PHYSICAL REVIEW B, VOLUME 65, 014113

Complete listing of order parameters for a crystalline phase transition: A solution to the generalized inverse Landau problem

Dorian M. Hatch and Harold T. Stokes
Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602

(Received 24 August 2001; published 12 December 2001)

For a given group-subgroup transition, the complete set of order parameters, primary and secondary, describe the distortions that accompany this transition. The task of obtaining all order-parametric distortions for a group-subgroup pair is a long standing problem. An algorithm is presented here which obtains the irreducible representations and order parameter directions for an arbitrary transition. Examples are given for a variety of phase transitions showing the application and utility of the procedure. It is shown that a unique selection of primary order parameters is not always possible.

DOI: 10.1103/PhysRevB.65.014113 PACS number(s): 64.70.Kb, 02.20.−a, 63.20.−e

I. INTRODUCTION

In two papers of the middle 1970's Ascher and Kobayashi[1,2] defined two problems of great interest in the study of phase transitions. The first is referred to as the direct Landau problem: given the symmetry group H of a high symmetry phase, find all the possible order parameters (OP's); for each of these determine the symmetries L of possible low symmetry phases; write down the thermodynamic potentials that describe the phases and the transitions between them and find a suitable way of classifying these potentials. In these papers[1,2] they stated they did not want to face this problem in its full generality but would instead study a less ambitious problem, the inverse Landau problem: given a group H and a subgroup L, find the irreducible representation (IR) of H determined by this transition.

Finding the IR of the symmetry reduction is important since it defines the cause of the transition. In the Landau philosophy an OP is a vector in an IR space. This vector will determine a set of symmetry elements in H which leave the vector invariant, thus determining an isotropy subgroup L (epikernel in the terminology of Ascher) and thus a relationship between the two groups. The search for the isotropy subgroup and the associated OP in the IR has been studied in several contexts. For space groups, listings of isotropy subgroups have been given by Toledano and Toledano[3] and by Stokes and Hatch.[4] These publications addressed the direct Landau problem for crystalline materials. Isotropy subgroups of OP directions in the context of other symmetry changes have also been studied, e.g., in non-Kekulé-type isoelectronic molecules,[5] for the breakdown of translational symmetry of a polyethylene chain,[6] and for the formation of cubic phases in complex fluids.[7]

The free energy of a crystal can be expanded as a sum of individually invariant polynomial forms of the OP components. The values of the OP at the minimum of the free energy determine the OP direction and therefore the resulting isotropy subgroup. The OP vector corresponds to a physical property or distortion of the high symmetry structure (symmetry H). When the OP becomes nonzero it determines the structure of reduced symmetry (symmetry L).

Often only a single OP is referred to in the description of a group-subgroup transition. The OP which defines the transition and determines the symmetry of the lower symmetry phase is called the primary OP. Quite generally, however, OP's associated with multiple IR's are coupled causing both primary and secondary OP's to be significant for a given structural transition. A secondary OP is one which couples to the primary OP in a very specific way. The coupling is always of the form linear in the secondary OP and quadratic or higher in the primary OP. At the phase transition the primary OP becomes nonzero. The secondary OP also becomes nonzero because of this coupling with the primary OP. These secondary OP's are invariant under L, and in fact are left invariant by a supergroup[8] of L. The terminology of "improper" is often used when the property appears as a secondary order parameter. For example, an improper ferroelastic is one in which the strain is a secondary OP. There also exist group-subgroup relationships where a single primary OP is not sufficient for defining the group-subgroup relationship, and multiple (coupled) primary OP's induce the transition.[8] Then it is necessary to have two or more primary OP's drive the transition.

In this paper we present our approach to the solution of the generalized inverse Landau problem, i.e., given a group H and a subgroup L, find all irreducible representations and OP directions of H determined by this transition. Up to now there is no published solution to this problem. In Sec. II we describe an algorithm used to obtain the IR's associated with a given group-subgroup pair. Primary IR's as well as all secondary IR's are obtained and there is no limitation that the IR's must be at points of symmetry of the Brillouin zone. Thus a complete listing of IR's associated with the transition are given. In addition we obtain OP directions within the IR space. We refer to this algorithm as the complete order parameter listing (COPL) algorithm. In Sec. III we give some examples to which the algorithm has been applied. We show that the choice of OP(s) may be arbitrary in a given case, since two or more distinct selections of the (multiple) primary OP's may determine the same subgroup. The algorithm has been implemented and is part of the ISOTROPY software[9] available on the internet.

