Landau Potentials for Multiferroic Mn$_2$GeO$_4$

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Abstract

It is shown how to adapt the results of ISODISTORT to a more convenient form. For the case of Mn$_2$GeO$_4$ we characterize the complex magnetic phase that exists at temperature below 5.5K, by order parameters for both the commensurate ordering and the incommensurate ordering. For the incommensurate ordering we are forced to consider the transformation properties which interrelate magnetic modes at different noncollinear members of the star of the incommensurate wave vector. The transformation properties of the order parameters and of the underlying magnetic wave functions are developed. These results are applied to construct the high order invariants in the free energy which have been used elsewhere to describe the characteristics of switching between different domains.

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I. INTRODUCTION

The last dozen years have seen an explosion in the study of multiferroic systems in which incommensurate magnetic order induces ferroelectricity, following the pioneering work of Refs. 1, 2, and 3. Shortly thereafter a microscopic model was developed based on the idea of a “spin current.” This mechanism has been widely cited in terms of a picture in which the spin structure is characterized as being a magnetic spiral. However, this idealized picture is not always easy to identify when the spiral is only weakly formed, when there are several different spirals in the unit cell, or indeed when this picture actually does not make the correct prediction. In early studies on Ni$_3$V$_2$O$_8$ and on TbMnO$_3$ a phenomenological Landau theory was developed which invoked a trilinear magnetoelectric interaction. The virtue of this theory was that it showed exactly how the crystal structure controlled the direction of the spontaneous polarization, a phenomenon which had not been understood prior to Refs. 9, 10, and 6. Perhaps due to its simplicity, the subsequent Mostovoy picture has been frequently applied. However, as we shall see here, in the present more complicated situation, this easily visualized picture is hard to apply. Accordingly, in the case we discuss here concerning the switching properties in Mn$_2$GeO$_4$ (MGO) the phenomenological approach comes into its own. Since the application of Landau theory is not trivial in this case, the present paper will give a detailed explanation as to how such a phenomenological theory is developed for MGO to characterize the complex switching phenomena that occur at temperatures below 5.5K.

In Sec. II, we discuss how order parameters are introduced to characterize the magnetic structure when it is nontrivial, having several magnetic sublattices of noncollinear spins. The magnetic order at zero wave vector is characterized by order parameters of a standard type and requires only a brief discussion. We show how the incommensurate magnetic ordering throughout the crystal is specified in terms of a normalized wave function which gives the distribution of magnetization within a unit cell and the associated amplitudes which give rise to complex-valued order parameters. This description is based on the mode structure and therefore provides a convenient description of the symmetry of the complicated incommensurate magnetic structure. It is necessary, of course, to appropriately describe the wave functions and order parameters of the different possible domains consistent with the
star of the wave vector. The discussion of the incommensurate magnetic modes is carried out mostly in an appendix and we will rely on the symmetry analysis of the suite of computer programs “ISODISTORT,”16 (whose results we verified by hand) use of which automatically performs the symmetry analysis of the magnetic ordering into sublattices. We use the present example to illustrate the use of this program, whose output is not guaranteed to be in a form most conveniently suited to an order parameter analysis.

In Sec. III we discuss how the order parameters and the wave functions for the various modes transform under the symmetry operations of the crystal.17 In the case of MGO one has two possible wave-vector domains, characterized by \( \mathbf{k}_A = (k_x, k_y, 0) \) and \(-\mathbf{k}_A\), and the other by \( \mathbf{k}_B = (k_x, -k_y, 0) \) and \(-\mathbf{k}_B\). Since the order parameters incorporate the symmetry properties of the incommensurate magnetic structure, they provide a natural way to discuss the properties of this complex magnetic system. Because the order parameters are explicitly defined in terms of the magnetic modes, one can identify transformations of the order parameters with actual transformation of the magnetic structure.

Having analyzed how the order parameters transform under the symmetry operations of the crystal, we construct, in Sec. IV, the invariants which make up the magnetic free energy. In principle a Landau theory could be developed to discuss the ordering process. However, this program is not our main objective because the first-order transition at \( T = 5.5\text{K} \) is quite complex. Instead, we describe here the construction of the invariant potentials which were used in Ref. 11 to explain the switching processes which take the system from one domain structure to another. The methodology used here may well be useful in the description of other complex incommensurate magnetic systems.

II. CRYSTAL SYMMETRY AND MODES

A. CRYSTAL SYMMETRY

For these discussions we record the symmetry operations of the orthorhombic space group for MGO, namely Pnma = No. 62 in Ref. 18, where \( x, y, \) and \( z \) refer to the \( a, b, \) and \( c \) crystal axes:

\[
\mathcal{E} = (x, y, z), \quad \mathcal{I} = (\overline{x}, \overline{y}, \overline{z})
\]
TABLE I: Symmetry properties of the two active zero-wave-vector magnetic order parameters $X_n$ for the irrep $\Gamma_n$. Both these order parameters (OP) are odd under time reversal.

| OP   | $m_x$ | $m_y$ | $m_z$ |
|------|-------|-------|-------|
| $X_1$ | 1     | 1     | 1     |
| $X_3$ | -1    | -1    | +1    |

\[ m_x = (x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}), \quad 2_x = (x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}) \]

\[ m_y = (x, y + \frac{1}{2}, z) , \quad 2_y = (x, y + \frac{1}{2}, z) \]

\[ m_z = (x + \frac{1}{2}, y, z + \frac{1}{2}), \quad 2_z = (x + \frac{1}{2}, y, z + \frac{1}{2}). \] (1)

We will also need to refer to the inverse operations:

\[ m_x^{-1} = (x + \frac{1}{2}, y - \frac{1}{2}, z - \frac{1}{2}) , \quad 2_x^{-1} = (x + \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2}) \]

\[ m_y^{-1} = (x, y + \frac{1}{2}, z), \quad 2_y^{-1} = (x, y - \frac{1}{2}, z) \]

\[ m_z^{-1} = (x - \frac{1}{2}, y, z + \frac{1}{2}), \quad 2_z^{-1} = (x + \frac{1}{2}, y, z - \frac{1}{2}). \] (2)

The eight sites in the unit cell are:

\[ \tau_1 = (0,0,0) , \quad \tau_2 = (1/2,0,1/2) \]

\[ \tau_3 = (1/2,1/2,1/2) , \quad \tau_4 = (0,1/2,0) \]

\[ \tau_5 = (a,1/4,\epsilon) , \quad \tau_6 = (a + 1/2,1/4,1/2 - \epsilon) \]

\[ \tau_7 = (1 - a,3/4,-\epsilon) , \quad \tau_8 = (1/2 - a,3/4,1/2 + \epsilon) . \] (3)

where $\epsilon \approx 0.0$ and $a \approx 0.275$.

**B. ZERO WAVE VECTOR MODES**

Two zero wave vector irreducible representations (irreps) are active: $\Gamma_1$ and $\Gamma_3$. Their parity under the mirror operations is given in Table I. The actual wave functions for these modes, given in the Supplemental Material to Ref. 12, are not needed for our symmetry analysis. However, it is helpful to note that the phase with $X_1$ is a type of antiferromagnetic ordering and $X_3$ ordering has a net magnetic moment along the $z$-axis.
C. INCOMMENSURATE MODES

In Appendix A, based on results from ISODISTORT\textsuperscript{16} we show that the magnetization throughout a domain of wave vector $k_A$ for the irrep $D^{(\sigma=1)}$ can be written as

$$M^{(A,1)}_\alpha(N + \tau_1) = a_\alpha e^{-i[N + \tau_1] \cdot k_A + i\phi} + \text{c. c.}$$
$$M^{(A,1)}_\alpha(N + \tau_2) = \mu_\alpha a_\alpha e^{-i[N + \tau_2] \cdot k_A + i\phi} + \text{c. c.}$$
$$M^{(A,1)}_\alpha(N + \tau_3) = b_\alpha e^{-i[N + \tau_3] \cdot k_A + i\phi} + \text{c. c.}$$
$$M^{(A,1)}_\alpha(N + \tau_4) = \mu_\alpha b_\alpha e^{-i[N + \tau_4] \cdot k_A + i\phi} + \text{c. c.}$$
$$M^{(A,1)}_\alpha(N + \tau_5) = z_\alpha e^{-i[N + \tau_5] \cdot k_A + i\phi} + \text{c. c.}$$
$$M^{(A,1)}_\alpha(N + \tau_6) = \mu_\alpha z_\alpha e^{-i[N + \tau_6] \cdot k_A + i\phi} + \text{c. c.}$$
$$M^{(A,1)}_\alpha(N + \tau_7) = z_\alpha^* e^{-i[N + \tau_7] \cdot k_A + i\phi} + \text{c. c.}$$
$$M^{(A,1)}_\alpha(N + \tau_8) = \mu_\alpha z_\alpha^* e^{-i[N + \tau_8] \cdot k_A + i\phi} + \text{c. c.}$$

(4)

where $N \equiv (N_x, N_y, N_z)$ specifies the integer coordinates (we always use rlu) of the unit cell, $a_\alpha$ and $b_\alpha$ are real-valued, $z_\alpha$ is complex-valued, $\mu_x = \mu_y = -\mu_z = -1$, the superscripts label the wave vector and the irrep, and the subscript is the component label, $\alpha = x, y,$ or $z$. For economy in notation we write Eq. (4) as

$$M^{(A,1)}_\alpha(N + \tau_n) = e^{i\phi_\alpha} [a_\alpha, \mu_\alpha a_\alpha, b_\alpha, \mu_\alpha b_\alpha; z_\alpha, \mu_\alpha z_\alpha, z_\alpha^*; \mu_\alpha z_\alpha^*]_n e^{-i[N + \tau_n] \cdot k_A} + \text{c. c.}$$

(5)

In this notation the magnetization for irrep $D^{(\sigma=2)}$ is given by

$$M^{(A,2)}_\alpha(N + \tau_n) = e^{i\phi_\alpha} [c_\alpha, -\mu_\alpha c_\alpha, d_\alpha, -\mu_\alpha d_\alpha; w_\alpha, -\mu_\alpha w_\alpha, w_\alpha^*; -\mu_\alpha w_\alpha^*]_n e^{-i[N + \tau_n] \cdot k_A} + \text{c. c.}$$

(6)

Note that we use different constants for irreps 1 and 2. We do this to emphasize the fact that the wave functions for different symmetries are not related, just as atomic s and p functions are not related to each other by symmetry.

