

SELECTION RULES AND SYMMETRY BREAKING*

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Abstract

A brief precis is given of group theory aspects of two major theoretical approaches to symmetry breaking in phase transitions in solids: the thermodynamically based Landau theory and the Renormalization Scaling methods. A connection is made with the type of selection rules discussed in my other paper at this Conference (see these Proceedings). Results are given for some important physical systems such as high temperature superconductors with space group $Pm3n$ exhibiting a structural phase transition, and systems in the perovskite $Pm3m$ family, such as $PrAlO_3$ which show a sequence of phase transitions.

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1. Introduction

This report has as a major purpose to provide an introduction to the use of group theory - particularly representation theory of crystallographic space groups - in the investigation of symmetry breaking in "continuous" or Ehrenfest "Second Order" phase transitions in crystals. For these transitions the system is always characterized by a single thermodynamic quantity: the Gibbs Function, or Thermodynamical Potential Φ . It is assumed that the system is a "single" homogeneous crystal whose symmetry is characterized by a crystallographic space group G , when the external conditions such as temperature and pressure or external fields or generalized stresses are specified. If the external conditions are changed to some new temperature and pressure, the Gibbs Function Φ will change continuously. This defines a continuous phase transition. According to the Ehrenfest classification the order of a phase transition is the lowest ordinal derivative of Φ which is discontinuous. A second order transition then means continuous Φ , and first derivative, with Φ' discontinuous.

At a phase transition point, however, symmetry changes discontinuously. For example, discrete elements of symmetry may be lost, or gained. The crystal symmetry group changes to a subgroup of the initial group. Landau was the first to attempt to reconcile these apparently mutually contradictory features, and we shall give a synopsis of his thermodynamically based theory in what follows. This theory is still in active use, and has been validated by recent microscopically based theories which demonstrate its domain of validity.

One of the most powerful of the modern theories of phase transitions is the Renormalization or Scaling Theory. This theory was developed mostly by Kadanoff, Wilson and Fisher. It is concerned with a microscopic, quantum, theory of the properties of the crystal

in the vicinity of the phase transition. This theory emphasizes the calculation of physical response functions such as specific heat, susceptibility, correlation length of fluctuations and similar quantities. It particularly emphasizes the temperature dependent part of these response functions, certain of which typically show a power law divergence of form $(T-T_c)^p$ ($p < 0$) as $T \rightarrow T_c$, and can also establish whether a transition is continuous or not if fluctuations are included.

This is the setting in which the present report should be considered. The two major approaches to the theory of phase transitions are:

- The Thermodynamic-Based - Landau Theory;
- The Renormalization (Scaling) Theory of Kadanoff-Wilson and Fisher.

I recently reviewed the Thermodynamic-Based Landau Theory at the Sixth International Colloquium on Group Theory (Tubingen 1977) with particular attention to the Group Theory aspects of the theory.¹ I refer the reader to that report for many details. Here I shall give a precis of that paper paying particular attention to the selection rules appropriate to the Landau Theory as applied to crystals, since this paper can be viewed as closely related to my other contribution in the present volume. An illustration of structural transitions will be presented.

Several reviews have appeared recently² on the Renormalization Scaling methods of obtaining "critical" behavior of the physical response functions in the vicinity of the phase transition point. The reader is referred to them for details about this method and its applications.

We reiterate for clarity that the continuous change of "physical" properties of the system undergoing second order transition refers to the energy, or free energy. The abrupt change of the system regarding symmetry implies that at temperature $T > T_c$ the system is "disordered": if c^j is some order parameter, its average value or expectation value $\langle c^j \rangle = 0$. For $T < T_c$, the expectation value $\langle c^j \rangle \neq 0$. Thus some "order" is present and the previous isotropy in the

order parameter space is broken - only those symmetry elements g which preserve the ordered configuration are now in the isotropy group of the system. These are a subset of the previous set.

Returning to thermodynamics recall that $\partial \Phi / \partial T = S$, the entropy. Hence at T_c entropy is continuous. But $T(\partial^2 \Phi / \partial T^2)_P = c_P$ the specific heat at constant volume. This is in general discontinuous - a jump, or "λ singularity" of specific heat at T_c . Since

$$(\Delta c_P / T) / (\partial P / \partial T) = \Delta (\partial V / \partial T)$$

there can be a discontinuity in the thermal expansion coefficient at T_c , even though no volume discontinuity occurs.

For a true first order transition $\Delta S \neq 0$, and $\Delta V \neq 0$ at T_c . A major rearrangement of atoms may occur. As a rule this type of transition occurs because of a crossing of two different functions ϕ_1 and ϕ_2 both of which refer to the system in different domains of variables $(T; P)$ but coincident at a point. Perhaps in a true first order transition from space group $G_1 \rightarrow$ space group G_2 the system must pass through a state of total isotropy: $G_1 \rightarrow O(3) \rightarrow G_2$?

