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Symmetry and phase transitions: the inverse Landau problem

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Abstract. For a phase transition between two phases of symmetries H and $L < H$, we reconsider the problem of finding the irreducible representation T_i of H that (according to Landau's theory) determines the transition. We show how this representation can be found directly (without going into the intricacies of the theory of induced representations and Landau's theory) from the permutation representation of H determined by the pair $L < H$. In all the examples considered, the group L is maximal with respect to the property that it acts trivially on some non-zero subspace of the representation space M_i of T_i.

1. Introduction

This is the first of a series of papers in which we shall discuss what can be said about phase transitions simply on the basis of symmetry considerations and the laws of thermodynamics.

The problem in its general form is the following: given the symmetry group H of a disordered, high-symmetry (and usually high-temperature) phase, find all the possible order parameters; for each of these determine the symmetries L of the possible ordered, low-symmetry (and usually low-temperature) phases; write down the thermodynamic potentials that describe these phases and the transitions between them and find a suitable way of classifying these potentials.

We shall name this problem the *Landau problem.* Indeed, the best known, and successful, theory which attempts to solve this problem is that of Landau (see e.g. Landau and Lifschitz 1958). According to Landau, the symmetry group L of each of the possible ordered phases is a subgroup of the symmetry group H (of the disordered phase) determined by one of those irreducible representations of H that fulfil a series of conditions (see e.g. Goldrich and Birman 1968). In this theory, thermodynamics and symmetry are intimately interwoven, perhaps even too much so. To some extent, we shall try to disentangle the threads and not invoke thermodynamics where group theory (or more generally mathematics) will suffice.

Another simple but powerful method is that based on *Curie's principle* (Curie 1894) as revived by the Russian school of crystal physicists (e.g. Zhëludev and Shuvalov 1957). It may be that this interpretation of the principle is too permissive. Our own version, which may be called the *maximum principle,* was formulated originally for such types of order parameter as electrical polarization, magnetization and current density or vector potential (Ascher 1966a, b), and admits a smaller number of possible symmetries for the ordered phases. In the following paper (Ascher 1977) we shall give a generalization of both principles.

2. The inverse Landau problem

In this paper we do not want to face the Landau problem in its full generality. Instead, as preparation, we shall study a less ambitious question, one that nevertheless is of great practical interest on its own. It is the following: given a group H (of the disordered phase) and a subgroup L of H (that describes the ordered phase), find the irreducible representation of H determined by this transition. We term this the *inverse Landau problem.* From its solution, much can be learned about the 'direct' Landau problem.

The inverse Landau problem is usually solved by a method of trial and error resting on the theory of induced representations. From the change in the translational symmetry, one determines the wavevector k and then, using the theory of induced representations, one finds all the irreducible representations of H corresponding to k. One then examines whether these fulfil the various conditions required by Landau theory (see e.g. Birman 1966, Dvorak 1971). For the admissible representations one then has to find the corresponding low-symmetry group L (if Landau's theory actually explains the phase transition in question).

Here we propose the following solution to the inverse Landau problem. Given two symmetry groups H and L (of the disordered and ordered phase, respectively) such that L is a subgroup of H, we form the permutation representation of H on the co-sets of L. If n is the index of L in N, this gives a homomorphism

$$\pi_L : H \rightarrow \mathrm{S}_n \qquad n = |H:L|$$

of H into the symmetric group S_n on n symbols. The image G of π_L is a subgroup of S_n and is isomorphic to the quotient group formed by the left co-sets of the kernel $\mathrm{Ker}\pi_L$ in H:

$$G \simeq H/\mathrm{Ker}\pi_L.$$

G is the *group determined by the phase transition.* Now, in principle, three cases may arise:

(i) G has no faithful irreducible representation,

(ii) G has exactly one faithful irreducible representation, and

(iii) G has more than one faithful irreducible representation.

In the following examples we shall find that the group G determined by the transition has one single faithful irreducible representation τ. This then is *the irreducible representation of H, determined by the transition.* It can also be characterized as the G-faithful irreducible component of the permutation representation π_L (which is always reducible). A general discussion of the trilemma will be given in a subsequent paper.

The method indicated here is straightforward. In the following example we shall give more information, however, than is strictly needed for the determination of the group G and the irreducible representation τ of H determined by the transition $H \rightarrow L$. Indeed these examples will also have to serve as illustrations of the theory that will be developed in subsequent papers.

3. First example: Nb_3Sn

As a first example we choose to discuss the diffusionless phase transition observed at low temperatures in compounds having the β-tungsten structure. In the case of Nb_3Sn, Shirane and Axe (1971) have found at (45·2 ± 0·3) K the change of symmetry

$$H = Pm3n \rightarrow P4_2^z/mmc = : L.$$

The index of L in H is 3:

$$|Pm3n : P4_2/mmc| = 3.$$

The kernel of the homomorphism

$$\pi_L : Pm3n \rightarrow \mathrm{S}_3$$

is *Pmmm*:

$$\mathrm{Ker}\ \pi_L = Pmmm.$$

(The group *Pmmm* is the intersection of the three *Pm*3*m*-conjugate subgroups $P4_2^x/mmc$, $P4_2^y/mmc$ and $P4_2^z/mmc$.) The *group G determined by the transition is*

$$Pm3n/Pmmm = \mathrm{D}_3.$$

Here D_3 denotes an abstract group and has no special crystallographic meaning, i.e. not necessarily $\mathrm{D}_3 = 32$. In general, the letters C, D, A and S will denote abstract groups having the structure of the cyclic, dihedral, alternating or symmetric group, respectively. The group D_3 has one faithful irreducible representation, namely E. This is *the irreducible representation of Pm3n determined by the transition.*