To describe the magnetization distribution for a single irrep requires specifying the 13 real-valued parameters, namely $a_\alpha$, $b_\alpha$, $\Re(z_\alpha)$, $\Im(z_\alpha)$ for $\alpha = x, y, z$ and the global phase $\phi$. A similar analysis was given in the Supplemental Material to Ref. 12, but it appears to allow more adjustable parameters than those given here, although our set of parameters is allowed by their analysis. There the actual values of the parameters obtained from experiment are given, but they are not needed here.
In the simplest situation only a single irrep is activated. In that case, the above
description of the incommensurate magnetization holds throughout the range of existence of the
phase (i.e. as long as no phase boundary has been crossed), but the parameters of the wave
function (i.e. the $a$'s, $b$'s and $z$'s) depend on temperature. If incommensurate magnetic or-
dering appears below a continuous phase transition, then the temperature-dependence of the
wavefunction when the ordering initially develops gives rise mainly to a change of scale of the
coefficients. Accordingly, we describe the wave function as an amplitude times a normalized
wave function. In so doing, we incorporate the phase factor $\exp(i\phi)$ in the amplitude, thus
giving rise to a complex-valued amplitude known as the order parameter, here denoted
$Q^{(\sigma)}_X(\sigma)$, for the irrep $\sigma$ at wave vector $k_X$, where $X = \pm A$ or $X = \pm B$ (and $k_{-X}$ denotes $-k_X$).

Of course, it is an approximation to assume that the temperature dependence of the wave
function merely induces a temperature dependence of the order parameter. However, since
this approximation correctly describes the symmetry of the phase, it is often useful and can
form the basis for a renormalization group treatment of the critical behavior. Furthermore,
as shown in Appendix B, corrections due to the additional temperature dependence of the
wave function can be generated within the Landau formulation of the order parameter which
we describe here.

In the present situation we are interested in describing a system which can have both
irreps simultaneously present. This means that order parameters for the two irreps can
simultaneously be nonzero. In what follows each mode is characterized by its order parameter
$Q^{(\sigma)}_X$ which has its own magnitude and phase. Thus we write the contribution to the $\alpha$-
component of the magnetization from irrep 1 at wave vector $k_A$ to be

$$M^{(A,1)}_\alpha(N + \tau_n) = Q^{(1)}_A [a_\alpha, \mu_\alpha a_\alpha, b_\alpha, \mu_\alpha b_\alpha; z_\alpha, \mu_\alpha z_\alpha, z^*_\alpha, \mu_\alpha z^*_\alpha] e^{-ik_A [N+\tau_n]} + c. c. \equiv Q^{(1)}_A \Psi^{(A,1)}_{a,n} e^{-ik_A [N+\tau_n]} + c. c. \quad (7)$$

and that from irrep 2 at wave vector $k_A$ to be

$$M^{(A,2)}_\alpha(N + \tau_n) = Q^{(2)}_A [c_\alpha, -\mu_\alpha c_\alpha, d_\alpha, -\mu_\alpha d_\alpha; w_\alpha, -\mu_\alpha w_\alpha, w^*_\alpha, -\mu_\alpha w^*_\alpha] e^{-ik_A [N+\tau_n]} + c. c. \equiv Q^{(2)}_A \Psi^{(A,2)}_{a,n} e^{-ik_A [N+\tau_n]} + c. c. \quad (8)$$
where we require the wave functions $\Psi^{(A,m)}$ to be normalized:

$$\sum_\alpha \left[ 2a_\alpha^2 + 2b_\alpha^2 + 4|z_\alpha|^2 \right] = 1 \quad (9)$$

We can equally well write the equation for $M_{\alpha}^{(A,1)}(N + \tau_n)$ as

$$M_{\alpha}^{(A,1)}(N + \tau_n) = Q_A^{(1),*} \left[ a_\alpha, \mu_\alpha a_\alpha, b_\alpha, \mu_\alpha b_\alpha; z_\alpha^*, \mu_\alpha z_\alpha^*, z_\alpha, \mu_\alpha z_\alpha \right] e^{-i(-k_A)[N + \tau_n]} + c. c. \quad (10)$$

This leads us to write

$$Q^{(\sigma)}_{-X} = Q^{(\sigma)*}_X, \quad \Psi^{(-X,1)}_{\alpha,n} = \Psi^{(X,1)*}_{\alpha,n} \quad (11)$$

where the script $-X$ refers to the wave vector $-k_X$. We assume that the $\Psi^{(A,\sigma)}_{\alpha,n}$ have been determined by fitting experimental data, as in Ref. 12. Our aim is to obtain the transformation properties of the order parameters and to determine the wave functions for $\pm k_B$ from those of $\pm k_A$.

The results for $\Psi$ for the star of the wave vector will be collected in Table III. One can easily see that these two wave functions, $\Psi^{(\sigma=1)}$ and $\Psi^{(\sigma=2)}$, are orthogonal to one another. We should point out that there is some arbitrariness in choosing the sign of the order parameter $Q$. We could have chosen $\Psi$ to be the negative of that listed in Table III. This would induce a change of sign in the associated $Q$ and would give rise to an equally valid representation. This arbitrariness is also evident in the case of a two-sublattice antiferromagnet, where we arbitrarily choose the orientations of the sublattice magnetizations when the order parameter (the staggered magnetization) is positive.

Usually the absolute phase of an order parameter is not important. However, relative phases of order parameters can crucially affect observable quantities, such as the electric polarization. Also note that we have made an arbitrary choice to associate $Q_A^{(1)}$ with $\exp(-i[N_xk_x + N_yk_y])$ rather than with $\exp(i[N_xk_x + N_yk_y])$.

### III. TRANSFORMATION PROPERTIES OF THE ORDER PARAMETERS

We define the transformation of order parameters under an operator $\mathcal{O}$, by considering the effect of $\mathcal{O}$ on the distribution of magnetization over the system. We write

$$\mathbf{M}(N_x, N_y, N_z; \tau_n)' = \mathcal{O}^S \mathbf{M} \left( [\mathcal{O}^R]^{-1}[N_x, N_y, N_z; \tau_n] \right), \quad (12)$$
TABLE II: Wave functions $\Psi^{(X,\sigma)}_{\alpha n}$ for the star of the wave vector, where $X = A$ or $X = B$ and $\mu_\alpha = (-1, -1, +1)$ and $\lambda'_\alpha = (-1, +1, -1)$. The notation is as in Eq. (7). Here $a_\alpha$, $b_\alpha$, $c_\alpha$, and $d_\alpha$ are real-valued and $z_\alpha$ and $w_\alpha$ are complex-valued. The values of these parameters are not fixed by symmetry. The wave function for $k_B$ is of the form given in Eq. (32). Its explicit relation to that for $k_A$ (given here) is obtained in Eqs. (40) and (41).

| $n$ | $1$  | $2$  | $3$  | $4$  | $5$  | $6$  | $7$  | $8$  |
|-----|------|------|------|------|------|------|------|------|
| $\Psi^{(A,1)}_{\alpha n}$ | $a_\alpha$ | $\mu_\alpha a_\alpha$ | $b_\alpha$ | $\mu_\alpha b_\alpha$ | $z_\alpha$ | $\mu_\alpha z_\alpha$ | $z^*_\alpha$ | $\mu_\alpha z^*_\alpha$ |
| $\Psi^{(A,2)}_{\alpha n}$ | $c_\alpha$ | $-\mu_\alpha c_\alpha$ | $d_\alpha$ | $-\mu_\alpha d_\alpha$ | $w_\alpha$ | $-\mu_\alpha w_\alpha$ | $w^*_\alpha$ | $-\mu_\alpha w^*_\alpha$ |
| $\Psi^{(B,1)}_{\alpha n}/\lambda'_\alpha$ | $\mu_\alpha b_\alpha$ | $b_\alpha$ | $\mu_\alpha a_\alpha$ | $a_\alpha$ | $z_\alpha$ | $\mu_\alpha z_\alpha$ | $z^*_\alpha$ | $\mu_\alpha z^*_\alpha$ |
| $\Psi^{(B,2)}_{\alpha n}/\lambda'_\alpha$ | $\mu_\alpha d_\alpha$ | $-d_\alpha$ | $\mu_\alpha c_\alpha$ | $-c_\alpha$ | $-w_\alpha$ | $\mu_\alpha w_\alpha$ | $-w^*_\alpha$ | $\mu_\alpha w^*_\alpha$ |

where $O^S$ is the part of the operator $O$ that operates on spin and $O^R$ is the part of the operator $O$ that operates on the position of the spin. This equation says that the transformed magnetic moment (indicated by a prime) that was at $[O^R]^{-1}[N + \tau_n]$ has been transformed by $O^S$ and is placed at its final location at $N + \tau_n$. In this section we will consider the transformations under the three perpendicular mirror planes, since these operations can be taken to be the generators of the point group. In the course of this program we will identify the “coordinate system” or “unit vectors” which in this case is the set of wave functions for each wave vector. In Eqs. (7) and (8) we have already defined the wave function for the wave vector $k_A$ and in Eq. (11) for the wave vector $-k_A$. In subsection IIIC we will obtain those for wave vectors $\pm k_B$.

A. TRANSFORMATION BY INVERSION $I$

Perhaps the simplest operation is spatial inversion $I$. Since $I^{-1} = I$, Eq. (12) is

$$M(N_x, N_y, N_z; \tau_n)' = I^S M \left([I^R][N_x, N_y, N_z; \tau_n]\right) = M \left([I^R][N_x, N_y, N_z; \tau_n]\right),$$

where we used the fact that the magnetic moment is a pseudovector to write the second version of the above equation. Thus, for wave vector $k_A$ and irrep $\sigma$

$$M_\alpha(N_x, N_y, N_z; \tau_n)' = Q^{(\sigma)}_A I^R[\Psi^{(A,\sigma)}_{\alpha n} e^{-i k_A \cdot (N + \tau_n)}] + \text{c.c.}$$

