COUPLED ORDER PARAMETERS IN THE LANDAU THEORY OF PHASE TRANSITIONS IN SOLIDS

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We discuss the role of both primary and secondary order parameters in a transition between two solid phases. We show how microscopic distortions which appear at the transition can be calculated using group-theoretical methods. We also show how the form of the coupling term in the Landau free energy influences the behavior of secondary order parameters.

1 INTRODUCTION

The Landau theory (Landau and Lifshitz, 1980) forms the basis of a group-theoretical description of phase transitions in crystalline solids. In this theory, we introduce an order parameter associated with one of the irreducible representations (irreps) of the space group of the crystal's high-symmetry phase. The free energy of the crystal is then expanded in powers of that order parameter. Possible values of the order parameter at the minimum of the free energy determine the allowed space groups of the low-symmetry phase. In the original Landau theory, the free energy is expanded only to fourth degree and describes second order (continuous) phase transitions. In the "extended" Landau theory, the free energy is expanded to arbitrarily high order so that additional minima (and hence additional possible space groups of the low-symmetry phase) are included in the results. The additional subgroups result from first order (discontinuous) phase transitions.

Usually, in Landau theory, we only consider order parameters associated with a single irrep. Generally, however, order parameters associated with different irreps are coupled, causing both primary and secondary order parameters to be significant for any given phase transition. A ferroelastic phase transition is called proper if the strain transforms like the primary order parameter and is called improper if the strain transforms like a secondary order parameter.

In this paper, we discuss the relationship between primary and secondary order parameters, and we show how the form of the Landau free energy affects their behavior across the phase transition. We also show how to calculate microscopic distortions caused by these order parameters.

Many of our methods have been developed in a series of papers discussing transitions in specific materials. The description of transitions where the primary order parameter corresponds to an ordering process has been given for the grandite

garnets (Hatch and Griffen, 1989), bromoform (Hatch and Stokes, 1990), $MgSiO_3$ garnet (Hatch and Ghose, 1989a), leucite (Hatch, Ghose, and Stokes, 1990), and titanite (Ghose *et al.*, 1990). In these papers, the specific ordering distributions for the lower-symmetry phases are given as well as discussions of the secondary order parameters, including strain. Displacive and/or rotational transitions have been described for ilvaite (Ghose *et al.*, 1989), A_2BX_4 structures (Hatch, Stokes, Aleksandrov, and Misyul, 1989), anorthite (Hatch and Ghose, 1989b), $BaTiO_3$ (Hatch and Stokes, 1989), langbeinites (Hatch, Artmann, and Boerio-Goates, 1990), and cristobalite (Hatch and Ghose, 1990). Again, specific displacements and/or rotation modes are given in these papers, as well as discussions of secondary order parameter distortions. In this paper, we generalize and extend the symmetry approach taken in these previous papers.

2 PRIMARY ORDER PARAMETER

2.1 *Isotropy subgroups*

Consider a crystal with space group symmetry G. Let a phase transition in this crystal be driven by an order parameter $\boldsymbol{\eta} = (\eta_1, \eta_2, \ldots)$ associated with an irrep Γ_η of G. By "associated," we mean that if an element $g \in G$ operates on $\boldsymbol{\eta}$, the components of $\boldsymbol{\eta}$ transform in the following manner:

$$g\eta_i = \sum_j D_\eta(g)_{ij}\eta_j,$$

where $D_\eta(g)$ is the representative matrix of element g in irrep Γ_η.

Above the transition, in the high-symmetry phase, the components of $\boldsymbol{\eta}$ are all zero. As we pass through the phase transition, one or more components of $\boldsymbol{\eta}$ become nonzero. The direction of $\boldsymbol{\eta}$ below the transition determines the space group symmetry G_η of the crystal there. This space group G_η is an *isotropy subgroup* of G and consists of all elements of $g \in G$ which satisfy $g\boldsymbol{\eta} = \boldsymbol{\eta}$, i.e.,

$$\eta_i = \sum_j D_\eta(g)_{ij}\eta_j. \tag{1}$$

The order parameter which drives the phase transition and determines the symmetry of the crystal below the transition is called the primary order parameter.

As an example, consider the case of $G = Pm\bar{3}m$ and $\Gamma_\eta = R_4^+$. [The notation for irrep labels is from Miller and Love (1967) and Cracknell *et al.* (1979).] The irrep R_4^+ is three-dimensional, and therefore the order parameter $\boldsymbol{\eta}$ has three components. Suppose the direction of the order parameter is $\boldsymbol{\eta} = (a, a, 0)$ below the phase transition (a is an arbitrary constant). Equation (1) becomes, in this case,

$$a = aD_\eta(g)_{11} + aD_\eta(g)_{12}$$
$$a = aD_\eta(g)_{21} + aD_\eta(g)_{22}$$
$$0 = aD_\eta(g)_{31} + aD_\eta(g)_{32}.$$

Using the selection of matrices given in Stokes and Hatch (1988), we find that the only matrices D_η in R_4^+ which satisfy these equations are

$$
\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}, \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}.
$$

The elements $g \in G$ which are mapped by R_4^+ onto these matrices constitute an isotropy subgroup of G. In this case, we identify this subgroup to be $G_\eta = Imma$ with basis vectors $(1, 0, 1), (0, 2, 0), (\bar{1}, 0, 1)$. A rather exhaustive list of isotropy subgroups of the 230 space groups can be found in Stokes and Hatch (1988).