II. ALGORITHM

We now describe the COPL algorithm which finds all IR's and associated OP's which arise in a given phase transition

$H \rightarrow L$, where $L \subset H$. We assume that we know which of the elements of H are contained in L. In practice, this means that we know the space group symmetry of L, the lattice vectors of L in terms of the lattice vectors of H, and the origin of the space group setting of L with respect to that of H.

In general, an IR will be involved in a phase transition if the subduction frequency

$$n_s = \frac{1}{|L|} \sum_{h \in L} \chi(h) \tag{1}$$

is nonzero. In this expression, $\chi(h)$ is the character of the space group operator h, and $|L|$ is the order of L. (In practice, we sum over the operators which the IR maps onto distinct matrices, and $|L|$ becomes the number of these operators.) The subduction frequency n_s is nonzero if and only if there exists a nonzero solution $\vec{\eta}$ which satisfies the equation

$$D(h)\vec{\eta} = \vec{\eta}, \tag{2}$$

simultaneously for every operator $h \in L$. In this expression, $D(h)$ is the $n \times n$ matrix onto which the IR of H maps the operator h, and $\vec{\eta}$ is an n dimensional vector which points in the direction of the OP. In practice, $\vec{\eta}$ needs to satisfy Eq. (2) only for the generators of L. This usually results in a small number of simultaneous equations to be solved.

The space-group symmetry determined by the OP can be obtained by putting $\vec{\eta}$ back into Eq. (2) and trying every operator $h \in H$ (try *all* operators in H, not just those in L). The set of operators h which satisfy Eq. (2) form a group L' which is a supergroup (either proper or improper) of L, i.e., $L \subseteq L' \subseteq H$. If $L' = L$ the OP is primary; otherwise the OP is secondary. (This rule becomes more complicated in the case of coupled primary OP's. See the examples in the next section.)

In principle, we could find all OP's by simply evaluating Eq. (1) for every IR of H. When we find an IR for which $n_s \neq 0$, we could then find the direction of the order parameter using Eq. (2). In practice, a space group has an infinite number of IR's, so we must restrict the search in some way.

IR's are associated with stars of $\vec{k}$ vectors. A star of $\vec{k}$ vectors is a set of distinct (nonequivalent) $\vec{k}$ vectors generated by point operations in the space group, i.e., given a vector $\vec{k}$, its star is given by $\{\vec{k}, R_2\vec{k}, R_3\vec{k}, \ldots, R_m\vec{k}\}$, where R_i are point operators in H. The vectors $\vec{k}, R_2\vec{k}, R_3\vec{k}, \ldots, R_m\vec{k}$ are called "arms" of the star. We consider as arms of the star only distinct $\vec{k}$ vectors, i.e., those which are not related by a vector of the reciprocal lattice.

It can be shown that the subduction frequency n_s in Eq. (1) will be zero unless at least one of the arms of the star of $\vec{k}$ satisfies

$$\vec{k} \cdot \vec{t} = \text{integer} \tag{3}$$

for every lattice vector $\vec{t}$ of L (including vectors to any centered lattice points). This gives us a systematic way of limiting the number of IR's to be tested.

We write the primitive lattice vectors $\vec{t}_i$ of L as

$$\vec{t}_i = \sum_j A_{ij} \vec{a}_j, \tag{4}$$

where $\vec{a}_j$ are primitive lattice vectors of H. By primitive, we mean that integer linear combinations of the lattice vectors reach all lattice points, including any centered lattice points. Since $L \subset H$, the elements A_{ij} must be integers. Vectors $\vec{k}$ in reciprocal space are written as

$$\vec{k} = \sum_j B_j \vec{b}_j, \tag{5}$$

where $\vec{b}_j$ are reciprocal lattice vectors of H such that

$$\vec{b}_j \cdot \vec{a}_i = \delta_{ij}. \tag{6}$$

Equation (3) can now be written as

$$\vec{k} \cdot \vec{t}_i = \sum_j A_{ij} B_j = n_i, \tag{7}$$

where n_i are integers. We invert these equations and obtain an expression for the allowed values of B_j:

$$B_j = \sum_i A_{ji}^{-1} n_i. \tag{8}$$

Note that the elements A_{ji}^{-1} are not necessarily integers. Let m be the least common denominator of all of the elements of A^{-1}. This means that mA_{ji}^{-1} is an integer for every j,i. We see from Eq. (8) that if we increase (or decrease) any of the n_i by m, the value of B_j changes by an integer and therefore does not result in an additional nonequivalent $\vec{k}$ vector. Therefore a complete set of nonequivalent $\vec{k}$ vectors can be generated from values of n_i in the range $0 \leqslant n_i < m$. This requires solving Eq. (8) m^3 times.