To give this representation of *Pm*3*n* explicitly, it is necessary and sufficient to indicate the linear transformations corresponding to generators of *Pm*3*n*. (It is unfortunately a widespread custom not to consider all generators; the translations are usually forgotten. The required information is given, however, for some selected non-generators. While this is agreeable and useful, it does not compensate for the lack of what is necessary.) As generators of *Pm*3*n*, we take the six elements.

$$e_1 = \{1|100\}, \qquad e_2 = \{1|010\}, \qquad e_3 = \{1|001\}$$
$$\{4_z\} = (e_1 e_2 e_3)^{1/2} 4_z = \{4_z|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\}$$
$$\{2_a\} = (e_1 e_2 e_3)^{1/2} 2_a = \{2_a|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\}$$
$$\bar{1} = \{\bar{1}|000\}.$$

The representation is given in table 1. It may be identified as the representation R_5 of G_{48}^7 on page 252 in Bradley and Cracknell (1972).

We use the following abbreviations for special directions: $a = (011)$, $b = (01\bar{1})$, $c = (101)$, $d = (10\bar{1})$, $e = (110)$ $f = (1\bar{1}0)$, $\alpha = (1\bar{1}\bar{1})$, $\beta = (\bar{1}1\bar{1})$, $\gamma = (\bar{1}\bar{1}1)$ and $\delta = (111)$. In the double row starting with *Pm*3*n*, the six generators of the group may be found in

Table 1. Irreducible representation τ of *Pm*3*n* determined by the transition $Pm3n \rightarrow P4_2/mmc$.

*Pm*3*n*	Ker	Im		1	3_α	3_α^2	$\{2_a\}$	$\{2_b\}$	$\{2_c\}$
				$e_1, e_2, e_3, \bar{1}$				$\{4_z\}$	$\{2_a\}$
π_L	*Pmmm*	D_3	$\mathrm{A}_1 \oplus \mathrm{E}$	(1)(2)(3)	(123)	(132)	(1)(23)	(2)(31)	(3)(12)
τ	*Pmmm*	D_3	E	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \epsilon^2 & 0 \\ 0 & \epsilon \end{pmatrix}$	$\begin{pmatrix} \epsilon & 0 \\ 0 & \epsilon^2 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \epsilon \\ \epsilon^2 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \epsilon^2 \\ \epsilon & 0 \end{pmatrix}$
				2	−1	−1	0	0	0

the lower part; a few other elements are given in the upper part. In the row starting with π_L one finds the permutation representation, which consists here of the permutations forming S_3. The corresponding permutation matrices can be reduced as $A_1 \oplus E$ of D_3.

The group $P4_2/mmc$ of the low-temperature phase has some noteworthy properties. It is maximal with respect to the property of determining the faithful irreducible representation $E(D_3)$ of D_3. Indeed its minimal supergroup in the lattice of subgroups of $Pm3n$ is $Pm3n$ itself and this group determines the faithful irreducible A of C_1. However, $P4_2/mmc$ is not the only subgroup of $Pm3n$ that determines this representation $E(D_3)$—the normal subgroup $Pmmm$ is obviously another one. There are no other such groups, however.

The maximality of $P4_2/mmc$ can be expressed in yet another way. It is maximal with respect to the property that there exists a (non-zero) subspace of the two-dimensional representation space M_E of E that consists of fixed points. In this example, this subspace is one-dimensional, as can be seen from the decomposition $\pi_L = A \oplus E$.

We shall say that, in the transition $Pm3n \to P4_2/mmc$, the order parameter is two-dimensional with one active component. This defines the order parameter abstractly. To have a physical order parameter one also needs a physical interpretation of the representation space.

Thus $P4_2/mmc$ is a subgroup of $Pn3m$, maximal with respect to the property of leaving the order parameter invariant. A detailed discussion of these questions of maximality (and of associated minimality) will be given in a subsequent paper.

To close the discussion of this example, we introduce a diagrammatic representation which clearly shows the role and situation of the various groups introduced in the discussion. It is based on the fact that every space group contains a (maximal abelian) normal subgroup U of translations such that the quotient S/U is isomorphic to a point group K. We then say that S is an extension of U by K. The extension can be presented graphically by (the short exact sequence of groups)

$$U \rightarrowtail S \twoheadrightarrow K$$

(see Ascher and Janner 1965, 1968). Here, an arrow $\rightarrowtail$ denotes a monomorphism and $\twoheadrightarrow$ an epimorphism (these are, in the case of groups, homomorphisms that are respectively one-to-one and onto). It is useful to also introduce homomorphisms between extensions. Thus, the three space groups encountered in this example may usefully be put in the following diagram (extensions horizontally):

$$\begin{array}{ccccc}
P & \rightarrowtail & Pmmm & \twoheadrightarrow & mmm \\
\| & & \downarrow & & \downarrow \\
P & \rightarrowtail & P4_2/mmc & \twoheadrightarrow & 4/mmm \\
\| & & \downarrow & & \downarrow \\
P & \rightarrowtail & Pm3n & \twoheadrightarrow & m3m
\end{array}$$