The subduced representation $D_\eta \downarrow G_\eta$ is defined to be a representation of G_η formed from the matrix representatives $D_\eta(g)$ for $g \in G_\eta$. The subduction frequency n is the number of times the identity irrep of G_η is contained in $D_\eta \downarrow G_\eta$ and can be calculated using the characters $\chi_\eta(g)$ of Γ_η:

$$
n = \frac{1}{|G_\eta|} \sum_{g \in G_\eta} \chi_\eta(g),
$$

where $|G_\eta|$ is the number of elements in G_η. (In practice, this sum is only taken over the different matrices in $D_\eta \downarrow G_\eta$.) A subgroup G_η of G is an isotropy subgroup if and only if (1) the subduction frequency n is nonzero and (2) there exists no supergroup of G_η with the same subduction frequency. [These two conditions have been called the subduction and chain criteria (Birman, 1978; Jarić, 1981, 1982).] In the case of $G = Pm\bar{3}m$, $\Gamma_\eta = R_4^+$, and $\eta = (a, a, 0)$, there are only four different matrices in $D_\eta \downarrow G_\eta$ (given above), and the subduction frequency is equal to

$$
n = \tfrac{1}{4}(3 + 1 + 1 - 1) = 1.
$$

2.2 Microscopic distortions

Consider some site A in a crystal undergoing a phase transition. We can determine possible microscopic "distortions" in the crystal at that site (Hatch, Stokes, and Putnam, 1987). These "distortions" can include atomic displacements (Hatch and Stokes, 1989; Hatch and Ghose, 1989b; Ghose et al., 1989), molecular rotations (Hatch, Stokes, Aleksandrov, and Misyul, 1989; Hatch, Artmann, and Boerio-Goates, 1990; Hatch and Ghose, 1990), and site occupation probability (Hatch and Griffen, 1984; Hatch and Stokes, 1990; Hatch and Ghose, 1989a; Ghose et al., 1990).

The elements of $g \in G$ which do not move the point at site A (i.e., $gA = A$) form a point group H called the site symmetry. The distortions that can occur at A are associated with different irreps Γ_H of H. For example, atomic displacements are associated with "vector representations" of H, i.e., irreps Γ_H whose basis functions transform like components x, y, z of a polar vector. Similarly, molecular rotations are associated with irreps Γ_H whose basis functions transform like components S_x, S_y, S_z of an axial vector. Site occupation probabilities are associated with the unit irrep of H.

Consider a particular distortion at A associated with some irrep Γ_H of H. An irrep Γ_η of G can bring about this distortion at A if $\Gamma_\eta \downarrow H$ contains Γ_H. This condition can be restated in the following subduction frequency calculation:

$$n = \frac{1}{|H|} \sum_{g \in H} \chi_\eta(g)\chi_H(g), \tag{2}$$

where $\chi_\eta(g)$ is the character of the matrix $D_\eta(g)$ in the irrep Γ_η of the space group G and $\chi_H(g)$ is the character of the matrix $D_H(g)$ in the irrep Γ_H of the point group H. The summation is over elements g in G which form the point group H, and $|H|$ is the number of elements in H. If n is nonzero, then the irrep Γ_η allows distortions at site A associated with Γ_H. Furthermore, the subduction frequency n gives the number of independent modes which involve such distortions at A. [Tables of these subduction frequencies have been compiled (Putnam, 1985; Kovalev, 1986). See the appendix of this paper for a discussion on the use of Kovalev's tables. There are special considerations in the cases where either Γ_η or Γ_H is reducible (the physically irreducible representation formed from a complex irrep and its complex conjugate). We will not discuss that question here.]

As an example, consider displacements of an atom at the Wyckoff d position $(\frac{1}{2}, 0, 0)$ in space group $G = Pm\bar{3}m$ (see Hahn, 1983). The site symmetry is $H = 4/mmm$. There are 16 elements in H. They include (x, y, z), $(\bar{x} + 1, \bar{y}, \bar{z})$, $(x, \bar{z}, y)$, etc. Each of these operators keeps the point $(\frac{1}{2}, 0, 0)$ fixed.

The vector representations of $H = 4/mmm$ are $\Gamma_H = A_{2u}$ and $\Gamma_H = E_u$. For the irrep $G_\eta = R_4^+$, we find from Eq. (2) that $n = 0$ for $\Gamma_H = A_{2u}$ and $n = 1$ for $\Gamma_H = E_u$. Thus, the allowed displacements of atoms at the Wyckoff d position are those associated with the irrep E_u of $4/mmm$.

A more precise determination of the distortion at A (such as the *direction* of the displacement in the preceding example) can be made using projection operator techniques. Let ϕ be a distortion at A associated with Γ_H. We can project out basis functions ψ_i of Γ_η using the following calculation:

$$\psi_i = \sum_{g \in G} D_\eta(g)_{ij} g\phi. \tag{3}$$

Different values of the index j may give different sets of basis functions. The maximum number of independent sets of basis functions that can be projected out of ϕ is equal to the subduction frequency n calculated in Eq. (2). These independent sets can be obtained by trying different values of j in Eq. (3).

Consider the effect of the operator g on ϕ in Eq. (3). In general, $g\phi$ is a distortion at some site gA equivalent to A. Thus, we have started with a distortion ϕ at a particular site A and have produced basis functions that describe distortions at every site equivalent to A throughout the crystal. It is useful to break up the sum in Eq. (3) into parts that each describe a distortion at a particular site. For example, the terms that describe the distortion at site A itself are those for which $g \in H$:

$$\psi_i(A) = \sum_{g \in H} D_\eta(g)_{ij} g\phi. \tag{4}$$

(The notation $\psi_i(A)$ simply means the part of ψ_i which is nonzero at A and does not mean that ψ_i is a function of A. The symbol A is a label for the function, not a coordinate argument of the function.) The terms that describe the distortion at some other site $g'A$ are those for which $g \in g'H$.

$$\psi_i(g'A) = \sum_{g \in g'H} D_\eta(g)_{ij} g\phi = \sum_k D_\eta(g')_{ik} g'\psi_k(A). \qquad (5)$$

The distortion described by the basis functions ψ_i is the most general distortion allowed by the irrep Γ_η. The actual distortion which occurs at a particular phase transition is given by a linear combination of these basis functions,

$$\psi = \sum_i \eta_i \psi_i, \qquad (6)$$

where η_i are the components of the order parameter η below the transition.

