where $y_a = \xi_{o,a}$ and $\sigma^o = \sigma_e + \sigma_o$. These equations are strongly overdetermined. Accordingly, the fact that they have a solution is evidence that the wave functions, which formed the input to this calculation are correct. (Indeed, in order to arrive at a solution, it was necessary to correct an error in the table of wave functions of Ref. 9.) These equations have the solution for the wave functions of the 2D irrep phase in terms of those of the 1D irrep phase as

$$r_{1,a} = \left[ e^{-i\pi/4} s_{a,1} - \rho_o e^{-i\pi/4} s_{a,1} \right] / \sqrt{2},$$
(98)

$$r_{2,a} = \left[ - e^{-i\pi/4} s_{a,1} + \rho_o e^{i\pi/4} s_{a,1} \right] / \sqrt{2},$$
(99)

$$y_a = \left[ - e^{-i\pi/4} + \rho_o e^{-i\pi/4} \right] s_{a,2},$$
(100)

$$r_{5,a} = \left[ e^{i\pi/4} \Lambda^{1/2} s_{a,3} - \rho_o e^{-i\pi/4} \Lambda^{1/2} s_{a,3} \right] / \sqrt{2},$$
(101)

$$r_{6,a} = \left[ - e^{-i\pi/4} \Lambda^{1/2} s_{a,3} + \rho_o e^{i\pi/4} \Lambda^{1/2} s_{a,3} \right] / \sqrt{2},$$
(102)

The order parameters are related by

$$\sigma^+ = \left[ e^{i\pi/4} \sigma_1 - e^{-i\pi/4} \sigma_2 \right] / \sqrt{2},$$
(103)

$$\sigma^- = \left[ - e^{-i\pi/4} \sigma_1 + e^{i\pi/4} \sigma_2 \right] / \sqrt{2}.$$  
(104)

A strong check on these results is that the $r_{6,n}$ and $r_{5,n}$ are real ($\rho_x = \rho_y = 1$) and $r_{5,n}$ is imaginary ($\rho_z = 1$), all as required by the symmetry analysis of the CM phase.9

These results show how the order parameters of the 2D irrep are related to the order parameters of the 1D irreps. One should also note that by continuity, if the IC phase has a spontaneous polarization as $q_z \rightarrow 1/4$, the CM phase should also have one and vice versa. This is ensured by the fact that

$$|\sigma_1|^2 - |\sigma_2|^2 = i \left[ (\sigma_e^+ + \sigma_e^o)(\sigma_o^+ + \sigma_o^o) - (\sigma_e^- + \sigma_e^o)(\sigma_o^- + \sigma_o^o) \right].$$
(105)

Now we only keep terms that conserve wave vector when we go away from $q_z = 1/2$, in which case,

$$|\sigma_1|^2 - |\sigma_2|^2 = i \left[ \sigma_e^+ \sigma_o^- - \sigma_o^+ \sigma_e^- + \sigma_e^+ \sigma_o^- - \sigma_o^+ \sigma_e^- \right].$$
(106)

Thus the ME interaction of Eq. (53) goes smoothly into the ME interaction in the CM state.9,24,37

$$V_{\text{int}} = r \left| \sigma_1^2 - |\sigma_2|^2 \right| P_y.$$  
(107)

VI. CONCLUSION

We have performed a representation analysis of the magnetic order for the IC phase of the RnMn$_2$O$_5$ series by includ-
interactions have shown that higher-order and Umklapp magnetoelectric which is bilinear in the magnetic order parameters, explains herit from the wave functions. Using these symmetry prop-
determined the physically important order parameters and
have analyzed the transformation properties, which they in-
the wave functions. Using these symmetry prop-
have shown that higher-order and Umklapp magnetoelectric interactions (which are quartic in the spin variables) can in-
duce nonzero values for all components of the spontaneous polarization. However, since the order parameters are small in the relevant phases and since microscopic mechanisms tend to involve terms quadratic in the spin variables, these anomalous components to the spontaneous polarization may be very difficult to observe. We have also explicitly obtained the compatibility relations for the transition between the IC phase and the CM phase (or more generally the phase where the x component of wave vector is locked to its CM value).

ACKNOWLEDGMENTS

A.A. and O.E.W. acknowledge support from the Israel Science Foundation. M.K. acknowledges support by the Swiss National Science Foundation under Contract No. PP002-102831.