The identity sign $=\!=$ on the left-hand side of the diagram is there to remind us that everything takes place 'equitranslationally'. A further useful diagram introduces the permutation representation π_L and the group D_3 determined by the transition $Pm3n \to P4_2/mmc$:

$$\begin{array}{ccccc}
P & \rightarrowtail & Pmmm & \twoheadrightarrow & mmm \\
\Vert & & \big\downarrow & & \big\downarrow \\
P & \rightarrowtail & Pm3n & \twoheadrightarrow & m3m \\
 & & \pi \big\downarrow & & \big\downarrow \\
 & & D_3 & = & D_3.
\end{array}$$

Here we find extensions horizontally and vertically.

Such diagrams will prove especially useful in cases that are more complicated than the present one.

4. Second example: $Gd_2(MoO_4)_3$ and $NH_4H_2PO_4$

The first compound, usually referred to as GMO, undergoes a phase transition at 159 °C. The change of symmetry is from $H = P\bar{4}2_1m$ to $L = Pba2$ and the volume of the primitive unit cell is doubled. The low-temperature phase is ferroelectric. The index of $Pba2$ in $P\bar{4}2_1m$ is thus 4, the lowest possible index. In the lattice of subgroups of $P\bar{4}2_1m$, the only group between $P\bar{4}2_1m$ and $Pba2$ is $Cmm2$. (Note that, despite the notation, $P\bar{4}2_1m$ and $Cmm2$ contain the same translations, can be given the same primitive cell). The situation is thus the following:

$$\begin{array}{ccccc}
U & \rightarrowtail & Pba2 & \twoheadrightarrow & mm2 \\
2\big\downarrow & & \big\downarrow 2 & & \Vert \\
P & \rightarrowtail & Cmm2 & \twoheadrightarrow & mm2 \\
\Vert & & \big\downarrow 2 & & \big\downarrow 2 \\
P & \rightarrowtail & P\bar{4}2_1m & \twoheadrightarrow & \bar{4}2m
\end{array}$$

The number beside the sign for monomorphism indicates the index of the subgroup. Both $Pba2$ and $Cmm2$ are normal subgroups of $P\bar{4}2_1m$, and

$$P\bar{4}2_1m/Pba2 = C_4.$$

Thus *the group determined by the transition* is the cyclic group of order four.

$$\begin{array}{ccccc}
U & \rightarrowtail & Pba2 & \twoheadrightarrow & mm2 \\
\big\downarrow & & \big\downarrow & & \big\downarrow \\
P & \rightarrowtail & P\bar{4}2_1m & \twoheadrightarrow & \bar{4}2m \\
\big\downarrow & & \big\downarrow & & \big\downarrow \\
C_2 & \rightarrowtail & C_4 & \twoheadrightarrow & C_2
\end{array}$$

As generators of $P\bar{4}2_1m$ we choose

$$e_1 = \{1|100\}, \qquad e_2 = \{1|010\}, \qquad e_3 = \{1|001\}$$
$$\bar{4}_z = \{\bar{4}_z|000\}$$
$$\{2_x\} = (e_1e_2)^{1/2}2_x = \{2_x|\tfrac{1}{2}\ \tfrac{1}{2}\ 0\}.$$

For the subgroup *Pba*2 we take

$$
\begin{aligned}
a_1 &= e_1 e_2^{-1} = \{1|1{-}10\} = [1|100] \\
a_2 &= e_1 e_2 = \{1|110\} = [1|010] \\
a_3 &= e_3 = \{1|001\} = [1|001] \\
[2_z] &= e_2 \bar{4}_x^2 = \{2_z|010\} = [2_z|{-}\tfrac{1}{2}\tfrac{1}{2}0] \\
[m_x] &= \{2_x\}\bar{4}_z = \{m_f|\tfrac{1}{2}\tfrac{1}{2}0\} = [m_x|0\tfrac{1}{2}0].
\end{aligned}
$$

The non-primitive translation in the Seitz symbols within the braces are given with respect to the generating translations of the supergroup. In the symbols within square brackets everything is referred to the generating translations of the group *Pba*2; thus the $f = [110]$ direction with respect to the e_i becomes the direction $x = [\bar{1}00]$ with respect to the a_i.

A decomposition into left co-sets of *Pba*2 is

$$P\bar{4}2_1m = L + e_1^{-1}L + \{2_x\}L + e_1^{-1}\{2_x\}L.$$

The multiplication table of co-sets is of course that of C_4. This group has one single real faithful irreducible representation τ, *the representation determined by the transition.* The permutation representation π_L provides a monomorphism from C_4 into S_4 and can be decomposed into linear ones, as indicated in table 2, the co-sets having been numbered

Table 2. Irreducible representations of $P\bar{4}2_1m$ determined by the transitions $P\bar{4}2_1m \rightarrow Pba2$ and $P\bar{4}2_1m \rightarrow Pmm2$.