As an example, consider again $G = Pm\overline{3}m$, $\Gamma_\eta = R_4^+$, $\eta = (a, a, 0)$, and a displacement of an atom at the Wyckoff d position $(\tfrac{1}{2}, 0, 0)$. Using a displacement $\phi = (0, 1, 0)$ and $j = 1$, we calculate from Eq. (4), using matrices from Stokes and Hatch (1988),

$$\begin{aligned}
\psi_1(\tfrac{1}{2}, 0, 0) &= (0, 8, 0), \\
\psi_2(\tfrac{1}{2}, 0, 0) &= (0, 0, 0), \\
\psi_3(\tfrac{1}{2}, 0, 0) &= (0, 0, \overline{8}).
\end{aligned} \qquad (7)$$

From Eq. (6) we find the direction of the displacement of the atom to be

$$a(0, 8, 0) + a(0, 0, 0) + 0(0, 0, \overline{8}) = (0, 8a, 0),$$

or in the [010] direction. We denote this displacement by $(0, \delta, 0)$, where δ is some small distance.

Similarly, we can find the displacement of the atoms at the other d points in the crystal. There are three d points in the unit cell of $Pm\overline{3}m$. Since the primitive unit cell doubles in size in this phase transition, there are six of these points in the primitive unit cell of $G_\eta = Imma$, and it is sufficient to find the atomic displacement at each of these six points. For example, the element $g' = (\bar{y}, x, z)$ in $Pm\overline{3}m$ takes $a = (\tfrac{1}{2}, 0, 0)$ into $g'a = (0, \tfrac{1}{2}, 0)$. From Stokes and Hatch (1988), the matrix representative of $(\bar{y}, x, z)$ is

$$D_\eta(\bar{y}, x, z) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & \overline{1} \\ 0 & 1 & 0 \end{pmatrix}.$$

From Eqs. (7) and (5), we obtain

$$\begin{aligned}
\psi_1(0, \tfrac{1}{2}, 0) &= (\overline{8}, 0, 0), \\
\psi_2(0, \tfrac{1}{2}, 0) &= (0, 0, 8), \\
\psi_3(0, \tfrac{1}{2}, 0) &= (0, 0, 0),
\end{aligned}$$

and from Eq. (6), we obtain

$$a(\overline{8}, 0, 0) + a(0, 0, 8) + 0(0, 0, 0) = (-8a, 0, 8a)$$

Table 1 Atomic displacements in the phase transition $Pm\bar{3}m \to Imma$ at the Wyckoff position d associated with the irrep R_4^+ of $Pm\bar{3}m$. The local displacements are associated with the irrep E_u of the point group $4/mmm$ of the site.

Site	Γ_q	Γ_H	Atom	Displacement
d	R_4^+	E_u	$(\frac{1}{2}, 0, 0)$	$(0, \delta, 0)$
			$(0, \frac{1}{2}, 0)$	$(\bar{\delta}, 0, \delta)$
			$(0, 0, \frac{1}{2})$	$(0, \bar{\delta}, 0)$
			$(\frac{\bar{1}}{2}, 0, 0)$	$(0, \bar{\delta}, 0)$
			$(0, \frac{\bar{1}}{2}, 0)$	$(\delta, 0, \bar{\delta})$
			$(0, 0, \frac{\bar{1}}{2})$	$(0, \delta, 0)$

which is a displacement in the $[\bar{1}01]$ direction, denoted by $(\bar{\delta}, 0, \delta)$. The atomic displacements at each of the six points are given in Table 1.

Let us expand this example by considering a specific crystalline structure: the perovskite structure ABO_3 (for example, $BaTiO_3$). The A atoms are at the Wyckoff b position, the B atoms are at the Wyckoff a position, and the O atoms are at the Wyckoff d position. Above, we found the atomic displacements at the d positions (the O atoms). If we repeat the calculations for the a and b points, we find that the irrep R_4^+ does not allow any atomic displacements at those positions. The subduction frequencies in Eq. (2) are zero for every vector representation of H for both the a and b positions. The distortions described by the order parameter $\eta = (a, a, 0)$ associated with the irrep R_4^+ allow only displacements of the O atoms.

The displacements of the O atoms shown in Table 1 describe a *rotation* as though these six atoms formed a rigid molecule centered at the B atom. The site symmetry of the Wyckoff a position is $H = m\bar{3}m$. The basis functions of irrep $\Gamma_H = T_{1g}$ transform like components of an axial vector. We find, as expected, that at the Wyckoff a position, the subduction frequency n calculated in Eq. (2) for $\Gamma_\eta = R_4^+$ and $\Gamma_H = T_{1g}$ is equal to 1. Starting with a distortion ϕ along the direction of an axial vector, we obtain a distortion $(\delta, 0, \delta)$ at $(0, 0, 0)$. The six O atoms surrounding the B atom rotate about an axis along the $[101]$ direction. This is exactly equivalent to the displacements of the O atoms shown in Table 1.