We next identify the star of $\vec{k}$ to which each of these $\vec{k}$ vectors belong. This gives us a complete set of possible stars of $\vec{k}$ which can be involved in the phase transition. Only the IR's associated with these stars can satisfy Eq. (1).

Let us summarize the algorithm.

(1) Obtain a list of $\vec{k}$ vectors from Eq. (8), trying every integer $0 \leqslant n_i < m$. This means solving Eq. (8) m^3 times resulting in a list of m^3 $\vec{k}$ vectors.

(2) Determine which star each $\vec{k}$ vector belongs to.

(3) For each IR of each star, use Eq. (1) to determine if the IR is involved in the phase transition ($n_s \neq 0$).

(4) For each IR involved in the phase transition, determine the direction of the OP by solving simultaneously Eq. (2) for each generator h of L.

(5) Obtain the space-group symmetry L' determined by the OP by finding all operators $h \in H$ which satisfy Eq. (2) for the OP found in the previous step.

The COPL algorithm has been implemented using the data base of the ISOTROPY software. Specifically, a general implementation of the COPL algorithm requires information about space group settings, lattice vectors, reciprocal lattice vectors, stars of $\vec{k}$, IR's belonging to stars of $\vec{k}$, and matrices onto which the IR's map operators of the space group. These are not just the the matrices of the IR's of the little groups of $\vec{k}$ (which is what you usually find in tables of IR matrices), but the matrices of the complete IR of the space group.

III. EXAMPLES

After the discovery of its ferroelectricity in 1945, $BaTiO_3$ became one of the most widely investigated ferroelectric materials.[10] Both static and dynamic investigations studied the transitions in this material. It has the prototype perovskite structure above 120 °C and becomes tetragonal, then orthorhombic, and finally trigonal as temperature is lowered. The barium atoms are at the Wyckoff (a) site and the titanium atoms at the (b) site.[11] The change in symmetry from $Pm\bar{3}m$ to $P4mm$ occurs in the first transition. For this transition, $P4mm$ has the lattice vectors $(1,0,0),(0,1,0),(0,0,1)$, and origin at $(0,0,0)$ for one of the orientations of the tetragonal phase. The new lattice and origin are given here in terms of the parent group lattice vectors. The following is the complete listing of OP's and their directions for this specific $L \subset H$ pair obtained by the COPL algorithm

Γ_1^+	(a)	$Pm\bar{3}m$	1
Γ_3^+	$(a,0)$	$P4/mmm$	1
Γ_4^-	$(0,0,a)$	$P4mm$	1.

Here we indicate each IR determined by this group-subgroup pair, the direction of the OP in IR carrier space, the subgroup determined by the OP, and the relative size of the unit cell of the subgroup. The labeling of IR's is that of Miller and Love[12] and the specific form of the OP depends on the choice of matrices for the IR. We used our own matrices which may be obtained from ISOTROPY.[4,9] Symmetry does not determine the value of the OP but will specify lines, planes, general points, etc. For example, the symbol a in the OP for Γ_4^- represents an arbitrary constant and indicates that any point of the line along the third IR axis gives the same subgroup. The physical distortion associated with the $(0,0,a)$ direction of Γ_4^- is the onset of polarization in the z direction, with the $(a,0)$ direction of Γ_3^+ is the onset of tetragonal strain along z, and with the (a) direction of Γ_1^+ is a volume change. This example of the use of the COPL algorithm is straight forward and offers no surprises.

Ferroelectric perovskite $A(B'B'')O_3$ alloys are of importance lately because of their large piezoelectric properties and the discovery of a monoclinic phase[13] between the tetragonal and rhombohedral phases. An analysis of the experimental data of a Pb-based perovskite alloy has been given[14] based upon the symmetry adapted free energy functions for different phases obtained as subgroups of $Pm\bar{3}m$. The primary OP space is taken to be Γ_4^-, the same as that used in the preceding paragraph, and the different phases are obtained for different directions of the OP within that space. The OP direction for the monoclinic M_a phase lies in the plane (a,a,b),[4,9] and its symmetry is Cm. (a and b are independent arbitrary constants. We cannot determine the ratio of b/a using symmetry alone.) This subgroup can be realized as a minimum of the Landau free energy if one goes to high enough order in the expansion[4] but the transition cannot be continuous. We obtain the following complete listing of OP directions from the COPL algorithm for the (a,a,b) direction with lattice vectors $(1,1,0)$, $(-1,1,0),(0,0,1)$ and origin at $(0,0,0)$:

Γ_1^+	(a)	$Pm\bar{3}m$	1
Γ_3^+	$(a,0)$	$P4/mmm$	1
Γ_4^+	$(a,-a,0)$	$C2/m$	1
Γ_5^+	(a,b,b)	$C2/m$	1
Γ_2^-	(a)	$P\bar{4}3m$	1
Γ_3^-	$(a,0)$	$P\bar{4}2m$	1
Γ_4^-	(a,a,b)	Cm	1
Γ_5^-	$(0,a,-a)$	$Amm2$	1.

The Γ_4^- IR again corresponds to the onset of polarization. The IR's Γ_5^+ and Γ_3^+ correspond to shear and deviatoric strain respectively. This example is relatively straight forward and is of current scientific interest.

$BaAl_2O_4$ exhibits a ferroelectric phase transition at 396 K. The low symmetry phase is $P6_3$. Recently Abakumov *et al.*[15] investigated this transition by transmission electron microscopy. They found that the transition leads to a doubling of the hexagonal lattice parameter a so that the ferroelectric unit cell is four times larger. They proposed that the high temperature, high symmetry phase is $P6_322$ with origin $(0,0,0)$ and lattice vectors $(2,0,0),(0,2,0),(0,0,1)$. The COPL algorithm yields the following OP's:

Γ_1	(a)	$P6_322$	1
Γ_2	(a)	$P6_3$	1
M_1	(a,a,a)	$P6_322$	4
M_2	(a,a,a)	$P6_3$	4.

We note that the low symmetry phase (space group $P6_3$ and size 4) is fully determined by the IR M_2. Thus the OP (a,a,a) for M_2 is the primary OP. The OP's for IR's Γ_1 and M_1 are secondary OP's. All correspond physically to atomic displacement modes. This example is of interest because there is no published OP information for this transition.

Shape memory alloys are materials of practical importance as they are being used as actuators, couplers, smart materials, medical guide wires, and stents, and they are important scientifically as fertile grounds for new methods in the investigation of phase transitions. The prototype shape-memory alloys are Ni-Ti, Au-Cd, and other pseudo-binary alloys $\mathrm{Ti(Ni},X)(X=\mathrm{Fe, Al,Cu})$. These materials exhibit a phase transition from the $B2$ structure (symmetry $Pm\bar{3}m$) to the $B19'$ structure (symmetry $P2_1/m$).[16] The monoclinic phase has the lattice vectors $(1,1,0)(-1,1,0)(0,0,1)$ and origin $(0,\frac{1}{2},0)$ relative to the original simple cubic phase. From the COPL algorithm we obtain the following listing of OP's:

Γ_1^+	(a)	$Pm\overline{3}mm$	1
Γ_3^+	$(a,0)$	$P4/mmm$	1
Γ_4^+	$(a,-a,0)$	$C2/m$	1
Γ_5^+	(a,b,b)	$C2/m$	1
M_2^-	$(a,0,0)$	$P4/nmm$	2
M_3^-	$(a,0,0)$	$P4/nmm$	2
M_5^-	$(0,0,a,0,0,0)$	$Pmma$	2.

IR's Γ_1^+, Γ_3^+, and Γ_5^+ yield strain contributions to the transition while IR's M_2^-, M_3^-, M_5^- define atomic displacement distortions. This example is of interest because the description of this transition has not included the full complement of OP's and the corresponding distortions that accompany them.[17] It is also interesting in that the transition cannot be induced by a single IR. Notice that no single OP gives the subgroup $P2_1/m$. However, there are sets of two coupled OP's which do. The selection of the pair M_5^-,M_2^- gives $P2_1/m$ as does the pair M_5^-,M_3^- $(Pmma\cap P4/nmm = P2_1/m)$ with the same origin and basis. The choice of these two primary OP's is arbitrary in that either pair can be used as the primary driving mechanisms for this transition.