$P\bar{4}2_1m$	Ker	Im		Elements of $P\bar{4}2_1m$			
	*Pba*2	C_4		e_3 $\{m_f\}$	$\{2_x\}$ $\bar{4}_z^2$	e_1, e_2 $2_z, \{m_e\}$	$\bar{4}_z$ $\{2y\}$
	*Pmm*2	C_4	$A \oplus B \oplus E$	e_3 $\{m_e\}$	$\{2_x\}, \bar{4}$	e_1, e_2 $2_z, \{m_f\}$	$\{2y\}$
π_L		C_4	$A + B + E$	(1) (2) (3) (4)	(1234)	(13) (24)	(1423)
τ			E	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$

in the order given above. The generators e_1 and e_2 belong to the co-sets e_1L which is the second-order element in C_4; e_3 belongs to the unit element L. This reflects the fact that the representation corresponds to a 'wavevector' $k = (\tfrac{1}{2}\tfrac{1}{2}0)$. The generators $\bar{4}_z$ and $\{2_x\}$ belong to the fourth-order co-sets $\{2_x\}e_1^{-1}L$ and $\{2_x\}L$, respectively.

From the preceding discussion it is also clear that the group *Pba*2 is maximal with respect to the property of determining the faithful irreducible representation E of C_4. Indeed, *Cmm*2 would give the representation *B* of C_2. (Since *Pba*2 is a normal subgroup, it is also minimal with respect to the above property.) Again, as in the preceding example, it is maximal with respect to the property of leaving invariant the order parameter of the transition—here any element of the two-dimensional representation space of E.

It is instructive to consider briefly all the subgroups of index 4 of $P\bar{4}2_1m$ with a change of translational symmetry corresponding to the wavevector $k = (\tfrac{1}{2}\tfrac{1}{2}0)$. These are the four groups of *Cmm*2 obtained by a loss of centring of *Cmm*2: *Pmm*2, *Pma*2, *Pbm*2 and *Pba*2 (see Neubüser and Wondratschek 1965). The first and the last are normal subgroups. They both determine as groups of the transition C_4 and as representation $E(C_4)$, although the non-translational elements of the space groups do not belong to the same co-sets in the two cases (see table 2). The difference comes from the fact that now

$\pi_L \bar{4}_z = (1234)$. Since the kernels are not isomorphic in the two cases, one has in fact two inequivalent real irreducible representations of $P\bar{4}2_1m$; these are denoted T_1 and T_2 by Dvorak (1971), where they are determined by *Pba*2 and *Pmm*2, respectively; our result in Table 2 gives the other pairing. It is in fact a matter of taste (read labelling) which pairing one chooses. Furthermore, the thermodynamic potentials are the same for both representations.

The situation is quite different for the two isomorphic groups *Pma*2 and *Pbm*2. They are inequivalent as extensions (of P by $mm2$) and conjugate as subgroups of $P\bar{4}2_1m$, and their intersection is the group $P2$ of index two in each of them. Thus the group

$$G = P\bar{4}2_1m/Pma2$$

determined by a transition $P\bar{4}2_1m \rightarrow Pma2$ is of order eight. There are five such groups. To find G we determine the permutation representation π_L afforded by $L = Pma2$. The co-set decomposition is the same as before and the generator of the translations are the same, but the two other generators are

$$[2_z] = [2_z|000] = \bar{4}_z^2$$
$$[m_x] = [m_x|\tfrac{1}{2}00] = e_2^{-1}\{2_x\}\bar{4}_z.$$

Thus one finds that the same permutations as before correspond to the translations, and also that the generator $\{2_x\}$ is represented by an unchanged permutation

$$\pi_L\{2_x\} = (1234);$$

the element that makes the difference is $\bar{4}_z$:

$$\pi_L \bar{4}_z = (12)(34).$$

The two elements (1234) and (12)(34) generate the dihedral group D_4. The situation is summarized in the following diagram of extensions:

$$\begin{array}{ccccc}
U & \rightarrowtail & P2 & \twoheadrightarrow & 2 \\
\downarrow & & \downarrow & & \downarrow \\
P & \rightarrowtail & P\bar{4}2_1m & \twoheadrightarrow & \bar{4}2m \\
\downarrow & & \downarrow & & \downarrow \\
C_2 & \rightarrowtail & D_4 & \twoheadrightarrow & D_2.
\end{array}$$

Further details are contained in table 3. The usual omission of the generators of the translations suppresses the character -2 and makes it difficult to recognize the irreducible representation τ of $P\bar{4}2_1m$ as the faithful representation E of D_4.

Let us now turn to the compound $NH_4H_2PO_4$ (ADP). It becomes antiferroelectric at $-125°C$, the symmetry changing from $H = I\bar{4}2d$ to $L = P2_12_12_1$. The situation is the following:

$$\begin{array}{ccccc}
P & \rightarrowtail & P2_12_12_1 & \twoheadrightarrow & 222 \\
{\scriptstyle 2}\downarrow & & {\scriptstyle 2}\downarrow & & \| \\
U & \rightarrowtail & I2_12_12_1 & \twoheadrightarrow & 222 \\
\| & & \downarrow{\scriptstyle 2} & & \downarrow{\scriptstyle 2} \\
U & \rightarrowtail & I\bar{4}2d & \twoheadrightarrow & \bar{4}2m.
\end{array}$$