3 SECONDARY ORDER PARAMETERS

In a given phase transition $G \to G_\eta$, we must consider all distortions consistent with the symmetry of G_η. However, not all such distortions can be described by an order parameter associated with the irrep Γ_η. Some are described by order parameters $\mathbf{q} = (q_1, q_2, \ldots)$ associated with other irreps Γ_q of G. These are called secondary order parameters.

In the low-symmetry phase, a secondary order parameter $\mathbf{q}$ must satisfy, for every element $g \in G_\eta$, the equation $g\mathbf{q} = \mathbf{q}$, or

$$q_i = \sum_j D_q(g)_{ij} q_j, \tag{8}$$

where $D_q(g)$ is the representative matrix of element g in irrep Γ_q. The direction of $\mathbf{q}$ which satisfies this equation also determines an isotropy subgroup G_q of G. In general, G_q is a supergroup of G_η. The action of $\mathbf{q}$ does not break the symmetry of G_η. However, it does cause additional distortions in the crystal which cannot be described by η alone.

If $\mathbf{q}$ satisfies Eq. (8), then the representation $D_q \downarrow G_\eta$ must contain the identity irrep of G_η at least once. In other words, the subduction frequency,

$$n = \frac{1}{|G_\eta|} \sum_{g \in G_\eta} \chi_q(g), \tag{9}$$

must be nonzero. All secondary order parameters must obey this equation. [The determination of these secondary order parameters has been called the inverse Landau problem (Ascher, 1977).]

Let us return to the example, $G = Pm\bar{3}m$, $\Gamma_\eta = R_4^+$, $\eta = (a, a, 0)$, and $G_\eta = Imma$. There are four irreps of G (besides R_4^+) which give nonzero subduction frequencies. These are listed in Table 2, along with the order parameter $\mathbf{q}$ and the isotropy subgroup G_q determined by that order parameter. In each case, G_q is a supergroup of $Imma$. Each of those four secondary order parameters onset at the phase transition simultaneously with the primary order parameter $\eta = (a, a, 0)$. Each order parameter also has a unique contribution to the distortion of the crystal at the phase transition. For example, the order parameter $\mathbf{q} = (a, \bar{a}, 0)$ associated with irrep $\Gamma_q = R_5^+$ allows atomic displacements at both the Wyckoff b and d positions. These are determined in the same way as for the primary order parameter, using Eqs. (2) through (6), substituting q for η in every equation. The results are shown in Table 3.

For the phase transition $Pm\bar{3}m \to Imma$ in the perovskite structure ABO_3, Tables 1 and 3 give a complete list of all possible atomic displacements which can accompany the phase transition. The displacements given in Table 1 are associated with the primary order parameter, and those given in Table 3 are associated with secondary order parameters.

Table 2 The secondary order parameters $\mathbf{q}$ for the phase transition $Pm\bar{3}m \to Imma$, along with their isotropy subgroups G_q.

Γ_q	$\mathbf{q}$	G_q	Basis vectors
Γ_1^+	(a)	$Pm\bar{3}m$	$(1, 0, 0), (0, 1, 0), (0, 0, 1)$
Γ_3^+	$(a, \sqrt{3}\bar{a})$	$P4/mmm$	$(0, 0, 1), (1, 0, 0), (0, 1, 0)$
Γ_5^+	$(0, 0, a)$	$Cmmm$	$(1, 0, 1), (1, 0, \bar{1}), (0, 1, 0)$
R_5^+	$(a, \bar{a}, 0)$	$Imma$	$(1, 0, 1), (0, 2, 0), (\bar{1}, 0, 1)$

Table 3 Atomic displacements in the phase transition $Pm\bar{3}m \rightarrow Imma$ associated with irreps $\Gamma_q \neq R_4^+$. We list the Wyckoff position (site), the irrep Γ_q of $Pm\bar{3}m$, the irrep Γ_H of the site symmetry point group H, the atomic positions, and the displacements.

Site	Γ_q	Γ_H	Atom	Displacement
b	R_5^+	T_{1u}	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(\bar{\delta}, 0, \delta)$
			$(\frac{3}{2}, \frac{1}{2}, \frac{1}{2})$	$(\delta, 0, \bar{\delta})$
d	R_5^+	E_u	$(\frac{1}{2}, 0, 0)$	$(0, \delta, 0)$
			$(0, \frac{1}{2}, 0)$	$(\delta, 0, \bar{\delta})$
			$(0, 0, \frac{1}{2})$	$(0, \bar{\delta}, 0)$
			$(\bar{\tfrac{1}{2}}, 0, 0)$	$(0, \bar{\delta}, 0)$
			$(0, \bar{\tfrac{1}{2}}, 0)$	$(\bar{\delta}, 0, \delta)$
			$(0, 0, \bar{\tfrac{1}{2}})$	$(0, \delta, 0)$

Components ε_{ij} of macroscopic strain may also be treated by the same methods discussed above. These are always associated with irreps at the zone center (Γ irreps). We find, for $Pm\bar{3}m$, that irrep Γ_3^+ has basis functions that transform like $x^2 + y^2 - 2z^2$ and $\sqrt{3}(x^2 - y^2)$. Thus, $\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz}$ and $\sqrt{3}(\varepsilon_{xx} - \varepsilon_{yy})$ form a pair of basis functions of Γ_3^+. We find in Table 2 that for this irrep, $\mathbf{q} = (a, -\sqrt{3}a)$ in the *Imma* phase. Thus, a nonzero strain component,

$$(\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz}) - \sqrt{3}[\sqrt{3}(\varepsilon_{xx} - \varepsilon_{yy})] = -2\varepsilon_{xx} + 4\varepsilon_{yy} - 2\varepsilon_{zz},$$

appears at the phase transition.