1 E. F. Bertaut, J. Phys. (Paris), Colloq. 32, C1-462 (1971).
2 J. Rossat-Mignod, in Methods of Experimental Physics, edited by K. Skold and D. L. Price (Academic, New York, 1987), Vol. 23, Chap. 20, p. 69.
3 L. D. Landau and E. M. Lifshitz, Statistical Physics (Pergamon, New York, 1978), Sec. 139.
4 J. Schweizer, J. Villain, and A. B. Harris, Eur. Phys. J.: Appl. Phys. 38, 41 (2007).
5 P. G. Radaelli and L. C. Chapon, Phys. Rev. B 76, 054428 (2007).
6 G. Lawes, A. B. Harris, T. Kimura, N. Rogado, R. J. Cava, A. Aharony, O. Entin-Wohlman, T. Yildirim, M. Kenzelmann, C. Broholm, and A. P. Ramirez, Phys. Rev. Lett. 95, 087205 (2005).
7 M. Kenzelmann, A. B. Harris, S. Jonas, C. Broholm, J. Schefer, S. B. Kim, C. L. Zhang, S. W. Cheong, O. P. Vajk, and J. W. Lynn, Phys. Rev. Lett. 95, 087206 (2005).
8 M. Kenzelmann, A. B. Harris, A. Aharony, O. Entin-Wohlman, T. Yildirim, Q. Huang, S. Park, G. Lawes, C. Broholm, N. Rogado, R. J. Cava, K. H. Kim, G. Jorge, and A. P. Ramirez, Phys. Rev. B 74, 014429 (2006).
9 A. B. Harris, Phys. Rev. B 76, 054447 (2007); A. B. Harris, ibid. 77, 019901(E) (2008).
10 The very low-temperature IC phases may be long wave length IC phases. See Refs. 11 and 12.
11 S. Kobayashi, H. Kimura, Y. Noda, and K. Kohn, J. Phys. Soc. Jpn. 74, 468 (2005).
12 S. Kobayashi, T. Osawa, H. Kimura, Y. Noda, I. Kagomiya, and K. Kohn, J. Phys. Soc. Jpn. 73, 1593 (2004).
13 K. Saito and K. Kohn, J. Phys.: Condens. Matter 7, 2855 (1995).
14 A. Inomata and K. Kohn, J. Phys.: Condens. Matter 8, 2673 (1996).
15 I. Kagomiya, K. Kohn, and T. Uchiyama, Ferroelectrics 280, 131 (2002).
16 I. Kagomiya, S. Matsumoto, K. Kohn, Y. Fukuda, T. Shobu, H. Kimura, Y. Noda, and N. Ikeda, Ferroelectrics 286, 167 (2003).
17 S. Kobayashi, T. Osawa, H. Kimura, Y. Noda, I. Kagomiya, and K. Kohn, J. Phys. Soc. Jpn. 73, 1031 (2004).
18 H. Kimura, Y. Kamada, Y. Noda, K. Kaneko, N. Metoki, and K. Kohn, J. Phys. Soc. Jpn. 75, 113701 (2006).
19 S. Kobayashi, T. Osawa, H. Kimura, Y. Noda, N. Kasahara, S. Mitsuda, and K. Kohn, J. Phys. Soc. Jpn. 73, 3439 (2004).
20 D. Higashiyama, S. Miyasaka, N. Kida, T. Arima, and Y. Tokura, Phys. Rev. B 70, 174405 (2004).
21 D. Higashiyama, S. Miyasaka, and Y. Tokura, Phys. Rev. B 72, 064421 (2005).
22 H. Kimura, S. Kobayashi, Y. Fukuda, T. Osawa, Y. Kamada, Y. Noda, I. Kagomiya, and K. Kohn, J. Phys. Soc. Jpn. 76, 074706 (2007).
23 For a phase directly connected to the paramagnetic phase via a continuous transition, we ignore the possibility of accidentally degenerate irreps, so only one irrep can appear. If a phase is reached by passing through two continuous phase transitions, then we similarly assume the presence of two irreps.
24 A. B. Harris, A. Aharony, and O. Entin-Wohlman, Phys. Rev. Lett. 100, 217202 (2008).
25 S. Quezel-Abrunaz, E. F. Bertaut, and G. Buissin, C. R. Acad. Sci. Paris 258, 3025 (1964).
26 A. J. C. Wilson, International Tables for Crystallography (Klu-
er, Dordrecht, 1995), Vol. A.
27 G. Buissin, Phys. Status Solidi A 16, 533 (1973).
28 G. Buissin, Phys. Status Solidi A 17, 191 (1973).
29 J. A. Alonso, M. T. Casais, M. J. Martinez-Lope, J. L. Martinez, and M. T. Fernandez-Diaz, J. Phys.: Condens. Matter 9, 8515 (1997).
30 L. C. Chapon, P. G. Radaelli, G. R. Blake, S. Park, and S.-W. Cheong, Phys. Rev. Lett. 96, 097601 (2006).
31 R. A. Ewings, A. T. Boothroyd, D. F. McMorrow, D. Mannix, H. C. Walker, and B. M. R. Wanklyn, Phys. Rev. B 77, 104415 (2008).
32 W. Ratcliff, V. Koryukhin, M. Kenzelmann, S. H. Lee, R. Erwin, J. Schefer, N. Hur, S. Park, and S. W. Cheong, Phys. Rev. B 72, 060407(R) (2005).
33 G. R. Blake, L. C. Chapon, P. G. Radaelli, S. Park, N. Hur, S.-W. Cheong, and J. Rodriguez-Carvajal, Phys. Rev. B 71, 214402 (2005).
34 M. Uga, N. Iwata, and K. Kohn, Ferroelectrics 219, 55 (1998).
35 N. Hur, S. Park, P. A. Sharma, JU. S. Ahn, S. Guha, and S.-W.
EFFECT OF INVERSION SYMMETRY ON THE…