8
The effect of $\mathcal{I}$ on $\tau_n$ is given in Table II.

| $n$ | $\tau_n$ | $\mathcal{I}\tau_n$ | $\Rightarrow$ | $\tau'_n$ |
|-----|----------|----------------|-------------|---------|
| 1   | (0, 0, 0) | (0, 0, 0) | (0, 0, 0) | $\tau_1$ |
| 2   | ($\frac{1}{2}$, 0, $\frac{1}{2}$) | ($-\frac{1}{2}$, 0, $-\frac{1}{2}$) | ($\frac{1}{2}$, 0, $\frac{1}{2}$) | $\tau_2$ |
| 3   | ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) | ($-\frac{1}{2}$, $-\frac{1}{2}$, $-\frac{1}{2}$) | ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) | $\tau_3$ |
| 4   | (0, $\frac{1}{2}$, 0) | (0, $-\frac{1}{2}$, 0) | (0, $\frac{1}{2}$, 0) | $\tau_4$ |
| 5   | ($a, \frac{1}{2}, \epsilon$) | ($-a, \frac{1}{2}, -\epsilon$) | (1, $a, \frac{3}{2}, \epsilon$) | $\tau_5$ |
| 6   | ($a + \frac{1}{2}, \frac{3}{2}, \frac{1}{2} - \epsilon$) | ($-a - \frac{1}{2}, -\frac{1}{2}, \frac{1}{2} + \epsilon$) | ($\frac{1}{2} - a, \frac{3}{2}, \frac{1}{2} + \epsilon$) | $\tau_6$ |
| 7   | ($1 - a, \frac{3}{2}, -\epsilon$) | ($a - 1, -\frac{3}{2}, \epsilon$) | ($a, \frac{1}{2}, \epsilon$) | $\tau_7$ |
| 8   | ($\frac{1}{2} - a, \frac{3}{2}, \frac{1}{2} + \epsilon$) | ($a - \frac{1}{2}, -\frac{3}{2}, \frac{1}{2} - \epsilon$) | ($a + \frac{1}{2}, \frac{3}{2}, \frac{1}{2} - \epsilon$) | $\tau_8$ |

$$= Q_A^{(\sigma)} [\mathcal{I}^R \Psi_{\alpha n}^{(A, \sigma)}] e^{-i[-k_A \cdot (N + \tau_n)]} + \text{c. c.} \quad (14)$$

This is of the form

$$M_{\alpha}(N_x, N_y, N_z; \tau_n)' = Q_A^{(\sigma)} [\bar{\Psi}_{\alpha n}^{(A, \sigma)}] e^{-i[-k_A \cdot (N + \tau_n)]} + \text{c. c.} \quad (16)$$

with

$$Q_A^{(\sigma)} \equiv \mathcal{I} \bar{Q}_A^{(\sigma)} = Q_A^{(\sigma)} = [Q_A^{(\sigma)}]^*, \quad \Psi_{\alpha n}^{(A, \sigma)} = [\Psi_{\alpha n}^{(A, \sigma)}]^* \quad (18)$$

consistent with Eq. (11). The analogous result holds for $k_B$. So in all we have

$$\mathcal{I} \bar{Q}_X^{(\sigma)} = Q_X^{(\sigma)} = Q_X^{(\sigma)}* \quad (19)$$

We may consider the order parameter to be a four-component column vector $\bar{Q}_\sigma$ with components $(Q_\sigma)_1 = Q_A^{(\sigma)}, (Q_\sigma)_2 = Q_B^{(\sigma)}, (Q_\sigma)_3 = Q_A^{(\sigma)}*, (Q_\sigma)_4 = Q_B^{(\sigma)}*$. We summarize our
results for the effect of inversion by writing

\[
\mathcal{I} \bar{Q}_\sigma \equiv \mathcal{I} \begin{bmatrix} Q_A^{(1)} \\ Q_B^{(1)} \\ Q_{-A}^{(1)} \\ Q_{-B}^{(1)} \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} Q_A^{(1)} \\ Q_B^{(1)} \\ Q_{-A}^{(1)} \\ Q_{-B}^{(1)} \end{bmatrix} \equiv \mathcal{M}_\sigma(\mathcal{I}) \bar{Q}_\sigma .
\] (20)

In general, if \( \mathcal{O} \) is an operator, then we write

\[
\mathcal{O}(Q_\sigma)_n = \sum_m [\mathcal{M}_\sigma(\mathcal{O})]_{nm}(Q_\sigma)_m .
\] (21)

B. TRANSFORMATION BY \( m_z \)

Since \( m_z \) leaves the wave vector \( k \) invariant, we consider it next. We start by considering the case when \( k = \mathbf{k}_A \). Thus we apply Eq. (12) when \( k = \mathbf{k}_A \) and \( \mathcal{O} = m_z \):

\[
M_\alpha(N_x, N_y, N_z; \tau_n)' = \lambda_\alpha M_\alpha \left( [m_z^R]^{-1}[N_x, N_y, N_z; \tau_n] \right) ,
\] (22)

where, since \( \mathbf{M} \) is a pseudovector, \( \lambda_\alpha = (-1, -1, +1) \). Thereby we find that

\[
M_\alpha(N_x, N_y, N_z; \tau_n)' = \lambda_\alpha \left( [m_z^R]^{-1} \Psi_{\alpha n}^{(A,1)} \right) e^{-ik_A \cdot [m_z^R]^{-1}[N+\tau_n]} Q_A^{(1)} + \text{c. c.} .
\] (23)

To evaluate the exponential for \( k_z = 0 \), note that acting on a vector of the form \( (v_x, v_y, 0) \), we have \( [m_z^R]^{-1}(v_x, v_y, 0) = (v_x - 1/2, v_y, 0) \). So

\[
M_\alpha(N_x, N_y, N_z; \tau_n)' = \lambda_\alpha \left( [m_z^R]^{-1} \Psi_{\alpha n}^{(A,1)} \right) e^{-ik_A \cdot [N+\tau_n]} e^{ix_z/2} Q_A^{(1)} + \text{c. c.} .
\] (24)

Now we consider \( [m_z^R]^{-1} \Psi_{\alpha n}^{(A,1)} \). In Table IV we see that

\[
[m_z^R]^{-1} \Psi_{\alpha n}^{(A,1)} = \Psi_{\alpha \bar{n}}^{(A,1)} ,
\] (25)

where \( \bar{n} = n - 1 \) if \( n \) is even and \( \bar{n} = n + 1 \) if \( n \) is odd. But, since \( \mu_\alpha = 1/\mu_\lambda \), we have, from Eq. (5), that

\[
\Psi_{\alpha \bar{n}}^{(A,1)} = \mu_\alpha \Psi_{\alpha n}^{(A,1)} .
\] (26)

Note that \( \mu_\alpha \lambda_\alpha = 1 \), so that the final result is

\[
M_\alpha(N_x, N_y, N_z; \tau_n)' = e^{ik_z/2} \Psi_{\alpha n}^{(A,1)} e^{-ik_A \cdot [N+\tau_n]} Q_A^{(1)} + \text{c. c.} .
\] (27)
TABLE IV: As table III. Transformation of $\tau_n$ by $m_z$.

| $n$ | $\tau_n$ | $[m_z^R]^{-1}\tau_n$ | $\Rightarrow$ | $\tau'_n$ |
|-----|-----------|---------------------|-------------|------------|
| 1   | (0, 0, 0) | $(-\frac{1}{2}, 0, \frac{1}{2})$ | $(\frac{1}{2}, 0, \frac{1}{2})$ | $\tau_2$ |
| 2   | $(\frac{1}{2}, 0, \frac{1}{2})$ | (0, 0, 0) | (0, 0, 0) | $\tau_1$ |
| 3   | $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ | $(0, \frac{1}{2}, 0)$ | $(0, \frac{1}{2}, 0)$ | $\tau_4$ |
| 4   | $(0, \frac{1}{2}, 0)$ | $(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ | $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ | $\tau_3$ |
| 5   | $(a, \frac{1}{2}, 0)$ | $(a - \frac{1}{2}, \frac{1}{4}, \frac{1}{4})$ | $(a + \frac{1}{2}, \frac{1}{4}, \frac{1}{4})$ | $\tau_6$ |
| 6   | $(a + \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ | $(a, \frac{1}{4}, 0)$ | $(a, \frac{1}{4}, 0)$ | $\tau_5$ |
| 7   | $(1 - a, \frac{3}{4}, 0)$ | $(\frac{1}{2} - a, \frac{3}{4}, \frac{1}{2})$ | $(\frac{1}{2} - a, \frac{3}{4}, \frac{1}{2})$ | $\tau_8$ |
| 8   | $(\frac{1}{2} - a, \frac{3}{4}, \frac{1}{2})$ | $(-a, \frac{3}{4}, 0)$ | $(1 - a, \frac{3}{4}, 0)$ | $\tau_7$ |

This is of the form

$$M_A(N_x, N_y, N_z; \tau_n)' = Q_A^{(1)}\Psi_A^{(1)}e^{-ik_A[N_x+N_y]} + c. c. \quad (28)$$

In other words,

$$Q_A^{(1)} = m_zQ_A^{(1)} = e^{ik_z/2}Q_A^{(1)}. \quad (29)$$

For $\sigma = 2$ we have

$$m_zQ_A^{(2)} = -e^{ik_z/2}Q_A^{(2)}. \quad (30)$$

The difference in sign for $m_zQ_A^{(2)}$ occurs because, here, instead of Eq. (26), one has

$$\Psi_A^{(2)} = -\mu_A\Psi_A^{(2)}. \quad (31)$$

We now use the above results to obtain analogous results for wave vectors $k_B$. Since the value of $k$ does not appear explicitly, the wave functions of $k_B = (k_x, -k_y, 0)$ are of the form

$$\Psi^{(B,1)} = [a'_\alpha, \mu_\alpha a'_\alpha, b'_\alpha, \mu_\alpha b'_\alpha, z'_\alpha, \mu_\alpha z'_\alpha, z'^*_\alpha, \mu_\alpha z'^*_\alpha] \quad (32)$$

and similarly for $\Psi^{(B,2)}$. The relation between $(a', b', z')$ and $(a, b, z)$, given in Table II will
be derived later. Note that Eq. (29) holds when \( \mathbf{k}_A \) is replaced by \( \mathbf{k}_B \). Thus we obtain

\[
\begin{bmatrix}
Q_A^{(\sigma)} \\
Q_B^{(\sigma)} \\
Q_A^{(\sigma)} \\
Q_B^{(\sigma)}
\end{bmatrix}
= \begin{pmatrix}
e^{i k_x/2} & 0 & 0 & 0 \\
0 & e^{i k_x/2} & 0 & 0 \\
0 & 0 & e^{-i k_x/2} & 0 \\
0 & 0 & 0 & e^{-i k_x/2}
\end{pmatrix}
\begin{bmatrix}
Q_A^{(\sigma)} \\
Q_B^{(\sigma)} \\
Q_A^{(\sigma)} \\
Q_B^{(\sigma)}
\end{bmatrix}
= M_\sigma(m_z) \bar{Q}_\sigma \quad (33)
\]

Here we noted that \( Q_X^{(\sigma)} = [Q_X^{(\sigma)}]^* \) to obtain the lower half of the matrix.