Also, we find that irrep Γ_5^+ has basis functions that transform like xy, yz, xz. Thus, $\varepsilon_{xy}, \varepsilon_{yz}, \varepsilon_{xz}$ form a set of basis functions of Γ_5^+. We find in Table 2 that for this irrep, $\mathbf{q} = (0, 0, a)$ in the *Imma* phase. Thus, a nonzero strain component ε_{xz} appears at the phase transition. All of these strains that appear at the transition are secondary order parameters. Consequently, this is an improper ferroelastic transition (Wadhawan, 1982).

As one final example, consider ordering of atoms in a mixed crystal. This kind of "distortion" is associated with the unit irrep of H. We want to find irreps Γ_q such that the subduction frequency in Eq. (9) is nonzero for the case where Γ_H is a unit irrep. For the phase transition we have been considering in ABO_3, this subduction frequency is nonzero ($n = 1$) only for the case $\Gamma_q = \Gamma_3^+$ and $\Gamma_H = A_{1g}$ at the Wyckoff d position. Using Eqs. (4) and (5), we find that the distortion is $-\delta$ at $(\pm\frac{1}{2}, 0, 0)$ and $(0, 0, \pm\frac{1}{2})$ and 2δ at $(0, \pm\frac{1}{2}, 0)$, where δ represents either an increase or decrease in occupation probability. For example, consider the mixed crystal, $ABC_{3x}D_{3(1-x)}$, where the C and D atoms occupy the Wyckoff d position. The probability that a particular d point is occupied by a C atom would be equal to x above the transition (equal for all points). Below the transition, the probability would

be equal to $x - \delta$ for $\frac{2}{3}$ of the points and $x + 2\delta$ for $\frac{1}{3}$ of the points. This change in site occupation would be a secondary order parameter in the phase transition to *Imma*.

4   LANDAU FREE ENERGY

4.1   Linear coupling

Consider a phase transition driven by a primary order parameter η and a secondary order parameter $\mathbf{q}$. The leading terms in the Landau free energy are

$$\Phi = A(T - T_0)(\eta_1^2 + \eta_2^2 + \cdots) + B(q_1^2 + q_2^2 + \cdots) - C[q_1 P_1(\boldsymbol{\eta}) + q_2 P_2(\boldsymbol{\eta}) + \cdots] + \cdots,$$

$$(10)$$

where $P_i(\boldsymbol{\eta})$ are mth degree homogeneous polynomials of η_1, $\eta_2, \ldots$ The lowest-order term coupling η to $\mathbf{q}$ is linear in $\mathbf{q}$. This will always occur when we obtain a nonzero subduction frequency in Eq. (9) for the irrep Γ_q, i.e., whenever $\mathbf{q}$ is a secondary order parameter. [We do not know of a rigorous proof of this statement, but we have tested by computer its validity for all of the cases that occur among the 4777 irreps treated in Stokes and Hatch (1988).]

Minimizing Φ with respect to $\mathbf{q}$ ($\partial\Phi/\partial q_i = 0$) and keeping only terms lowest order in $\mathbf{q}$, we obtain,

$$q_i = \frac{C}{2B} P_i(\boldsymbol{\eta}).$$

$$(11)$$

In the high-symmetry phase, both η and $\mathbf{q}$ are zero. As we pass through the transition, one or more components of η become nonzero. If one or more of the polynomials $P_i(\boldsymbol{\eta})$ also become nonzero, then the corresponding components q_i of $\mathbf{q}$ also become nonzero. In this case, the order parameters η and $\mathbf{q}$ are driven to nonzero values at the *same* temperature. The linear coupling in the free energy guarantees that if η goes nonzero, then $\mathbf{q}$ must go nonzero also. Distortions due to secondary order parameters are not only *allowed* to be present at the phase transition, they are *forced* to be present (although perhaps in a very small degree) by the linear coupling term in the free energy. It is not optional to consider secondary order parameters in a phase transition; it is mandatory, if we want to fully understand the distortions accompanying the transition. [For discussions on linear coupling and secondary order parameters, see Hatch and Stokes (1990), Hatch, Stokes, and Ghose (1990), Hatch and Ghose (1989a), Levanyuk and Sannikov (1974), and Tolédano and Tolédano (1987).]

If the transition is second order (continuous), Landau theory predicts that the nonzero components of the primary order parameter η depend on temperature like $(T_c - T)^{1/2}$, a function which has an infinite slope at the transition temperature T_c. [T_c is not necessarily equal to the T_0 which appears in Eq. (10). The coupling generally affects the transition temperature.] Since $P_i(\boldsymbol{\eta})$ are mth degree homogeneous polynomials, we see from Eq. (11) that the nonzero components of the secondary order

parameter $\mathbf{q}$ depend on temperature like $(T_c - T)^{m/2}$. In the case of $m \geq 2$, this function has a *non-infinite* slope at the transition. Thus, although both $\boldsymbol{\eta}$ and $\mathbf{q}$ become nonzero at exactly the same temperature, the effect of $\boldsymbol{\eta}$ is much more pronounced than that of $\mathbf{q}$ near the transition. For example, in the phase transition $Pm\bar{3}m \to Imma$, the atomic displacements in Table 1 (primary order parameter) would be much more prominent than those in Table 3 (secondary order parameters). The degree m of the polynomials $P_i(\boldsymbol{\eta})$ is called the faintness index.