There is another phase transition in the Ni-Ti alloys which has attracted considerable attention. This is the transition from the $B2$ phase to the R phase $(P3)$.[16,18] The R phase has a cell size increase of 9, the origin is at (0,0,0), and the lattice vectors are $(2,-1,-1),(-1,2,-1),(1,1,1)$. From the COPL algorithm we get the following complete listing of OP's:

Γ_1^+		(a)	$Pm\overline{3}m$	1
Γ_2^+		(a)	$Pm\overline{3}$	1
Γ_4^+		(a,a,a)	$R\overline{3}$	1
Γ_5^+		(a,a,a)	$R\overline{3}m$	1
Γ_1^-		(a)	$P432$	1
Γ_2^-		(a)	$P\overline{4}3m$	1
Γ_4^-		(a,a,a)	$R3m$	1
Γ_5^-		(a,a,a)	$R32$	1
Λ_1	$(\frac{1}{3},\frac{1}{3},\frac{1}{3})$	$(a,0,0,0,b,0,0,0)$	$P3m1$	3
Λ_2	$(\frac{1}{3},\frac{1}{3},\frac{1}{3})$	$(a,0,0,0,b,0,0,0)$	$P3$	3
Σ_1	$(\frac{1}{3},\frac{1}{3},0)$	$(0,a,b,0,0,a,0,-b,0,0,a,b)$	$P312$	9
Σ_2	$(\frac{1}{3},\frac{1}{3},0)$	$(0,a,b,0,0,a,0,-b,0,0,a,b)$	$P3$	9
Σ_3	$(\frac{1}{3},\frac{1}{3},0)$	$(0,a,b,0,0,a,0,-b,0,0,a,b)$	$P3$	9
Σ_4	$(\frac{1}{3},\frac{1}{3},0)$	$(0,a,b,0,0,a,0,-b,0,0,a,b)$	$P312$	9.

In the above list the Λ and Σ IR's occur on lines of symmetry in the Brillouin zone. The coordinates of the $\vec{k}$ vector on those lines are given, following the IR symbol. This example is of interest because of its large number of OP's, and because the primary OP arises from a line of symmetry Σ, in the Brillouin zone. This example has additional interest because there is an ambiguity in selecting the primary OP. We see that each of the OP's $\Sigma_2(0,a,b,0,0,a,0,-b,0,0,a,b)$ and $\Sigma_3(0,a,b,0,0,a,0,-b,0,0,a,b)$ individually fully determine the $P3$ subgroup.

---

[1] E. Ascher and J. Kobayashi, J. Phys. C **10**, 1349 (1997).

[2] E. Ascher, J. Phys. C **10**, 1365 (1997).

[3] P. Tolédano and J. C. Tolédano, Phys. Rev. B **13**, 3097 (1976); **16**, 386 (1977); **21**, 1139 (1980); **25**, 1946 (1982).

[4] H. T. Stokes and D. M. Hatch, *Isotropy Subgroups of the 230 Crystallographic Space Groups* (World Scientific, Singapore, 1988).

[5] K. Yoshizawa, M. Hatanaka, Y. Matusuzaki, K. Tanaka, and T. Yamabe, J. Chem. Phys. **100**, 4453 (1994).

[6] M. Kuźma, B. Lulek, and T. Lulek, J. Phys.: Condens. Matter **3**, 7545 (1991).

[7] B. Mettout and P. Tolédano, Europhys. Lett. **46**, 357 (1999).

[8] H. T. Stokes and D. M. Hatch, Phase Transitions **34**, 53 (1991).

[9] The software package ISOTROPY is available at http://www.physics.byu.edu/~stokesh/isotropy.html.

[10] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon, Oxford, 1977).

[11] *International Tables for Crystallography*, edited by T. Hahn (Reidel, Boston, 1983).

[12] S. C. Miller and W. F. Love, *Tables of Irreducible Representations of Space Groups and Co-Representations of Magnetic Space Groups* (Pruett, Boulder, 1967).

[13] B. Noheda, D. E. Cox, G. Shirane, R. Guo, B. Jones, and L. E. Cross, Phys. Rev. B **63**, 014103 (2001).

[14] Y. Yamada, Y. Uesu, M. Matsuda, K. Fujishiro, D. E. Cox, B. Noheda, and G. Shirane, cond-mat/0106553 (unpublished).

[15] A. M. Abakumov, O. I. Lebedev, L. Nistor, G. Van Tendeloo, and S. Amelinckx, Phase Transitions **71**, 143 (2000).

[16] G. R. Barsch, T. Ohba, and D. M. Hatch, Mater. Sci. Eng., A **273-275**, 161 (1999).

[17] X. Huang, C. Bungaro, V. Godlevsky, and K. M. Rabe, cond-mat/0105278 (unpublished).

[18] W. Cai, Y. Murakami, and K. Otsuka, Mater. Sci. Eng., A **273-275**, 186 (1999).