Table 3. Irreducible representations of $P\bar{4}2_1m$ determined by the transitions $P\bar{4}2_1m \rightarrow Pma2$ and $P\bar{4}2_1m \rightarrow Pbm2$

$P\bar{4}2_1m$	Ker	Im		Elements of $P\bar{4}2_1m$							
	Pma2	D_4		$e_3, 2_z$	$\{2_x\}, \{2_y\}$		e_1, e_2	$\bar{4}_z, \bar{4}_z^3$		$\{m_e\}, \{m_f\}$	
	Pbm2	D_4		$e_3, 2_z$	$\{2_x\}, \{2_y\}$		e_1, e_2		$\bar{4}_z, \bar{4}_z^3$		$\{m_e\}, \{m_f\}$
π_L		D_4	$A \oplus B_2 \oplus E$	1	(1234)	(1432)	(13)(24)	(12)(34)	(14)(23)	(13)	(24)
τ		D_4	E	2	0	0	−2	0	0	0	0

Generators of $I\bar{4}2d$ are

$$
\begin{aligned}
a_1 &= (e_1^{-1}e_2e_3)^{1/2} = \{1|1000\}\\
a_2 &= (e_1e_2^{-1}e_3)^{1/2} = \{1|010\}\\
a_3 &= (e_1e_2e_3^{-1})^{1/2} = \{1|001\}\\
4_z &= \{4_z|000\}\\
\{2_x\} &= e_2^{1/2}e_3^{1/4}2_x = \{2_x|\tfrac{3}{4}\tfrac{1}{4}\tfrac{1}{2}\}.
\end{aligned}
$$

The elements a_1, a_2 and a_3 generate an FCC lattice U. The generators of the subgroup are e_1, e_2 and e_3 (generating the primitive cubic lattice P) and

$$
\begin{aligned}
(2_z) &= a_1a_2a_3\,4_z = (2_z|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\\
(2_x) &= a_3\{2_x\} = (2_x|\tfrac{1}{2},1,-\tfrac{1}{4}).
\end{aligned}
$$

This enables us to find the decomposition into co-sets:

$$H = L + \{m_e\}L + a_1a_2a_3L + \{m_e\}a_1a_2a_3L.$$

The co-sets form the cyclic group C_4:

$$
\begin{array}{ccccc}
P & \rightarrowtail & P2_12_12_1 & \twoheadrightarrow & 222\\
\downarrow & & \downarrow & & \downarrow\\
U & \rightarrowtail & I\bar{4}2d & \twoheadrightarrow & \bar{4}2m\\
\downarrow & & \downarrow & & \downarrow\\
C_2 & \rightarrowtail & C_4 & \twoheadrightarrow & C_2.
\end{array}
$$

The generators a_1, a_2, a_3 and $\{2_x\}$ belong to the co-set $a_1a_2a_3L$, the second-order element of C_4, while the 'wavevector' is $(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})$; the generator 4_z is an element of $\{m_e\}L$. Hence the table 4. Again, the subgroup $P2_12_12_1$ is maximal with respect to the property of leaving the two-dimensional order parameter invariant.

Table 4. Irreducible representation τ of $I\bar{4}2d$ determined by the transition $I\bar{4}2d \rightarrow P2_12_12_1$.

$I\bar{4}2d$	Ker	Im		$\{2_y\}$	$\{m_f\}$	2_z	$\bar{4}_z^{-3}, \{m_e\}$
					$\bar{4}_z$	$a_1, a_2, a_3, \{2_x\}$	
π_L	$P2_12_12_1$	C_4	A⊕B⊕E	(1)(2)(3)(4)	(1234)	(13)(24)	(1423)
τ			E	2	0	−2	0

Thus the physically different phase transitions in GMO and ADP determined the same irreducible representation E of C_4. Abstractly the order parameter is the same, physically it may be different. Yet through the physical differences the abstract sameness will manifest itself in the thermodynamic properties.

5. Third example: boracite, $Mg_3B_7O_{13}Cl$

At 265°C, boracite undergoes a phase transition. The volume of a primitive unit cell doubles and the symmetry group changes from $H = F\bar{4}3c$ to $L = Pca2_1$ of index 12.

This group is neither a normal nor an equitranslation subgroup. It is useful, as is done in the following diagram of (horizontal) extensions, to separate the change of crystal class from the change of the translational symmetry by introducing the intermediate