Sometimes all of the polynomials $P_i(\boldsymbol{\eta})$ are zero for the particular direction of $\boldsymbol{\eta}$ in G_{η}, even though the subduction frequency of Eq. (9) is nonzero. In that case, it is necessary to expand Φ to higher order and find other terms linear in $\mathbf{q}$ where the polynomials $P_i(\boldsymbol{\eta})$ do *not* vanish. This does not change any of the results above except that the effective faintness index is then greater than m.

The $m = 1$ case occurs only when $\Gamma_{\eta} = \Gamma_q$, i.e. when $\boldsymbol{\eta}$ and $\mathbf{q}$ are associated with the *same* irrep. In this case, $P_i(\boldsymbol{\eta}) = \eta_i$ and $\mathbf{q} = (C/2B)\boldsymbol{\eta}$ near the transition. Both $\boldsymbol{\eta}$ and $\mathbf{q}$ have the same temperature dependence. In this case, $\mathbf{q}$ is often called a pseudo-primary order parameter. The coupling is called "bilinear," and a number of examples of such coupling have been studied (Dobrzyński and Przystawa, 1981; Oleksy and Przystawa, 1983; Salje, 1985; Salje and Devarajan, 1986; Ghose, Tsukimura, and Hatch, 1989).

Let us return again to the example, $G = Pm\bar{3}m$ and $\Gamma_{\eta} = R_4^+$. There are ten irreps of $Pm\bar{3}m$ which allow a coupling term linear in $\mathbf{q}$. These are listed in Table 4. If we let $\boldsymbol{\eta} = (a, a, 0)$, we find that five of these terms vanish completely, leaving nonzero coupling terms only for R_4^+ and the four irreps listed in Table 2.

For example, the coupling term for Γ_3^+ evaluated at $\boldsymbol{\eta} = (a, a, 0)$ is equal to $a^2 q_1 - \sqrt{3}a^2 q_2$. From Eq. (11), we see that the components of $\mathbf{q}$ are proportional to the polynomials $P_i(\boldsymbol{\eta})$. The direction of $\mathbf{q}$ is thus written as $(a, -\sqrt{3}a)$ so that the

Table 4   Linear coupling terms in the Landau free energy for $G = Pm\bar{3}m$ and $\Gamma_{\eta} = R_4^+$. In each case, we give the irrep Γ_q and the degree m of the polynomials $P_i(\boldsymbol{\eta})$.

Γ_q	m	$\sum_i q_i P_i(\boldsymbol{\eta})$
Γ_1^+	2	$q_1(\eta_1^2 + \eta_2^2 + \eta_3^2)$
Γ_2^+	6	$q_1(\eta_1^4\eta_2^2 - \eta_1^4\eta_3^2 + \eta_2^4\eta_3^2 - \eta_2^4\eta_1^2 + \eta_3^4\eta_1^2 - \eta_3^4\eta_2^2)$
Γ_3^+	2	$q_1(2\eta_1^2 - \eta_2^2 - \eta_3^2) + q_2\sqrt{3}(\eta_3^2 - \eta_2^2)$
Γ_4^+	4	$q_1\eta_1\eta_3(\eta_1^2 - \eta_3^2) + q_2\eta_2\eta_1(\eta_2^2 - \eta_1^2) + q_3\eta_3\eta_2(\eta_3^2 - \eta_2^2)$
Γ_5^+	2	$q_1\eta_2\eta_3 + q_2\eta_3\eta_1 + q_3\eta_1\eta_2$
R_1^+	9	$q_1(\eta_1^5\eta_2^3\eta_3 - \eta_1^5\eta_2\eta_3^3 + \eta_2^5\eta_3^3\eta_1 - \eta_2^5\eta_3\eta_1^3 + \eta_3^5\eta_1^3\eta_2 - \eta_3^5\eta_1\eta_2^3)$
R_2^+	3	$q_1\eta_1\eta_2\eta_3$
R_3^+	5	$q_1\sqrt{3}\eta_1\eta_2\eta_3(\eta_2^2 - \eta_3^2) + q_2\eta_1\eta_2\eta_3(2\eta_1^2 - \eta_2^2 - \eta_3^2)$
R_4^+	1	$q_1\eta_1 + q_2\eta_2 + q_3\eta_3$
R_5^+	3	$q_1\eta_1(\eta_3^2 - \eta_2^2) + q_2\eta_2(\eta_1^2 - \eta_3^2) + q_3\eta_3(\eta_2^2 - \eta_1^2)$

components, a and $-\sqrt{3}a$ have the same ratio as the coefficients, a^2 and $-\sqrt{3}a^2$. This result agrees with the direction of $\mathbf{q}$ given in Table 2 for Γ_3^+.

There is one important case we should consider separately: the unit irrep Γ_1 which is one-dimensional with every representative matrix $D_1(g)$ equal to 1 (the 1×1 identity matrix). The Landau free energy for this case is given by

$$\Phi = A(T - T_c)(\eta_1^2 + \eta_2^2 + \cdots) - B_1 q + B_2 q^2 - Cq(\eta_1^2 + \eta_2^2 + \cdots) + \cdots.$$

The B_1 term did not appear in Eq. (10). This term is only allowed for the unit irrep. Minimizing Φ with respect to $\mathbf{q}$, we obtain

$$q = \frac{B_1}{2B_2} + \left(\frac{C_1}{2B_2}\right)(\eta_1^2 + \eta_2^2 + \cdots).$$

Here, q has a nonzero value even when $\mathbf{\eta} = 0$. Basis functions of the unit irrep are invariant with respect to *all* symmetry operations $g \in G$. Therefore $\mathbf{q}$ is allowed to be nonzero in the high-symmetry phase and is not usually considered to be an order parameter associated with the phase transition. However, because of the coupling with $\mathbf{\eta}$, a change in q does occur at the transition.