C. TRANSFORMATION BY \( m_y \)

To identify the modes for wave vector \( \mathbf{k}_B \) from those of wave vector \( \mathbf{k}_A \), we transform the wave functions for \( \mathbf{k}_A \) into those for \( \mathbf{k}_B = (k_x, -k_y, 0) \). Although symmetry allows the parameters of the wave function (e.g. \( a, b \), etc.) to be arbitrary, once they are fixed for wave vector \( \mathbf{k}_A \), they are implicitly fixed (to within a phase factor) for wave vector \( \mathbf{k}_B \). Under transformation by \( m_y \) we write Eq. (12) as

\[
M_\alpha(N_x, N_y, N_z; \tau_n)' = \lambda'_\alpha M_\alpha \left([m_y^R]^{-1}[N_x, N_y, N_z; \tau_n]\right), \quad (34)
\]

where, since \( \mathbf{M} \) is a pseudovector, \( \lambda'_\alpha = (-1, +1, -1) \). Thereby, for irrep \( \sigma \) we find that

\[
M_\alpha(N_x, N_y, N_z; \tau_n)' = \lambda'_\alpha \left([m_y^R]^{-1}\Psi_{\alpha n}^{(A, \sigma)}\right) e^{-i k_A : [m_y^R]^{-1}[N + \tau_n]} Q_A^{(\sigma)} + c. c., \quad (35)
\]

To evaluate the exponential for \( k_z = 0 \), note that acting on a vector of the form \((v_x, v_y, 0)\), we have \([m_y^R]^{-1}(v_x, v_y, 0) = (v_x, 1/2 - v_y, 0) \). So

\[
M_\alpha(N_x, N_y, N_z; \tau_n)' = \lambda'_\alpha \left([m_y^R]^{-1}\Psi_{\alpha n}^{(A, \sigma)}\right) e^{-i k_z(N_x + \tau_{nx}) + k_y(-N_y - \tau_{ny} + 1/2)} Q_A^{(\sigma)} + c. c. \quad (36)
\]

Now we consider \([m_y^R]^{-1}\Psi_{\alpha n}^{(A, \sigma)}\). In Table \[V\] we see that

\[
[m_y^R]^{-1}\Psi_{\alpha n}^{(A, \sigma)} = \Psi_{\alpha \pi}^{(A, \sigma)}, \quad (37)
\]

where \( \pi = 5 - n \) if \( n < 5 \) and \( \pi = n \) for \( n > 4 \). Then

\[
M_\alpha(N_x, N_y, N_z; \tau_n)' = \lambda'_\alpha e^{-i k_z/2} \Psi_{\alpha n}^{(A, \sigma)} e^{-i k_z(N_x + \tau_{nx}) + k_y(-N_y + \tau_{ny})} Q_A^{(\sigma)} + c. c. \quad (38)
\]

This is of the form
TABLE V: As Table III. Transformation of $\tau_n$ by $m_y$.

| $n$ | $\tau_n$ | $[m_y^R]^{-1}\tau_n$ | $\Rightarrow$ $\tau'_n$ |
|-----|-----------|---------------------|---------------------|
| 1   | (0, 0, 0) | (0, $\frac{1}{2}$, 0) | (0, $\frac{1}{2}$, 0) $\tau_4$ |
| 2   | ($\frac{1}{2}$, 0, $\frac{1}{2}$) | ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) | ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) $\tau_3$ |
| 3   | ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) | ($\frac{1}{2}$, 0, $\frac{1}{2}$) | ($\frac{1}{2}$, 0, $\frac{1}{2}$) $\tau_2$ |
| 4   | (0, $\frac{1}{2}$, 0) | (0, 0, 0) | (0, 0, 0) $\tau_1$ |
| 5   | ($a$, $\frac{1}{4}$, 0) | ($a$, $\frac{1}{4}$, 0) | ($a$, $\frac{1}{4}$, 0) $\tau_5$ |
| 6   | ($a + \frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{2}$) | ($a + \frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{2}$) | ($a + \frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{2}$) $\tau_6$ |
| 7   | (1 - $a$, $\frac{3}{4}$, 0) | (1 - $a$, - $\frac{1}{4}$, 0) | (1 - $a$, $\frac{3}{4}$, 0) $\tau_7$ |
| 8   | ($\frac{1}{2}$ - $a$, $\frac{3}{4}$, $\frac{1}{2}$ - $a$) | ($\frac{1}{2}$ - $a$, - $\frac{1}{4}$, $\frac{1}{2}$ - $a$) | ($\frac{1}{2}$ - $a$, $\frac{3}{4}$, $\frac{1}{2}$ - $a$) $\tau_8$ |

$M_\alpha(N_x, N_y, N_z; \tau_n) = Q_B^{(\sigma)}{\Psi^{(B, \sigma)}_\alpha} e^{-i[k_z(N_x+\tau_n)+(-k_y)(N_y+\tau_n)]} + c. c.$ . (39)

We choose the signs of the wave functions for $k_B$ such that

$\Psi^{(B_1)}_{\alpha n} = \lambda'_{\alpha} \Psi^{(A_1)}_{\alpha n} = \lambda'_{\alpha}[\mu_\alpha b_\alpha, b_\alpha, \mu_\alpha a_\alpha, a_\alpha; z_\alpha, \mu_\alpha z_\alpha, z^*_\alpha, \mu_\alpha z^*_\alpha]_n$ . (40)

$\Psi^{(B_2)}_{\alpha n} = -\lambda'_{\alpha} \Psi^{(A_2)}_{\alpha n} = \lambda'_{\alpha}[\mu_\alpha d_\alpha, -d_\alpha, \mu_\alpha c_\alpha, -c_\alpha; -w_\alpha, \mu_\alpha w_\alpha, -w^*_\alpha, \mu_\alpha w^*_\alpha]_n$ . (41)

As expected, $\Psi^{(B_1)}_{\alpha n}$ is of the form of Eq. (32), but now we have an explicit evaluation of $\Psi^{(B, \sigma)}_{\alpha n}$, given in Table III. With these definitions the transformed value of the order parameter $Q_B^{(\sigma)}$ is

$Q_B^{(\sigma)}' = m_y Q_B^{(\sigma)} = (-1)^{\sigma+1} Q_A^{(\sigma)} e^{-ik_y/2}$ . (42)

We repeat our previous warning about the phase. We could have defined $\Psi^{(B, \sigma)}_{\alpha n}$ to be the negative of its value in Eqs. (40) or (41). This possibility is analyzed in Appendix C, where we see that the choice of sign for the wave function implies a choice of sign for the order parameters, but does not affect the invariant potentials determined below.

To summarize: in terms of the order parameter vector $\bar{Q}_\sigma$ introduced in Eq. (20), we
have \((m_y \bar{Q}_\sigma)_n = \sum_m M_\sigma(m_y)_{nm} (\bar{Q}_\sigma)_m\), with
\[
M_\sigma(m_y) = (-1)^{\sigma+1} \begin{bmatrix}
0 & e^{ik_y/2} & 0 & 0 \\
e^{-ik_y/2} & 0 & 0 & 0 \\
0 & 0 & 0 & e^{-ik_y/2} \\
0 & 0 & e^{ik_y/2} & 0
\end{bmatrix}.
\] (43)

Equation (12) gives the 2,1 element of \(M_\sigma(m_y)\). The other matrix elements can be deduced by changing the sign of \(k_y\) or by complex conjugation.

D. Transformation by \(m_x\)

We now consider transformation by \(m_x\). We write Eq. (12) for irrep \(\sigma\) as
\[
M_\alpha(N + \tau_n)' = m_x^S M_\alpha^{(A,\sigma)} \left( [m_x^R]^{-1} [N_x, N_y, N_z; \tau_n] \right) .
\] (44)

Since \(M\) is a pseudovector we set \(m_x^S = \lambda''_\alpha\), with \(\lambda'' = (1, -1, -1)\). Then
\[
M_\alpha(N + \tau_n)' = \lambda''_\alpha \left( [m_x^R]^{-1} \psi^{(A,\sigma)}_{\alpha\pi} \right) e^{-ikA[m_x^R]^{-1}[N+\tau_n]} Q_A^{(\sigma)} + c. c. .
\] (45)

To evaluate the exponential for \(k_z = 0\), note that acting on a vector of the form \((k_x, k_y, 0)\), we have \([m_x^R]^{-1}(v_x, v_y, 0) = (1/2 - v_x, v_y - 1/2, -1/2)\). So
\[
M_\alpha(N_x, N_y, N_z; \tau_n)' = \lambda''_\alpha Q_A^{(\sigma)} \psi^{(A,\sigma)}_{\alpha\pi} e^{-i[k_x(-N_x)+k_yN_y]-i[k_x(-\tau_{n,x}+1/2)+k_y(\tau_{n,y}-1/2)]} + c. c. \\
= \lambda''_\alpha Q_A^{(\sigma)} \psi^{(A,\sigma)}_{\alpha\pi} e^{-i(-k_x)N_x+k_yN_y+(k_y(\tau_{n,y}-k_x\tau_{n,z})+(k_x-k_y)/2} + c. c. ,
\] (46)

where now \(\tau_\pi = m_x^R \tau_n\), so that
\[
\bar{1} = 3 , \quad \bar{2} = 4 , \quad \bar{3} = 1 , \quad \bar{4} = 2 , \quad \bar{5} = 8 , \quad \bar{6} = 7 , \quad \bar{7} = 6 , \quad \bar{8} = 5 .
\] (47)

Equation (46) is of the form
\[
M_\alpha(N_x, N_y, N_z; \tau_n)' = Q^{(\sigma)}_{-B} e^{-i[-k_B \cdot (N+\tau_n)]} \psi^{(-B,\sigma)} + c. c. .
\] (48)

Thus we have
\[
Q^{(\sigma)}_{-B} = m_x Q^{(\sigma)}_{-B} = \rho_\sigma Q_A^{(\sigma)} e^{-i(k_x-k_y)/2} , \quad \psi^{(-B,\sigma)} = \rho_\sigma \psi^{(A,\sigma)}_{\alpha\pi} \lambda''_\alpha .
\] (49)
Comparing Eqs. (40) and (50) we require that \( \rho \) be \( \pm 1 \) is because \( \Psi^{(B,\sigma)} \) was already fixed by Eqs. (40) and (41). Accordingly, here we have to choose the sign of \( \rho \) to be consistent with our previous definition of \( \Psi^{(B,\sigma)} \). Using Eq. (47) and taking \( \Psi^{(A,\sigma)} \) from Table II we find that Eq. (49) gives

\[
\rho_1 \lambda_1 \Psi^{(A,1)}_{\sigma \alpha} = \Psi^{(B,1)}_{\sigma \alpha} = \Psi^{(-B,1)}_{\sigma \alpha} 
\]

\[
\rho_2 \lambda_2 \Psi^{(A,2)}_{\sigma \alpha} = \Psi^{(B,2)}_{\sigma \alpha} = \Psi^{(-B,2)}_{\sigma \alpha} 
\]

Comparing Eqs. (40) and (50) we require that \( \rho_1 \lambda_1 = \lambda_1 \mu_\alpha \) which gives \( \rho_1 = +1 \). Comparing Eqs. (41) and (51) we require that \( \rho_2 \lambda_2 = \lambda_2 \mu_\alpha \) which gives \( \rho_2 = +1 \). The final result is that in terms of the order parameter vector \( \vec{Q}_\sigma \) introduced in Eq. (20), we have \( m_x \vec{Q}_\sigma = M_\sigma (m_x) \vec{Q}_\sigma \), with

\[
M_\sigma (m_x) = \begin{bmatrix}
0 & 0 & 0 & e^{i(k_x + k_y)/2} \\
0 & 0 & e^{i(k_x - k_y)/2} & 0 \\
0 & e^{-i(k_x + k_y)/2} & 0 & 0 \\
e^{-i(k_x - k_y)/2} & 0 & 0 & 0
\end{bmatrix}
\]

In Eq. (49) we have explicitly calculated the (4,1) matrix element of the matrix \( M_\sigma (m_x) \). The other matrix elements can be obtained by suitably changing the sign(s) of the components of the wave vector(s).