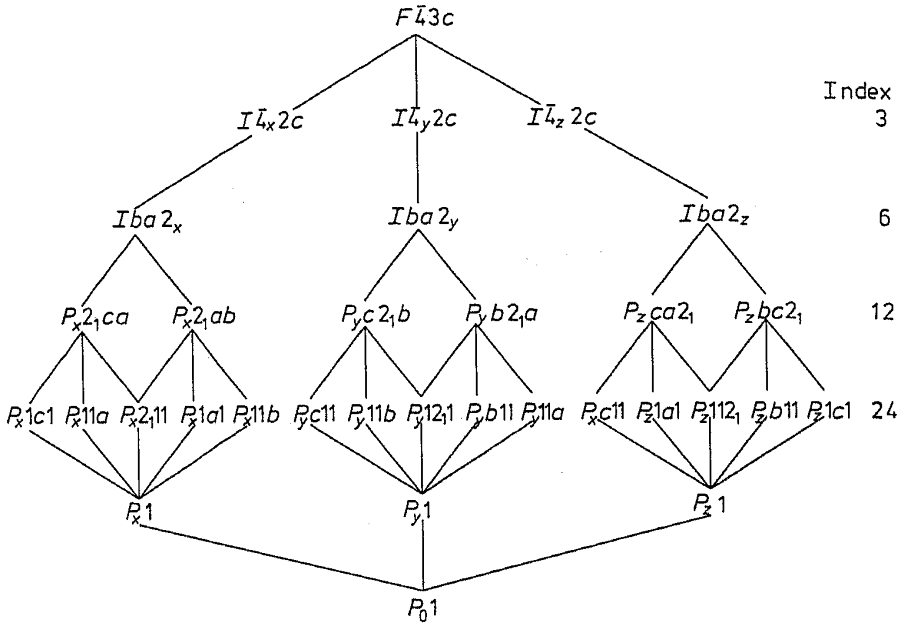
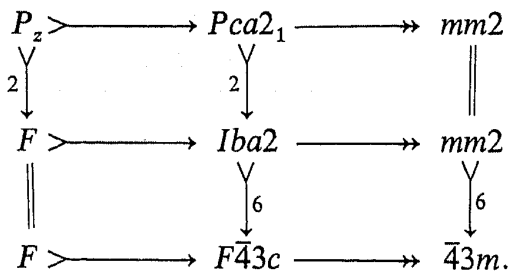


Figure 1. Lattice of subgroups between $F\bar{4}3c$ and P_01 (of index 96).

group $Iba2$, an equitranslation subgroup of $F\bar{4}3c$ and an equiclass supergroup of $Pca2_1$ (see also figure 1).



The elements of $F\bar{4}3c$ that are not translations are either of the form p or the form $(f_1f_2f_3)^{1/2}p$, where p is an element of the point group 23. As generators we choose the five following elements:

$$f_1 = (e_2e_3)^{1/2} = \{1|100\}$$
$$f_2 = (e_3e_1)^{1/2} = \{1|010\}$$
$$f_3 = (e_1e_2)^{1/2} = \{1|001\}$$
$$\{\bar{4}_z\} = (f_1f_2f_3)^{1/2}\bar{4}_z = \{1|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\}$$
$$\{m_a\} = (f_1f_2f_3)^{1/2}m_a = \{m_a|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\}.$$

The f_i generate a face-centred cubic lattice F, the e_i a simple cubic lattice P_0.

We pick the following five elements as generators of the subgroup $Pca2_1$:

$$
\begin{aligned}
c_1 &= f_1^{-1}f_2 = (e_1e_2)^{1/2} = \{1|1\bar{1}0\} = [1|100]\\
c_2 &= f_3 = (e_1e_2)^{1/2} = \{1|001\} = [1|010]\\
c_3 &= f_1f_2f_3^{-1} = e_3 = \{1|11\bar{1}\} = [1|001]\\
[2_z] &= f_1f_3^{-1}\{\bar{4}_z\}^2 = f_22_z = (e_3e_1)^{1/2}2_z = c_1c_2c_32_z = \{2_z|010\} = [2_z|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}]\\
[m_y] &= f_2f_3^{-1}\{\bar{4}_z\}^3\{m_a\}\{\bar{4}_z\}^2\{m_a\} = (f_1^{-1}f_2f_3)^{1/2}m_e = e_1^{1/2}m_e\\
&= (c_1c_2)^{1/2}m_e = \{m_e|\tfrac{\bar{1}}{2}\tfrac{1}{2}\tfrac{1}{2}\} = [m_y|\tfrac{1}{2}\tfrac{1}{2}0].
\end{aligned}
$$

The c_i generate a primitive orthorhombic lattice P_z. There are six subgroups that are conjugate in $F\bar{4}3C$ to $Pca2_1$, namely $P2_1ca$, $P2_1ab$, $Pc2_1b$, $Pb2_1a$, $Pca2_1$ and $Pbc2_1$ (note: six different groups, same setting). Their intersection, the largest normal subgroup of $F\bar{4}3c$ contained in each of them, is $P1 = P_0$, generated by the three translations e_1, e_2 and e_3 (see figure 1).

The three lattices F, P_z and P_0 are related in the following way:

$$F = P_z + f_1P_2 = (P_0 + c_2P_0) + f_1(P_0 + c_2P_0) = P_0 + f_3P_0 + f_1P_0 + f_1f_3P_0.$$

Since these co-sets multiply as D_2, we see that $U/W = D_2$. Thus we find that *the group G determined by the transition $F\bar{4}3c \to Pca2_1$ is given by the following diagram of extensions (horizontally and vertically)*:

$$
\begin{array}{ccccc}
P_0 & \rightarrowtail & P1 & \twoheadrightarrow & 1\\
\downarrow & & \downarrow & & \downarrow\\
F & \rightarrowtail & F\bar{4}3c & \text{———} & \bar{4}3m\\
\downarrow & & \downarrow & & \downarrow\\
D_2 & \rightarrowtail & G & \twoheadrightarrow & S_4
\end{array}
$$

The group G, of order 96, is an extension of D_2 by S_4. The problem now is to find the irreducible representation τ of $F\bar{4}3m$, i.e. the faithful irreducible representation of G, if indeed G has one single faithful irreducible representation. The example of boracite, to which we shall return in a subsequent paper, seems particularly instructive; we shall therefore give some details of the solution.