Cheong, Nature (London) 429, 392 (2004).

36 N. Hur, S. Park, P. A. Sharma, S. Guha, and S.-W. Cheong, Phys. Rev. Lett. 93, 107207 (2004).

37 A. B. Harris, A. Aharony, and O. Entin-Wohlman, J. Phys. Condens. Matter (to be published).

38 Throughout the paper $q_x$ is assumed to be near or at 1/2 and $q_z$ near or at 1/4.

39 W. Sikora, F. Bialas, and L. Pytlik, J. Appl. Crystallogr. 37, 1015 (2004).

40 The factor 2 occurs because positions are measured in lattice constants and wave vectors are in rlu’s.

41 A. B. Harris and J. Schweizer, Phys. Rev. B 74, 134411 (2006).

42 H. Katsura, N. Nagaosa, and A. V. Balatsky, Phys. Rev. Lett. 95, 057205 (2005).

43 I. A. Sergienko and E. Dagotto, Phys. Rev. Lett. 97, 227204 (2006).

44 Here we assume that the $e$ and $o$ order parameters condense at the same wave vector. This assumption is justified in Refs. 8, 37, and 24.

45 D. Frohlich, St. Leute, V. V. Pavlov, and R. V. Pisarev, Phys. Rev. Lett. 81, 3239 (1998).

46 M. Mostovoy, Phys. Rev. Lett. 96, 067601 (2006); M. Kenzelmann and A. B. Harris, ibid. 100, 089701 (2008).

47 D. Mukamel, Phys. Rev. B 13, 5065 (1976).

51 E. P. Wigner, Group Theory and its Application to the Quantum Mechanics of Atomic Spectra (Academic, New York, 1959), See Eq. (9.37).

52 J. J. Betouras, G. Giovannetti, and J. van den Brink, Phys. Rev. Lett. 98, 257602 (2007).

53 In Ref. 22 an analysis of the commensurate structures of YMn$_2$O$_5$, ErMn$_2$O$_5$, and HoMn$_2$O$_5$ was performed without using symmetry considerations to limit the determination of the spin structures. Accordingly, their structures show small deviations from those obtained by a fit (Ref. 37) to a structure with a single order parameter following Table IX. The resulting minor readjustment of the spin structure of YMn$_2$O$_5$ is discussed in detail in Sec. 3.5 of Ref. 37. More recently, similar results for the commensurate phase of YMn$_2$O$_5$ have been given in Ref. 54 and could probably be analyzed similarly but with a slightly poorer fit to a single order parameter. In addition, this reference also gives the spin structure of the low-temperature (10 K) incommensurate phase of YMn$_2$O$_5$. This phase may not be described by the order parameters of the present paper, since representation theory (on which this description is based) is not applicable if the phase is not connected via continuous transitions to the paramagnetic phase.

54 J.-H. Kim, S.-H. Lee, S. I. Park, M. Kenzelmann, J. Schefer, J.-H. Chung, C. F. Majkrzak, M. Takeda, S. Wakimoto, S. Y. Park, S.-W. Cheong, M. Matsuda, H. Kimura, Y. Noda, and K. Kakurai, arXiv:0803.1123 (unpublished).

55 R. M. Hornreich, M. Luban, and S. Shtrikman, Phys. Rev. Lett. 35, 1678 (1975).