### E. TRANSFORMATION BY 2z

We write for irrep \( \sigma = 1 \) and wave vector \( \vec{k}_A \) under transformation by 2z

\[
M_\alpha (N_x, N_y, N_z; \tau_n) = \lambda^{m}_\alpha \left[ \frac{2^R}{2z} \right]^{-1} \left[ N_x, N_y, N_z; \tau_n \right] 
\]

\[
= \lambda^{m}_\alpha \left[ \frac{2^R}{2z} \right]^{-1} \Psi^{(A,1)}_{\sigma \alpha} e^{-i k_A \cdot [2^R(1) - 1]} [N + \tau_n] \vec{Q}_A^{(1)} + \text{c. c.} 
\]

\[
= \lambda^{m}_\alpha \Psi^{(A,1)}_{\sigma \alpha} e^{-i k_x [N_x + \tau_{nx} + 1/2] - i k_y [N_y - \tau_{ny}]} \vec{Q}_A^{(1)} + \text{c. c.} 
\]

\[
= \lambda^{m}_\alpha \Psi^{(A,1)}_{\sigma \alpha} e^{-i(k_x) [N_x + \tau_{nx} - 1/2] - i(k_y) [N_y + \tau_{ny}]} \vec{Q}_A^{(1)} + \text{c. c.} 
\]

\[
= \lambda^{m}_\alpha \Psi^{(A,1)}_{\sigma \alpha} e^{-i(k_x) [N_x + \tau_{nx} - 1/2] - i(k_y) [N_y + \tau_{ny}]} \vec{Q}_A^{(1)} + \text{c. c.} 
\]

(53)
where $\bar{1} = 2$, $\bar{3} = 4$, $\bar{5} = 8$, $\bar{6} = 7$, and the inverse relations also hold, so that $\Psi_{\alpha_\pi}^{(A,1)} = \mu_\alpha \Psi_{\alpha\pi}^{(A,1)*}$. Also $\lambda''_\alpha = (-1, -1, +1)$, so that $\lambda''_\alpha = \mu_\alpha$. Thus Eq. (53) is of the form

$$M_\alpha(N_x, N_y, N_z; \tau_n)' = Q_{-A}^{(1)*} e^{-i[(\bar{k}_x)(N_x + \tau_{nx}) + (\bar{k}_y)(N_y + \tau_{ny})]} \ ,$$

with

$$Q_{-A}^{(1)*} = 2 \cdot Q_{-A}^{(1)} = Q_A^{(1)} e^{-ik_x/2} \ , \quad \Psi_{\alpha\pi}^{(-A,1)} = \lambda''_\alpha \Psi_{\alpha\pi}^{(A,1)} = \Psi_{\alpha\pi}^{(A,1)*} \ ,$$

in agreement with Eq. (11). Since $Q_{-B}^{(1)}$ has the same value of $k_x$, the above result implies that

$$Q_{-B}^{(1)*} = 2 \cdot Q_{-B}^{(1)} = Q_B^{(1)} e^{-ik_x/2} .$$

The transformation properties of $Q_X^{(1)}$ are obtained from those of $Q_{-X}^{(1)}$ by changing the sign of $k$. A similar analysis for irrep 2 (but with $\Psi_{\alpha\pi}^{(A,2)} = -\mu_\alpha \Psi_{\alpha\pi}^{(A,2)*}$) leads to the final result that $2 \cdot \bar{Q}_\sigma = M(2z) \bar{Q}_\sigma$, with

$$M_\sigma(2z) = (-1)^{\sigma+1} \begin{bmatrix} 0 & 0 & e^{ik_x/2} & 0 \\ 0 & 0 & 0 & e^{ik_x/2} \\ e^{-ik_x/2} & 0 & 0 & 0 \\ 0 & e^{-ik_x/2} & 0 & 0 \end{bmatrix} .$$

F. TRANSFORMATION BY OTHER OPERATIONS

Here we record the result for translation. For instance, apply Eq. (12) to the magnetization when the transformation operator is a translation $T$ through a lattice vector:

$$[M(N + \tau_n)]' = T^S M \left( [T^R]^{-1} [N + \tau_n] \right) \ ,$$

This gives, for translation $T$:

$$[M(N + \tau_n)]' = [M(N - T + \tau_n)]$$

$$= e^{i k \cdot T} [M(N + \tau_n)] .$$
When the translation $T$ is through an integer number of lattice constants in the three lattice directions, $N_x, N_y, N_z$, we write
\[
M_\sigma(T_{N_x,N_y,N_z}) = 
\begin{bmatrix}
  e^{i(k_xN_x+k_yN_y)} & 0 & 0 & 0 \\
  0 & e^{i(k_xN_x-k_yN_y)} & 0 & 0 \\
  0 & 0 & e^{i(-k_xN_x-k_yN_y)} & 0 \\
  0 & 0 & 0 & e^{i(-k_xN_x+k_yN_y)}
\end{bmatrix} . \tag{60}
\]

G. COMPOSITION RULES

If $O^{(1)}$ and $O^{(2)}$ are two operators, then we might write that
\[
O^{(1)} O^{(2)} (\tilde{Q}_\sigma)_n \equiv O^{(1)} \left[ O^{(2)} (\tilde{Q}_\sigma)_n \right] = O^{(1)} \left[ \sum_m \left( M_\sigma(O^{(2)}) \right)_{nm} (\tilde{Q}_\sigma)_m \right] \\
= \sum_m \sum_s \left( M_\sigma(O^{(2)}) \right)_{nm} \left( M_\sigma(O^{(1)}) \right)_{ms} (\tilde{Q}_\sigma)_s \\
\equiv \sum_s M_\sigma \left( O^{(1)} O^{(2)} \right)_{ns} (\tilde{Q}_\sigma)_s , \tag{61}
\]
from which we might conclude that
\[
M_\sigma(O^{(1)} O^{(2)}) = M_\sigma(O^{(2)}) M_\sigma(O^{(1)}) . \tag{62}
\]

One reason this result is wrong is that the first equation of Eq. (61) interprets $O^{(1)} O^{(2)} (\tilde{Q}_\sigma)_n$ to mean $O^{(1)}[O^{(2)}(\tilde{Q}_\sigma)_n]$, whereas Eq. (62) interprets it to mean $[O^{(1)} O^{(2)}](\tilde{Q}_\sigma)_n$. Another problem is that up to now, the operators $O^{(n)}$ operate on order parameters and not on each other. This situation is discussed in detail by Wigner. Instead we assert that
\[
M_\sigma(O^{(1)} O^{(2)}) = M_\sigma(O^{(1)}) M_\sigma(O^{(2)}) . \tag{63}
\]

As an example of Eq. (63) consider the relation from Eq. (1) that $2z = m_y m_x \neq m_x m_y$. Then, according to Eq. (63) we should have
\[
M_\sigma(2z) = M_\sigma(m_y) M_\sigma(m_x) \neq M_\sigma(m_x) M_\sigma(m_y) , \tag{64}
\]
which the reader can verify using Eqs. (57), (43), and (52).
IV. LANDAU FREE ENERGY

A. MINIMAL (UNCOPPELED) MODEL FOR ORDER PARAMETERS

We start by describing the symmetry of the model when the order parameters $X_1$ and $X_3$ at zero wave vector and $Q^{(σ)}_X$ at wave vector $k_X$ are not coupled to one another. We can imagine that ordering has developed via consecutive continuous transitions, as might happen for a suitable set of parameters having the same symmetry as MGO, but quite different in detail. Although this is not the experimental scenario, it will provide a correct description of the symmetries of the phase. Thus we imagine $X_1$ and $X_2$ to be governed by a free energy

$$ F_1, 3 = a_1(T - T_1)X_1^2 + u_1X_1^4 + a_3(T - T_3)X_3^2 + u_3X_3^4 , \quad (65) $$

and similarly the incommensurate order parameters to be governed by a free energy, the simplest form of which is

$$ F_X = a_{X,1}(T - T_1)(|Q^{(1)}_A|^2 + |Q^{(1)}_B|^2) + a_{X,2}(T - T_2)(|Q^{(2)}_A|^2 + |Q^{(2)}_B|^2) + O(|Q|^4) . \quad (66) $$

We point out that within such a simple theory and barring an unphysical accidental degeneracy, $Q^{(σ=1)}_X$ and $Q^{(σ=2)}_X$ would not have the same wave vector because the exchange interactions are never exactly isotropic in an orthorhombic crystal.

However, if the equilibrium value of the two wave vectors are almost equal in a simple approximation, then there are terms in the Landau free energy which lock the two wave vectors into equality\textsuperscript{21} and we assume this to be the case here. Then the nature of the ordered phase is dictated by the form of the quartic and higher order terms of the Landau free energy. Consider, for example, the quartic terms. In the space of $Q_A$ and $Q_B$ there are isotropic terms

$$ ΔF = \sum_σ u_σ \left[ |Q_A^{(σ)}|^2 + |Q_B^{(σ)}|^2 \right] . \quad (67) $$

This term would allow for an arbitrary superposition of both wave vectors, $k_A$ and $k_B$ within a single domain. However, it has been shown\textsuperscript{11} that each domain contains only a single wave vector. That indicates that the free energy includes the term

$$ ΔF = \sum_{σσ'} B_{σσ'}|Q_A^{(σ)}|^2|Q_B^{(σ')}|^2 . \quad (68) $$
TABLE VI: SYMMETRY OF THE BUILDING BLOCKS

| Operator | Transforms like |
|----------|----------------|
| $F_1 = X_1X_3$ | $m_xm_y$ |
| $F_2 = i\left[Q_A^{(1)}Q_A^{(2)*} - Q_A^{(1)*}Q_A^{(2)} - Q_B^{(1)}Q_B^{(2)*} + Q_B^{(1)*}Q_B^{(2)}\right]$ | $m_z$ |
| $F_3 = i\left[Q_A^{(1)}Q_A^{(2)*} - Q_A^{(1)*}Q_A^{(2)} + Q_B^{(1)}Q_B^{(2)*} - Q_B^{(1)*}Q_B^{(2)}\right]$ | $m_xm_ym_z$ |
| $F_4 = |Q_A^{(1)}|^2 - |Q_B^{(1)}|^2$ | $m_xm_y$ |
| $F_5 = |Q_A^{(2)}|^2 - |Q_B^{(2)}|^2$ | $m_z$ |
| $F_6 = P_z$ | $m_z$ |

which strongly disfavors having two wave vectors simultaneously present when $B_{\sigma\sigma'}$ is large and positive. Finally, we point out that we expect terms in the free energy to prevent irreps from having the same phase. At positions where one irrep is maximal, there is usually less phase space into which the other irrep can condense. This argument is reflected by the term:

$$\Delta F = A \sum_{X \leftrightarrow A,B} \left(Q_X^{(1)}[Q_X^{(2)*}]^2 + [Q_X^{(1)*}Q_X^{(2)}]^2\right)^2,$$

with $A > 0$. This term is proportional to $\cos^2(\Delta \phi)$, where $\Delta \phi$ is the phase difference between the complex-valued order parameters of the two irreps. We expect $A$ to be large and positive, in which case $\Delta \phi = \pm \pi/2$ is strongly favored. The effects we attribute here to quartic terms could equally well be attributed to higher order terms of similar symmetry.