First we must know more about the group G. We know that it is a subgroup of order 96 of the symmetric group S_{12}, but what are its generators and the relations between them? Let us find the decomposition of $F\bar{4}3c$ into co-sets of $Pca2_1$. We use the intermediary group $I = Iba2$. Since

$$\bar{4}3m = mm2_z + \bar{4}_z(mm2) + m_a(mm2) + m_b(mm2) + m_c(mm2) + m_d(mm2),$$

we have

$$F\bar{4}3m = I + \{\bar{4}_z\}I + \{m_a\}I + \{m_b\}I + \{m_c\}I + \{m_d\}I.$$

Furthermore, $Fca2_1 = L$ is an equiclass subgroup of I. The translations of the former generate P_z, those of the latter generate F. Therefore we have

$$Iba2 = L + f_1L,$$

giving altogether the decomposition

$$
\begin{aligned}
F\bar{4}3m = L &+ \{4_z\}L + \{m_a\}L + \{m_b\}L + \{m_c\}L + \{m_d\}L + a_1L + \{\bar{4}_z\}a_1L\\
&+ \{m_a\}a_1L + \{m_b\}a_1L + \{m_c\}a_1L + \{m_d\}a_1L.
\end{aligned}
$$

Numbering the co-sets in this order from 1 to 12, we find that the generators of $F\bar{4}3c$ are mapped onto the following permutations

$$\begin{aligned}
\pi_L f_1 &= : F_1 = (17)(28)(39)(4,10)(5)(6)(11)(12)\\
\pi_L f_2 &= : F_2 = (17)(28)(5,11)(6,12)(3)(4)(9)(10)\\
\pi_L f_3 &= : F_3 = (39)(4,10)(5,11)(6,12)(1)(2)(7)(8) = F_1F_2\\
\pi_L\{\bar{4}_z\} &= : X = (1278)(3,11,10,6)(4,12,9,5)\\
\pi_L\{m_a\} &= : Y = (13)(24)(6,12)(79)(8,10)(5)(11).
\end{aligned}$$

Thus, as we knew already, the translation group generated by f_1, f_2 and f_3 is mapped on to the dihedral group D_2 generated by F_1 and F_2. Since all non-primitive translations in $F\bar{4}3c$ are of form $(f_1f_2f_3)^{1/2}$, they are mapped by π_L onto the unity. Thus G should contain a subgroup G_0 isomorphic to $\bar{4}3m$ and indeed we find

$$X^4 = Y^2 = (XY)^3 = 1,$$

showing that X and Y generate a group isomorphic to $\bar{4}3m$. Thus G is a semidirect product $D_2 \dot{\times} G_0$ of D_2 by G_0. The action of the latter on the former is given by

$$\begin{aligned}
XF_1X^{-1} &= F_2 \qquad & YF_1Y^{-1} &= F_1\\
XF_2X^{-1} &= F_1 \qquad & YF_2Y^{-1} &= F_1F_2.
\end{aligned}$$

From now on we shall identify the elements of G_0 with the corresponding elements of $\bar{4}3m$.

The group G has the ten conjugate classes given in table 5. The second column gives the cycle structure of the elements and the last column indicates the number of elements in the class. The symbol m_{a-f} stands for the six elements m_a, m_b, m_c, m_d, m_e and m_f; other similar symbols have similar meanings.

Table 5. Conjugation classes of G.

K_1	1^{12}	1	1
K_2	2^6	$2_x, 2_y, 2_z$	3
K_3	2^6	F_12_x, F_22_y, F_32_z	3
K_4	1^22^5	$m_{a-f}, F_1m_a, F_2m_b, F_2m_c, F_2m_d, F_3m_e, F_3m_f$	12
K_5	1^42^4	F_1, F_2, F_3	3
K_6	1^42^4	$F_12_y, F_12_z, F_22_z, F_22_x, F_32_x, F_32_y$	6
K_7	3^4	$3^{\pm}_{\alpha-\delta}, F_13^{\pm}_{\alpha-\delta}, F_23^{\pm}_{\alpha-\delta}, F_33^{\pm}_{\alpha-\delta}$	32
K_8	4^3	$\bar{4}^{\pm}_{x-z}, F_1\bar{4}^{\pm}_x, F_2\bar{4}^{\pm}_y, F_3\bar{4}^{\pm}_z$	12
K_9	4^3	$F_1\bar{4}_y, F_1\bar{4}_z, F_2\bar{4}_z, F_2\bar{4}_x, F_3\bar{4}_x, F_3\bar{4}_y$	12
K_{10}	$1^22^14^2$	$F_1m_{c,d,e,f}, F_2m_{e,f,a,b}, F_3m_{a,b,c,d}$	12

Table 6. Normal subgroups of G.

N_i	$\sum K_i$		G/N_i
N_0	G	$D_2 \dot{\times} S_4$	C_1
N_1	$K_1 + K_2 + K_3 + K_5 + K_6 + K_7$	$D_2 \dot{\times} A_4$	C_2
N_2	$K_1 + K_2 + K_3 + K_5 + K_6$	$D_2 \times D_2$	D_3
N_3	$K_1 + K_5$	D_2	S_4
N_4	$K_1 + K_3$	D_2	S_4
N_5	$K_1 + K_2$	D_2	S_4
N_6	K_1	C_1	G

From table 5 we read off the seven normal subgroups of G given in table 6. The second column indicates the classes of G that compose the normal subgroup, while in the third column the abstract structure of the subgroup is given (the symbol $\dot{\times}$ standing for semidirect product).