The volume of the crystal is an example of an order parameter associated with Γ_1. The volume is invariant under all symmetry operations $g \in G$. At a continuous phase transition, an extra contribution to the volume appears which is linear in temperature ($m = 2$) causing the response function $\partial V / \partial T$ to be discontinuous at the transition (Hatch, Artmann, and Boerio-Goates, 1990).

4.2 Nonlinear coupling

Consider the coupling of two order parameters, $\mathbf{\eta}$ and $\mathbf{\xi}$, associated with irreps, Γ_η and Γ_ξ, respectively. In the Landau free energy, there always exists a term of the form,

$$(\eta_1^2 + \eta_2^2 + \cdots)(\xi_1^2 + \xi_2^2 + \cdots).$$

This term is nonlinear in both $\mathbf{\eta}$ and $\mathbf{\xi}$. If this term is strong enough (large negative coefficient), it is possible for a first-order (discontinuous) phase transition to occur where the effect of *both* $\mathbf{\eta}$ and $\mathbf{\xi}$ are prominent. (Holakovský, 1973; Imry, 1975; Gene *et al.*, 1977; Gufan and Larin, 1980; Hatch and Stokes, 1990; Hatch, Ghose and Stokes, 1990; Salje and Devarajan, 1986; Levanyuk and Sannikov, 1968; Larin, 1984; Redfern *et al.*, 1988.) In that case, $\mathbf{\eta}$ and $\mathbf{\xi}$ are *both* primary order parameters even though they are associated with *different* irreps of G. This can happen whether or not linear coupling terms also exist.

The symmetry $G_{\eta\xi}$ of the crystal below the transition is determined by the direction of *both* $\mathbf{\eta}$ and $\mathbf{\xi}$ and is simply the intersection of G_η and G_ξ. As an example consider the case of $G = Pm\bar{3}m$, $\Gamma_\eta = R_4^+$, and $\Gamma_\xi = X_1^+$, with $\mathbf{\eta} = (a_1, a_1, 0)$ and $\mathbf{\xi} = (0, a_2, a_2)$. The direction of $\mathbf{\eta}$ determines the isotropy subgroup $G_\eta = Imma$ with basis vectors $(1, 0, 1), (0, 2, 0), (\bar{1}, 0, 1)$ as given previously. The direction of $\mathbf{\xi}$ determines the isotropy subgroup $G_\xi = P4/mmm$ with basis vectors $(0, 0, 2), (2, 0, 0), (0, 1, 0)$. The intersection of these two groups is $G_{\eta\xi} = Cmcm$ with basis vectors $(2, 0, 2), (2, 0, \bar{2}), (0, 2, 0)$.

parameter $\mathbf{q}$ depend on temperature like $(T_c - T)^{m/2}$. In the case of $m \geq 2$, this function has a *non-infinite* slope at the transition. Thus, although both $\mathbf{\eta}$ and $\mathbf{q}$ become nonzero at exactly the same temperature, the effect of $\mathbf{\eta}$ is much more pronounced than that of $\mathbf{q}$ near the transition. For example, in the phase transition $Pm\bar{3}m \rightarrow Imma$, the atomic displacements in Table 1 (primary order parameter) would be much more prominent than those in Table 3 (secondary order parameters). The degree m of the polynomials $P_i(\mathbf{\eta})$ is called the faintness index.

Sometimes all of the polynomials $P_i(\mathbf{\eta})$ are zero for the particular direction of $\mathbf{\eta}$ in G_η, even though the subduction frequency of Eq. (9) is nonzero. In that case, it is necessary to expand Φ to higher order and find other terms linear in $\mathbf{q}$ where the polynomials $P_i(\mathbf{\eta})$ do *not* vanish. This does not change any of the results above except that the effective faintness index is then greater than m.

The $m = 1$ case occurs only when $\Gamma_\eta = \Gamma_q$, i.e. when $\mathbf{\eta}$ and $\mathbf{q}$ are associated with the *same* irrep. In this case, $P_i(\mathbf{\eta}) = \eta_i$ and $\mathbf{q} = (C/2B)\mathbf{\eta}$ near the transition. Both $\mathbf{\eta}$ and $\mathbf{q}$ have the same temperature dependence. In this case, $\mathbf{q}$ is often called a pseudo-primary order parameter. The coupling is called "bilinear," and a number of examples of such coupling have been studied (Dobrzyński and Przystawa, 1981; Oleksy and Przystawa, 1983; Salje, 1985; Salje and Devarajan, 1986; Ghose, Tsukimura, and Hatch, 1989).

Let us return again to the example, $G = Pm\bar{3}m$ and $\Gamma_\eta = R_4^+$. There are ten irreps of $Pm\bar{3}m$ which allow a coupling term linear in $\mathbf{q}$. These are listed in Table 4. If we let $\mathbf{\eta} = (a, a, 0)$, we find that five of these terms vanish completely, leaving nonzero coupling terms only for R_4^+ and the four irreps listed in Table 2.

For example, the coupling term for Γ_3^+ evaluated at $\mathbf{\eta} = (a, a, 0)$ is equal to $a^2 q_1 - \sqrt{3}a^2 q_2$. From Eq. (11), we see that the components of $\mathbf{q}$ are proportional to the polynomials $P_i(\mathbf{\eta})$. The direction of $\mathbf{q}$ is thus written as $(a, -\sqrt{3}a)$ so that the

Table 4 Linear coupling terms in the Landau free energy for $G = Pm\bar{3}m$ and $\Gamma_\eta = R_4^+$. In each case, we give the irrep Γ_q and the degree m of the polynomials $P_i(\mathbf{\eta})$.