B. COUPLING TERMS IN THE FREE ENERGY

Before proceeding to higher order we emphasize that we only want to enumerate the lowest order terms which have each possible allowed symmetry. To construct such higher than quadratic order terms which are allowed by symmetry, we formulate the following rules. Rule 1: we do not allow a term which includes a factor which itself transforms like unity, such as $X_n^2$ or $|Q_X^{(\sigma)}|^2$, because the term without this factor should already be in our list of allowed terms. Such terms do not lead to a different symmetry. They only make a quantitative change in the response of the system. Rule 2: Due to translational invari-
ance, an allowed term must conserve wave vector. In view of Rule 1, this rule implies that the incommensurate order parameters can only occur in the combination $Q^{(σ)}_X [Q^{(σ')}_X]^*$.  

Rule 3: due to time reversal invariance any term must contain an even number of magnetic order parameters. In view of the previous rules, $X_1$ and $X_3$ can only occur in the product $X_1X_3$. To summarize: the allowed building blocks for invariants are a) $X_1X_3$, b) $i(Q^{(1)}_X [Q^{(2)}_X]^* – [Q^{(1)}_X]^* Q^{(2)}_X)$, c) $|Q^{(σ)}_A|^2 – |Q^{(σ)}_B|^2$, d) components of the electric polarization, $P$ or magnetization $M$. Similar terms in which $P$ is replaced by the applied electric field or $M$ is replaced by the applied magnetic field are also possible, but are not considered here.

Note: the term $(Q^{(1)}_X [Q^{(2)}_X]^* + [Q^{(1)}_X]^* Q^{(2)}_X)$ is excluded by the potential of Eq. (69). In Table VI we list the symmetry of the various building blocks. To verify these results use Eqs. (33), (43), and (52) to write

$$m_x Q^{(1)}_A Q^{(2)*}_A = Q^{(1)*}_B Q^{(2)}_B, \quad m_x Q^{(1)}_B Q^{(2)*}_B = Q^{(1)*}_A Q^{(2)}_A,$$

$$m_y Q^{(1)}_A Q^{(2)*}_A = -Q^{(1)*}_B Q^{(2)}_B, \quad m_y Q^{(1)}_B Q^{(2)*}_B = -Q^{(1)*}_A Q^{(2)}_A,$$

$$m_z Q^{(1)}_A Q^{(2)*}_A = -Q^{(1)*}_A Q^{(2)}_A, \quad m_z Q^{(1)}_B Q^{(2)*}_B = -Q^{(1)*}_B Q^{(2)}_B.$$  \hfill (70)

One can check that, in agreement with Table VI,

$$m_x F_2 = m_y F_2 = -m_z F_2 = F_2, \quad m_x F_3 = m_y F_3 = m_z F_3 = -F_3.$$  \hfill (71)

The simplest invariant is

$$U = aF_2 F_6 = ia \left[ Q^{(1)}_A Q^{(2)*}_A – Q^{(1)*}_A Q^{(2)}_A – Q^{(1)*}_B Q^{(2)}_B + Q^{(1)}_B Q^{(2)*}_B \right] P_z,$$  \hfill (72)

which is the usual trilinear magnetoelastic interaction which induces a nonzero equilibrium value of $P_z$.  

Then we have the invariants

$$V_1 = b_1 F_1 F_4 = b_1 X_1 X_3 \left[ |Q^{(1)}_A|^2 – |Q^{(1)}_B|^2 \right]$$  \hfill (73)

$$V_2 = b_2 F_1 F_5 = b_2 X_1 X_3 \left[ |Q^{(2)}_A|^2 – |Q^{(2)}_B|^2 \right].$$  \hfill (74)

In principle we could also list $F_4 F_5$. But when each domain only has a single wave vector, this term is not interesting. Finally we have $W \equiv F_1 F_3 F_6$:

$$W = ic X_1 X_3 P_z \left[ Q^{(1)}_A Q^{(2)*}_A – Q^{(1)*}_A Q^{(2)}_A + Q^{(1)*}_B Q^{(2)}_B – Q^{(1)}_B Q^{(2)*}_B \right].$$  \hfill (75)
Again, we omit the terms $F_3 F_4 F_5$ and $F_3 F_5 F_6$ because when each domain only has a single wave vector, these interactions are not interesting. The consequences of the potentials $U$, $V$, and $W$ for the switching behavior of MGO are discussed in detail in Ref. 11.

We should also note the existence of the invariant

$$Y = eX_1X_3 + \sum_\sigma f_\sigma \left( |Q_\sigma^A|^2 - |Q_\sigma^B|^2 \right) P_x P_y.$$ (76)

This term shows that in this phase the electric susceptibility tensor has off-diagonal $x$-$y$ elements induced by the magnetic ordering which depend on the wave vector of the domain and on $X_3$, the $z$-component of magnetization.

C. EQUILIBRIUM PHASES

In this section we minimize the free energy including coupling terms and thereby determine the various equilibrium domains that are possible. This discussion is not equivalent to discussing the switching between equilibrium states. To illustrate the difference between these two analyses consider the following two scenarios. In scenario I, one simply cools into the lowest temperature phase and then asks if there is any correlation between the orientation of the net magnetization and that of the net ferroelectric polarization: i.e. in any arbitrarily selected domain are these two collinear vectors always parallel or always antiparallel to one another? The experimental answer is “no”:\footnote{12} in some domains the two vectors are parallel and in other domains they are antiparallel. In scenario II, one asks a different question: if the magnetic field is used to reverse the direction of the magnetization in a domain, will that always cause the direction of the ferroelectric polarization in that domain to reverse? The experimental answer to that question is “yes.”\footnote{11}

Here we only consider the equilibrium properties and we rely on the experimental observation that each domain contains only one of the two possible wave vectors.\footnote{11} So we have therefore two choices for domains: they have either wave vector $\pm k_A$ or wave vector $\pm k_B$. We assume that the magnitudes of the order parameters $Q_X^{(\sigma)}$ are fixed by the terms in the free energy which only depend on these variables, and domains A and B are related by $|Q_A^{(\sigma)}| = |Q_B^{(\sigma)}|$. We assume that the magnitudes of $X_1$ and $X_3$ (but not their algebraic signs) are similarly fixed. When we minimize the $U$, $V$, and $W$ terms it is obvious that we will only be able to determine the product of $X_1$ and $X_3$. Accordingly, we will have domains in
which the sign and magnitude of $X_1X_3$ is determined so as to minimize the free energy, but
the algebraic sign of $X_3$, the magnetization, can be chosen arbitrarily while keeping the sign
of the product $X_1X_3$ fixed. Finally, since the free energy clearly does not depend on the
sign of the ferroelectric polarization, $P_z$, we will have domains with either sign of $P_z$. So in
all, these three independent binary choices gives rise to eight possible distinct domains, as
already noted in Ref. [11].

Accordingly, for a domain of wave vector $k_X$ we introduce the variables $\eta_X$ and $\zeta_X$ by

$$
\eta_X \equiv X_1X_3/|X_1X_3|, \quad Q_X^{(1)}/Q_X^{(2)*} - Q_X^{(1)*}/Q_X^{(2)} = 2i\zeta_X |Q_X^{(1)}Q_X^{(2)}|
$$

so that in the domain of $k_X$ $\eta_X = \pm 1$ is the phase of the staggered magnetization relative
to that of the ferromagnetic moment and $\zeta_X = \pm 1$ is the phase of $Q_X^{(1)}$ relative that of $Q_X^{(2)}$
in units of $\pi/2$ (which is the definition of the helicity). We first consider the situation in the
domain of wave vector $k_A$. There we have the free energy

$$
F_A \equiv U + V_1 + V_2 + W = -2aP_z\zeta_A|Q_A^{(1)}Q_A^{(2)}| + \eta_A \left[b_1|Q_A^{(1)}|^2 + b_2|Q_A^{(2)}|^2\right]|X_1X_3|
-2c\eta_A P_z|X_1X_3||Q_A^{(1)}Q_A^{(2)}| + \frac{1}{2\chi_E}P_z^2,
$$

where we have now included the free energy due to the polarization in terms of the electric
polarizability $\chi_E$. We minimize the free energy $F_A$ with respect to $P_z$, so that

$$
\chi_E^{-1}P_z = 2\zeta_A \left(a + c\eta_A|X_1X_3|\right)|Q_A^{(1)}Q_A^{(2)}|,
$$

in which case the equilibrium free energy becomes (since $\zeta_A^2 = 1$)

$$
F_A = -2\chi_E \left(a + c\eta_A|X_1X_3|\right)^2|Q_A^{(1)}Q_A^{(2)}|^2
+ \eta_A \left[b_1|Q_A^{(1)}|^2 + b_2|Q_A^{(2)}|^2\right]|X_1X_3|.
$$

As expected, $F_A$ does not depend on the sign of the helicity $\zeta_A$ which determines the sign of
$P_z$. We need to minimize this with respect to $\eta_A$. We write

$$
F_A = -2\chi_E \left(a^2 + c^2|X_1X_3|^2\right)|Q_A^{(1)}Q_A^{(2)}|^2
+ \eta_A |X_1X_3| \left(b_1|Q_A^{(1)}|^2 + b_2|Q_A^{(2)}|^2 - 4\chi_Eca|Q_A^{(1)}Q_A^{(2)}|^2\right),
$$

so that $\eta_A = -\mathcal{R}_A/|\mathcal{R}_A|$, where

$$
\mathcal{R}_X = b_1|Q_X^{(1)}|^2 + b_2|Q_X^{(2)}|^2 - 4\chi_Eca|Q_X^{(1)}Q_X^{(2)}|^2,
$$

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where $X$ is either $A$ or $B$. Thus in a domain of wave vector $\mathbf{k}_A$

$$\chi_E^{-1} P_z = 2\zeta_A (a - cR_A |X_1X_3/R_A|) |Q_A^{(1)} Q_A^{(2)}|.$$  

The analysis for wave vector $\mathbf{k}_B$ is similar and yields the result

$$\chi_E^{-1} P_z = -2\zeta_A (a - cR_B |X_1X_3/R_B|) |Q_B^{(1)} Q_B^{(2)}|.$$  

All domains have the same magnitude of $P_z$, but its sign varies from domain to domain.