Now the simple characters of G can easily be found. Each faithful irreducible representation Γ of G/N_i gives an irreducible representation of G with kernel N_i. If G/N_i has no faithful irreducible representation, there is no irreducible representation of G with kernel N_i. It turns out that each normal subgroup of G provides the kernel for at least one irreducible representation. In this way we find the characters of nine of the ten irreducible representations. The tenth, the one in which we are interested, is faithful and its characters can now be found from the well-known relations between simple characters. The result is shown in table 7. The last line row of this table gives the character of the (reducible) permutation representation π_L.

Table 7. Simple characters of G.

τ_i	N_i	G/N_i	Γ	K_1	K_2	K_3	K_4	K_5	K_6	K_7	K_8	K_9	K_{10}
τ_0	G	C_1	A	1	1	1	1	1	1	1	1	1	1
τ_1	N_1	C_2	B	1	1	1	−1	1	1	1	−1	−1	−1
τ_2	N_2	D_3	E	2	2	2	0	2	2	−1	0	0	0
τ_3	N_3	S_4	T_1	3	−1	−1	−1	3	−1	0	1	1	−1
τ_3'	N_3	S_4	T_2	3	−1	−1	1	3	−1	0	−1	−1	1
τ_4	N_4	S_4	T_1	3	−1	3	−1	−1	−1	0	1	−1	1
τ_4'	N_4	S_4	T_2	3	−1	3	1	−1	−1	0	−1	1	−1
τ_5	N_5	S_4	T_1	3	3	−1	−1	−1	−1	0	−1	1	1
τ_5	N_5	S_4	T_2	3	3	−1	1	−1	−1	0	1	−1	−1
τ	C_1	G	τ	6	−2	−2	0	−2	2	0	0	0	0
π_L	C_1	G		12	0	0	2	4	4	0	0	0	2

We have thus found *the irreducible representation τ of $F\bar{4}3c$, determined by the phase transition* $F\bar{4}3c \rightarrow Pca2_1$. Furthermore, we can see how the permutation representation π_L of $F\bar{4}3c$ decomposes into linear irreducible representations:

$$\pi_L = \tau_0 \oplus \tau_2 \oplus \tau_3' \oplus \tau.$$

The fact that the faithful τ occurs once shows that the subspace of the six-dimensional representation space of τ that is left invariant by $L = Pca2_1$ is one-dimensional; the six-dimensional order parameter has one active component.

Again $Pca2_1$ is maximal with respect to the property of leaving the order parameter invariant. The minimal supergroup of $Pca2_1$ in the lattice of figure 1 is $Iba2_z$. This is an equitranslation subgroup of $F\bar{4}3c$. Therefore, the transition $F\bar{4}3c \rightarrow Iba2$ cannot leave the same order parameter invariant. (This translation determines the representation T_2 of $\bar{4}3m$.)

Many other aspects of phase transitions in boracite are revealed by this treatment and will be treated in a separate paper.

6. Slight generalizations

Often one meets a situation where neither of two groups, L_1 and L_2, related by a phase transition is a subgroup of the other. The transition is then necessarily of first order.

However, this situation can be reduced to that of the inverse Landau problem. It suffices to find a group containing L_1 and L_2 as subgroups. The smallest such group is the group $L_1 \vee L_2$ generated by L_1 and L_2. As an illustration, let us examine the well known case of $BaTiO_3$. There are two transitions between ferroelectric phases at 278 K between $L_1 = P4mm$ and $L_2 = Bmm2$, and at 183 K between L_2 and $L_3 = R3m$. $L_1 \vee L_2 \vee L_3 = Pm3m$. This last group is indeed the high-temperature symmetry group H of $BaTiO_3$. The transition from H to L_1 takes place at 393 K and, although from group to subgroup, it is of first order. Above 1733 K (or when quenched from these temperatures), $BaTiO_3$ has the hexagonal symmetry $L_0 = P6_3/mmc$. The group $E = L_0 \vee L_1$ generated by L_0 and L_1 is the Euclidean group, a symmetry group of liquid $BaTiO_3$. The index of L_0 or L_1 in E is infinite. The first-order phase transition $L_0 \rightarrow L_1$ is a recrystallization (a reconstructuve phase transition).

Furthermore, in many cases the group H may be the symmetry of a 'mean structure' or a reference structure, that is, strictly speaking, not really observed.

Finally, the transitions considered need not be phase transitions, but simply transitions between states of different symmetry in a given system.

7. Concluding remarks

The examples of phase transitions presented in this paper show the advantages of using permutation representations. A more systematic study, together with complete tables of space groups resulting from transitions with conserved translations, will be given in the following paper (Ascher 1976). Work on canonical forms for equations describing the phase transitions for given symmetries $L < H$ is in progress.

The more general significance of this approach to phase transitions is that it provides a pattern for the handling of the symmetry aspects of bifurcation problems for a large class of nonlinear operators.

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