Γ_q	m	$\sum_i q_i P_i(\mathbf{\eta})$
Γ_1^+	2	$q_1(\eta_1^2 + \eta_2^2 + \eta_3^2)$
Γ_2^+	6	$q_1(\eta_1^4\eta_2^2 - \eta_1^4\eta_3^2 + \eta_2^4\eta_3^2 - \eta_2^4\eta_1^2 + \eta_3^4\eta_1^2 - \eta_3^4\eta_2^2)$
Γ_3^+	2	$q_1(2\eta_1^2 - \eta_2^2 - \eta_3^2) + q_2\sqrt{3}(\eta_3^2 - \eta_2^2)$
Γ_4^+	4	$q_1\eta_1\eta_3(\eta_1^2 - \eta_3^2) + q_2\eta_2\eta_1(\eta_2^2 - \eta_1^2) + q_3\eta_3\eta_2(\eta_3^2 - \eta_2^2)$
Γ_5^+	2	$q_1\eta_2\eta_3 + q_2\eta_3\eta_1 + q_3\eta_1\eta_2$
R_1^+	9	$q_1(\eta_1^5\eta_2^3\eta_3 - \eta_1^5\eta_2\eta_3^3 + \eta_2^5\eta_3^3\eta_1 - \eta_2^5\eta_3\eta_1^3 + \eta_3^5\eta_1^3\eta_2 - \eta_3^5\eta_1\eta_2^3)$
R_2^+	3	$q_1\eta_1\eta_2\eta_3$
R_3^+	5	$q_1\sqrt{3}\eta_1\eta_2\eta_3(\eta_2^2 - \eta_3^2) + q_2\eta_1\eta_2\eta_3(2\eta_1^2 - \eta_2^2 - \eta_3^2)$
R_4^+	1	$q_1\eta_1 + q_2\eta_2 + q_3\eta_3$
R_5^+	3	$q_1\eta_1(\eta_3^2 - \eta_2^2) + q_2\eta_2(\eta_1^2 - \eta_3^2) + q_3\eta_3(\eta_2^2 - \eta_1^2)$

Considering other irreps, we could make a table, similar to Tables 1 and 3, showing all of the atomic displacements caused by both primary and secondary order parameters in this phase transition.

APPENDIX   USING THE TABLES OF KOVALEV

The most recent edition of Kovalev's tables of irreps (Kovalev, 1986) includes the subduction frequencies calculated by Eq. (2). As an example of how to use these tables, consider atomic displacements in the hypothetical phase transition $Pm\bar{3}m \rightarrow Imma$ in the perovskite structure ABO_3. The atoms are at Wyckoff positions a, b, and d. The irreps associated with the primary and secondary order parameters in this transition are Γ_3^+, Γ_5^+, R_4^+, and R_5^+. From Table 7 of Stokes and Hatch (1988), we find that these irreps in the notation of Kovalev are $K12T5$, $K12T7$, $K13T9$, and $K13T7$, respectively.

The site symmetry of Wyckoff positions a and b are both $m\bar{3}m$. From the point group character tables in Appendix 1 of Kovalev, we find that the vector irrep of $m\bar{3}m$ is $F_{1u} = \Gamma10$. In §15 of Kovalev, we find the subduction frequencies listed for $Pm\bar{3}m$ for the various Wyckoff positions. We are looking for entries like $K12: \Gamma10 - T5$, $K12: \Gamma10 - T7$, $K13: \Gamma10 - T9$, or $K13: \Gamma10 - T7$. We find none of these for Wyckoff position a, but for position b we find $K13: \ldots \Gamma10 - T7$. Thus for position b, the subduction frequency is $n = 1$ for irrep $K13T7 = R_5^+$. Atomic displacements associated with that irrep are allowed for atoms at Wyckoff position b, as shown in Table 3 of this paper.

The site symmetry of Wyckoff position d is $4/mmm$. From the point group character tables in Appendix 1 of Kovalev, we find that the vector irreps of $4/mmm$ are $A_{2u} = \Gamma4$ and $E_u = \Gamma10$. Thus, we are looking for entries like $K12: \Gamma4 - T5$, $K12: \Gamma4 - T7$, $K13: \Gamma4 - T9$, $K13: \Gamma4 - T7$, $K12: \Gamma10 - T5$, $K12: \Gamma10 - T7$, $K13: \Gamma10 - T9$, or $K13: \Gamma10 - T7$ for Wyckoff position d. We find the entry $K13: \ldots \Gamma10 - T7 - T9$ which means that the subduction frequency is $n = 1$ for both irreps $K13T7 = R_5^+$ and $K13T9 = R_4^+$. Atomic displacements asociated with those irreps are allowed for atoms at Wyckoff position d, as shown in Table 3 of this paper.

As a second example of using Kovalev's tables, consider the possible ordering of atoms in this same phase transition. This kind of distortion is associated with the unit irrep of the point group. In Appendix 1 of Kovalev, we find that the unit irrep is always denoted $\Gamma1$. Thus we are looking for entries like $K12: \Gamma1 - T5$, $K12: \Gamma1 - T7$, $K13: \Gamma1 - T9$, or $K13: \Gamma1 - T7$. We find no entries like this for positions a and b. For position c, we find the entry $K12: \Gamma1 - T5$ which means that the subduction frequency is $n = 1$ for irrep $K12T5 = \Gamma_3^+$. Atomic ordering associated with that irrep is allowed for atoms at Wyckoff position d.

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