To summarize: each domain is characterized by 1) the axis of the wave vector, $\hat{k}_A$ or $\hat{k}_B$, 2) the sign of $P_z$ [or equivalently, according to Eq. (79), the sign of the helicity $\zeta_X$], and 3) the sign of the net magnetization along $\hat{c}$. But all domains are symmetry-related to one another.

V. CONCLUSIONS

Many of our results for the system Mn$_2$GeO$_4$ (MGO) have useful analogs for other non-collinear magnetic incommensurate systems. For instance, note the way we simplified the output of ISODISTORT in the Appendix A. Secondly, the case of MGO illustrates how one introduces order parameters as the amplitudes of the magnetic “modes.” This formulation is reminiscent of the description of lattice vibration in terms of normal modes amplitudes and the symmetry analysis that follows here parallels that of phonon modes. A significant advantage of introducing order parameters is that they conveniently carry with them the symmetry properties of the modes. In the usual scenario involving magnetic order parameters, the symmetry is trivial. Here in a more complex setting, the analysis is more involved and one has to keep track of what is called here the “wave function.” The wave function gives meaning to the order parameters. This end result is well illustrated by the application of the results of this paper to the switching phenomena described in Ref. [11].

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Appendix A: Modes for $k_A$

1. Modes for Irreps $D^{(1)}$ and $D^{(2)}$

In Tables VII and VIII we show the modes for irrep $D^{(1)}$ for $k_A = (k_x, k_y, 0)$. Table IX and X give the analogous data for irrep $D^{(2)}$. From these tables (taken from ISODISTORT) we obtain the magnetization distribution throughout a domain for irrep $\sigma$ as

$$M(N + \tau_n) = m^{(\sigma)}(\tau_n)e^{i\chi - ik(N + \tau_n)} + \text{c. c.} \ . \quad (A1)$$

We allow the modes to have an arbitrary overall phase factor, $\exp(i\chi)$, because the origin of the incommensurate excitation is arbitrary. We now write the results of ISODISTORT given in Tables I and II in a simpler, but equivalent form. For irrep $D^{(1)}$ for the ch sites we make the cosmetic replacement

$$m^{(1)}_\alpha(\tau_1) = a_\alpha , \quad m^{(1)}_\alpha(\tau_2) = \mu_\alpha a_\alpha , \quad m^{(1)}_\alpha(\tau_3) = b_\alpha , \quad m^{(1)}_\alpha(\tau_4) = \mu_\alpha b_\alpha , \quad (A2)$$

where $(\mu_x, \mu_y, \mu_z) = (-1, -1, +1)$. For the pl sites, the situation is more complicated. Table VIII gives the terms from ISODISTORT which depend on $Z_3$ and $Z_4$ as

$$m^{(1)}_x(\tau_5) = (Z_3 - iZ_4)e^{i\phi} , \quad m^{(1)}_x(\tau_6) = -(Z_3 - iZ_4)e^{i\phi} ,$$

$$m^{(1)}_x(\tau_7) = (Z_3 + iZ_4)e^{-i\phi} , \quad m^{(1)}_x(\tau_8) = -(Z_3 + iZ_4)e^{-i\phi} . \quad (A3)$$

Note that this is a parametrization in terms of three parameters. However, this is an over-parametrization: if $\phi$ is arbitrarily varied, $m_x$ can remain unchanged by a suitable rotation in the complex $(Z_3, Z_4)$ plane. Accordingly, we reproduce these results via a two-parameter representation in terms of the complex-valued variable $z_x = (Z_3 - iZ_4)e^{i\phi}$, so that

$$m^{(1)}_x(\tau_5) = z_x , \quad m^{(1)}_x(\tau_6) = -z_x , \quad m^{(1)}_x(\tau_7) = z_x^* , \quad m^{(1)}_x(\tau_8) = -z_x^* . \quad (A4)$$

Similarly, we can reproduce the results of Table VIII from ISODISTORT for $m_y$ on the pl sites by setting $z_y = (Z_1 - iZ_2)e^{i\phi}$ in which case

$$m^{(1)}_y(\tau_5) = (Z_1 - iZ_2)e^{i\phi} = z_y , \quad m^{(1)}_y(\tau_6) = -(Z_1 - iZ_2)e^{i\phi} = -z_y ,$$

$$m^{(1)}_y(\tau_7) = (Z_1 + iZ_2)e^{-i\phi} = z_y^* , \quad m^{(1)}_y(\tau_8) = -(Z_1 + iZ_2)e^{-i\phi} = -z_y^* , \quad (A5)$$
TABLE VII: Structure of the six modes for $k = k_A \equiv (0.138, 0.211, 0)^{16}$ irrep $D^{(1)}$, for ch sites $\tau_1$ - $\tau_4$ from ISODISTORT for space group Pnma = No. 62 in Ref. 18. The magnetic moment distribution is $M(R + \tau_n) = e^{-i\mathbf{k} \cdot (R + \tau_n)}m(\tau_n)$, where the first column lists the real-valued amplitudes which give $m(\tau_n)$, where the $m(\tau_n)$ are listed in the form $(R, \theta) \equiv R \exp(i\theta)$. An arbitrary overall phase, the same for ch and pl sites, is not included in these tables.

| AMP | $m_x$ | $m_y$ | $m_z$ | $m_x$ | $m_y$ | $m_z$ |
|-----|-------|-------|-------|-------|-------|-------|
| $Y_1$ | $\tau_1$ | (1, 0) | (0, 0) | (0, 0) | $\tau_2$ | (1, 180) | (0, 0) | (0, 0) |
| $Y_2$ | $\tau_3$ | (1, 0) | (0, 0) | (0, 0) | $\tau_4$ | (1, 180) | (0, 0) | (0, 0) |
| $Y_3$ | $\tau_1$ | (0, 0) | (1, 0) | (0, 0) | $\tau_2$ | (0, 0) | (1, 180) | (0, 0) |
| $Y_4$ | $\tau_3$ | (0, 0) | (1, 180) | (0, 0) | $\tau_4$ | (0, 0) | (1, 0) | (0, 0) |
| $Y_5$ | $\tau_1$ | (0, 0) | (0, 0) | (1, 0) | $\tau_2$ | (0, 0) | (0, 0) | (1, 0) |
| $Y_6$ | $\tau_3$ | (0, 0) | (0, 0) | (1, 180) | $\tau_4$ | (0, 0) | (0, 0) | (1, 180) |

a) We will reparametrize: $Y_6 \rightarrow -Y_6$ and $Y_4 \rightarrow -Y_4$, so that these phases are regularized.

and for $M_z$ on the pl sites by setting $z_z = (Z_5 - iZ_6)e^{i\phi}$ in which case

$$ m_z^{(1)}(\tau_5) = (Z_5 - iZ_6)e^{i\phi} = z_z \, , \quad m_z^{(1)}(\tau_6) = (Z_5 - iZ_6)e^{i\phi} = z_z \, , $$

$$ m_z^{(1)}(\tau_7) = (Z_5 + iZ_6)e^{-i\phi} = z_z^* \, , \quad m_z^{(1)}(\tau_8) = (Z_5 + iZ_6)e^{-i\phi} = z_z^* \, , $$

(A6)

Similar identifications are mode for irrep $D^{(2)}$ and we obtain Eqs. (5) and (6).

**Appendix B: TEMPERATURE DEPENDENCE OF MODES**

Look at Eq. (4). There one sees that each mode involves 12 real parameters. Thus, there are actually 11 additional modes having the same symmetry as the mode we focus upon. Thus we introduce corresponding mode amplitudes $Q_n$, with $n = 1, 12$, where the free energy at quadratic order due to the irrep in question in the disordered phase is

$$ F = \sum_{n=1}^{12} F_n(T_n - T)|Q_n|^2 \, , $$

(B1)

where $T_1$ is the largest $T_n$, so that the mode labeled “1” is the one that first condenses as the temperature is lowered. To study the mean-field temperature-dependence for $T$ just below
TABLE VIII: As Table VII. Mode structure for \( \mathbf{k} = (0.138, 0.211, 0) \), irrep \( D^{(1)} \), for pl sites. ISODISTORT sets \( \phi = 327.55 \), but as we discuss, this value has no significance.

| AMP  | \( m_x \) | \( m_y \) | \( m_z \) | \( m_x \) | \( m_y \) | \( m_z \) |
|------|-----------|-----------|-----------|-----------|-----------|-----------|
| \( Z_1 \) | \( \tau_5 \) | (0, 0) | (1, \( \phi \)) | (0, 0) | \( \tau_6 \) | (0, 0) | (1, \( \phi - 180 \)) | (0, 0) |
|       | \( \tau_7 \) | (0, 0) | (1, 360 - \( \phi \)) | (0, 0) | \( \tau_8 \) | (0, 0) | (1, 540 - \( \phi \)) | (0, 0) |
| \( Z_2 \) | \( \tau_5 \) | (0, 0) | (1, \( \phi - 90 \)) | (0, 0) | \( \tau_6 \) | (0, 0) | (1, \( \phi - 270 \)) | (0, 0) |
|       | \( \tau_7 \) | (0, 0) | (1, 450 - \( \phi \)) | (0, 0) | \( \tau_8 \) | (0, 0) | (1, 630 - \( \phi \)) | (0, 0) |
| \( Z_3 \) | \( \tau_5 \) | (1, \( \phi \)) | (0, 0) | (0, 0) | \( \tau_6 \) | (1, \( \phi - 180 \)) | (0, 0) | (0, 0) |
|       | \( \tau_7 \) | (1, 360 - \( \phi \)) | (0, 0) | (0, 0) | \( \tau_8 \) | (1, 540 - \( \phi \)) | (0, 0) | (0, 0) |
| \( Z_4 \) | \( \tau_5 \) | (1, \( \phi - 90 \)) | (0, 0) | (0, 0) | \( \tau_6 \) | (1, \( \phi - 270 \)) | (0, 0) | (0, 0) |
|       | \( \tau_7 \) | (1, 450 - \( \phi \)) | (0, 0) | (0, 0) | \( \tau_8 \) | (1, 630 - \( \phi \)) | (0, 0) | (0, 0) |
| \( Z_5 \) | \( \tau_5 \) | (0, 0) | (0, 0) | (1, \( \phi \)) | \( \tau_6 \) | (0, 0) | (0, 0) | (1, \( \phi \)) |
|       | \( \tau_7 \) | (0, 0) | (0, 0) | (1, 360 - \( \phi \)) | \( \tau_8 \) | (0, 0) | (0, 0) | (1, 360 - \( \phi \)) |
| \( Z_6 \) | \( \tau_5 \) | (0, 0) | (0, 0) | (1, \( \phi - 90 \)) | \( \tau_6 \) | (0, 0) | (0, 0) | (1, \( \phi - 90 \)) |
|       | \( \tau_7 \) | (0, 0) | (0, 0) | (1, 450 - \( \phi \)) | \( \tau_8 \) | (0, 0) | (0, 0) | (1, 450 - \( \phi \)) |

TABLE IX: As Table VII. Mode structure for \( \mathbf{k} = (0.138, 0.211, 0) \) for irrep \( D^{(2)} \)

| AMP  | \( m_x \) | \( m_y \) | \( m_z \) | \( m_x \) | \( m_y \) | \( m_z \) |
|------|-----------|-----------|-----------|-----------|-----------|-----------|
| \( Y_1 \) | \( \tau_1 \) | (1, 270) | (0, 0) | (0, 0) | \( \tau_2 \) | (1, 270) | (0, 0) | (0, 0) |
| \( Y_2 \) | \( \tau_3 \) | (1, 270) | (0, 0) | (0, 0) | \( \tau_4 \) | (1, 270) | (0, 0) | (0, 0) |
| \( Y_3 \) | \( \tau_1 \) | (0, 0) | (1, 270) | (0, 0) | \( \tau_2 \) | (0, 0) | (1, 270) | (0, 0) |
| \( Y_4 \) | \( \tau_3 \) | (0, 0) | (1, 90) | (0, 0) | \( \tau_4 \) | (0, 0) | (1, 90) | (0, 0) |
| \( Y_5 \) | \( \tau_1 \) | (0, 0) | (0, 0) | (1, 270) | \( \tau_2 \) | (0, 0) | (0, 0) | (1, 90) |
| \( Y_6 \) | \( \tau_3 \) | (0, 0) | (0, 0) | (1, 90) | \( \tau_4 \) | (0, 0) | (0, 0) | (1, 270) |
TABLE X: As Table VII. Mode structure for \( k = (0.138, 0.211, 0) \) for irrep D\(^{(2)}\).

| AMP | \( m_x \) | \( m_y \) | \( m_z \) | \( m_x \) | \( m_y \) | \( m_z \) |
|-----|--------|--------|--------|--------|--------|--------|
| \( Z_1 \) | \( \tau_5 \) | \( (0, 0) \) | \( (1, \phi) \) | \( (0, 0) \) | \( \tau_6 \) | \( (0, 0) \) | \( (1, \phi) \) | \( (0, 0) \) |
| \( \tau_7 \) | \( (0, 0) \) | \( (1, 540 - \phi) \) | \( (0, 0) \) | \( \tau_8 \) | \( (0, 0) \) | \( (1, 540 - \phi) \) | \( (0, 0) \) |
| \( Z_2 \) | \( \tau_5 \) | \( (0, 0) \) | \( (1, \phi - 90) \) | \( (0, 0) \) | \( \tau_6 \) | \( (0, 0) \) | \( (1, \phi - 90) \) | \( (0, 0) \) |
| \( \tau_7 \) | \( (0, 0) \) | \( (1, 630 - \phi) \) | \( (0, 0) \) | \( \tau_8 \) | \( (0, 0) \) | \( (1, 630 - \phi) \) | \( (0, 0) \) |
| \( Z_3 \) | \( \tau_5 \) | \( (1, \phi) \) | \( (0, 0) \) | \( (0, 0) \) | \( \tau_6 \) | \( (1, \phi) \) | \( (0, 0) \) | \( (0, 0) \) |
| \( \tau_7 \) | \( (1, 540 - \phi) \) | \( (0, 0) \) | \( (0, 0) \) | \( \tau_8 \) | \( (1, 540 - \phi) \) | \( (0, 0) \) | \( (0, 0) \) |
| \( Z_4 \) | \( \tau_5 \) | \( (1, \phi - 90) \) | \( (0, 0) \) | \( (0, 0) \) | \( \tau_6 \) | \( (1, \phi - 90) \) | \( (0, 0) \) | \( (0, 0) \) |
| \( \tau_7 \) | \( (1, 630 - \phi) \) | \( (0, 0) \) | \( (0, 0) \) | \( \tau_8 \) | \( (1, 630 - \phi) \) | \( (0, 0) \) | \( (0, 0) \) |
| \( Z_5 \) | \( \tau_5 \) | \( (0, 0) \) | \( (0, 0) \) | \( (1, \phi) \) | \( \tau_6 \) | \( (0, 0) \) | \( (0, 0) \) | \( (1, \phi - 180) \) |
| \( \tau_7 \) | \( (0, 0) \) | \( (0, 0) \) | \( (1, 540 - \phi) \) | \( \tau_8 \) | \( (0, 0) \) | \( (0, 0) \) | \( (1, 360 - \phi) \) |
| \( Z_6 \) | \( \tau_5 \) | \( (0, 0) \) | \( (0, 0) \) | \( (1, \phi - 90) \) | \( \tau_6 \) | \( (0, 0) \) | \( (0, 0) \) | \( (1, \phi - 270) \) |
| \( \tau_7 \) | \( (0, 0) \) | \( (0, 0) \) | \( (1, 630 - \phi) \) | \( \tau_8 \) | \( (0, 0) \) | \( (0, 0) \) | \( (1, 450 - \phi) \) |

At \( T_1 \) we go to higher order:

\[
F = -a_1(T_1 - T)|Q_1|^2 + \sum_{n>1}(T_n - T)|Q_n|^2 + u|Q_1|^4 + V , \tag{B2}
\]

where \( T_1 < T, T_n > T \) for all \( n > 1 \), and \( u > 0 \). Thereby we find the standard result:

\[ \langle Q_1 \rangle = 0, \text{ for } T > T_1 \text{ and for } T < T_1 \]

\[ |\langle Q_1 \rangle| = \left[ a_1/(2u) \right]^{1/2} |T_1 - T|^{1/2} , \tag{B3} \]

where \( \langle \ldots \rangle \) denotes an equilibrium value. In the present case, the terms which modify the critical wave function associated with \( Q_1 \) are all even order in the order parameters. The quadratic terms are diagonal by construction of the normal modes. So the leading term which give corrections to the wave function of the critical mode is of the form

\[
V = \sum_{n>1}|Q_n|^2 \left[ c_n Q_1 Q_n^* + c_n^* Q_1^* Q_n \right] , \tag{B4}
\]

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where $c_n$ need not be real-valued. For $T < T_1$ the effect of this term is approximately the same as that of

$$V = 2 \sum_{n>1} |\langle Q_1 \rangle|^2 [c_n Q_1 Q_n^* + c_n^* Q_n^* Q_1], \quad (B5)$$

Thus we see that at quartic order there is a mixing of modes governed by the temperature dependent prefactor proportional to the equilibrium value, $|\langle Q_1 \rangle|^2$, which in mean field theory is proportional to $T_1 - T$. Of course, this mixing only takes place within the space of modes having the same symmetry as $Q_1$.

**Appendix C: PHASE FACTORS**

In this section we discuss how the definition of order parameters is subject to inclusion of arbitrary phase factors. As mentioned, this ambiguity is similar to that encountered in a two-sublattice antiferromagnet where one defines the staggered magnetization order parameter $N$ in terms of the sublattice magnetizations, either as $N = M_1 - M_2$ or as $N = M_2 - M_1$. A macroscopic observable will not depend on the sign of $N$. We now see how such a phase factor affects our analysis. Equations (41) and (42) define the wave functions $\Psi_{(B,\sigma)}^{(A,\alpha)}$. In principle we can introduce arbitrary phases $\exp(i\phi_\sigma)$ as prefactors in these definitions. It is not useful to go to that level of generality. So we will modify these definitions by writing

$$\Psi_{(B,\sigma)}^{(A,1)} = \xi_1 \lambda_\alpha \Psi_{(A,1)}^{(A,1)} = \xi_1 \lambda_\alpha [\mu_1 \beta, \mu_1 \alpha, \mu_1 \alpha; \mu_1 \alpha, \mu_1 \alpha, \mu_1 \alpha]_n,$$

$$\Psi_{(B,\sigma)}^{(A,2)} = -\xi_2 \lambda_\alpha \Psi_{(A,2)}^{(A,2)} = -\xi_2 \lambda_\alpha [\mu_2 \beta, -\mu_2 \alpha, -\mu_2 \alpha; -\mu_2 \alpha, -\mu_2 \alpha, -\mu_2 \alpha]_n. \quad (C1)$$

with each $\xi_\sigma = \pm 1$. Then, in this version of the theory we have

$$\mathcal{M}_\sigma(m_y) = (-1)^{\sigma+1} \begin{bmatrix} 0 & \xi_1 e^{ik_y/2} & 0 & 0 \\ \xi_2 e^{-ik_y/2} & 0 & 0 & 0 \\ 0 & 0 & \xi_2 e^{ik_y/2} & 0 \\ 0 & 0 & 0 & \xi_1 e^{-ik_y/2} \end{bmatrix}. \quad (C3)$$
These modification do not affect $M_\sigma(m_z)$ or $M_\sigma(2z)$ because $m_z$ and $2z$ transform wave functions into themselves. Similarly, we now have the modified result

$$M_\sigma(m_x) = (-1)^{\sigma+1} \begin{bmatrix} 0 & 0 & 0 & \xi_2 e^{i(k_x+k_y)/2} \\ 0 & 0 & \xi_1 e^{i(k_x-k_y)/2} & 0 \\ 0 & \xi_2 e^{-i(k_x+k_y)/2} & 0 & 0 \\ \xi_1 e^{-i(k_x-k_y)/2} & 0 & 0 & 0 \end{bmatrix}. \quad (C4)$$

One can verify that these choices of phase to not affect Eq. $(70)$ and thus do not affect the results for the invariant potential $U$, $V_n$, and $W$.

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23 The exact values of the nonzero components of the wave vector clearly do not influence the mode structure. The value of $k_x = 0.136$ differs slightly from $k_x = 0.138$ given in Ref. 12.