A weakly first order transition with $\Delta S \sim 0$, $\Delta V \sim 0$ may be incorporated into the thermodynamically based Landau Theory: it is "nearly" second order.

2. Discrete Symmetry Breaking in Continuous Phase Transitions

The thermodynamically based Landau theory is concerned with several aspects of phase transitions. It is a theory in which the abrupt, or discrete loss of one or more symmetry elements at a phase transition point is reconciled with the continuity of Φ and Φ' at the transition. It is also a theory in which the critical behavior is obtained. It thus appears to have the capability of dealing with all of the important matters of interest. Unfortunately the theory is not universal because of the neglect of fluctuations (or if one prefers to look from a different viewpoint), of inhomogeneities in the system which play an important and in some cases decisive role very near to the transition point. It would take us too far from the topic of this paper to attempt to enumerate classes of situations in which this theory

can be rigorously shown to be applicable. The reader is referred to references given in general reference 2 for further discussion.

The thermodynamic-Landau Theory can give answers to the following questions concerning a particular group-subgroup pair: $G_0 \supset G'$;

Can a continuous transtion $G_0 \rightarrow G'$ occur?

What "order parameters" can be the physical entities producing this transition?

In what follows we show how this question can be answered within the confines of the Landau Theory, and we shall give an illustration of application of the general theory to structural phase transitions.

We remark also that part of the formal structure of the Landau Theory applies as well in the context of Renormalization methods.

Landau introduced a density functional $\rho(\vec{r})$ which has the significance that $\rho(\vec{r}) d\vec{r}$ is the probability that in the volume element $d\vec{r}$ about \vec{r} there is a particle of a certain type. This density functional will serve also as a test function for symmetry. The symmetry group of the system G is the isotropy group of $\rho(\vec{r})$:

$$G: \{g; g\rho(\vec{r}) = \rho(\vec{r})\}$$

Now if G_0 is the initial symmetry group of $\rho(\vec{r})$ symmetry breaking occurs if some elements $\bar{g} \in G_0$ are lost. The new isotropy group G' will be subgroup of G_0

$$G' \subset G_0; G_0 = G' + \bar{g}_2 G' + \dots$$

using \bar{g}_α to denote the coset representatives which were "lost".

Thermodynamic stability of the system can be investigated by constructing the Gibbs Free Energy Φ and using the extremum principal of classical thermodynamics to determine the values of any "unconstrained" parameters $\{c^j\}$. For stability Φ must be an extremum with respect to variation of any such parameter. Physically, these internal "order parameters" readjust themselves spontaneously to produce the extremum. For stable equilibrium, Φ must be minimum. Analytically, at T_c :

$$\partial \Phi / \partial c_{\alpha}^j = 0 ; \quad \partial^2 \Phi / \partial c_{\alpha}^j \partial c_{\beta}^j > 0.$$

The idea is to select the set of order parameters

$$\{c_{\alpha}^j\} , \quad \alpha = 1 \dots \ell_j$$

so that c_{α}^j are bases for a single irreducible representation D^j of G_0 :

$$\{c_{\alpha}^j\} \rightarrow D^j \text{ of } G_0 ; \dim D^j = \ell_j .$$

Then use $\{c_{\alpha}^j\}$ both as unconstrained parameters in Φ , and as a linear (symmetry) expansion parameter in $\rho(\vec{r})$. Recall that any function can be expanded in terms of a "complete" set of functions which are partners in all irreducible representations of a group G_0 :³ Hence

$$\rho(\vec{r}, \{c^j\}) = \rho_0(\vec{r}, \{c^j\}) + \delta \rho(\vec{r}, \{c^j\})$$

where

$$\delta \rho(\vec{r}, \{c^j\}) \equiv \sum_{\alpha} c_{\alpha}^j \phi_{\alpha}^j(\vec{r})$$

Here $\phi_{\alpha}^j(\vec{r})$ are basis functions for D^j

$$\begin{aligned} P_g \phi_{\alpha}^j(\vec{r}) &= \phi_{\alpha}^j(g^{-1}\vec{r}) \\ &= \sum_{\beta} D^j(g)_{\beta\alpha} \phi_{\beta}^j(\vec{r}) . \end{aligned}$$

The essential point is that the symmetry breaking term $\delta \rho$ is a linear functional of the order parameter which we take as the set $\{c_{\alpha}^j\}$.

The Free Energy Φ is taken as a functional of the set $\{c_{\alpha}^j\}$ which are bases of the single irreducible representation D^j . Φ is expanded in a power series

$$\begin{aligned} \Phi(T, P, \{c^j\}) &= \Phi^0 + A f^{(2)}(\{c^j\}) \\ &+ B f^{(3)}(\{c^j\}) + \sum_Y D_Y f_Y^{(4)}(\{c^j\}) + \dots \end{aligned}$$

The $f_Y^{(s)}$ are G_0 -invariant polynomials of s^{th} degree, and distinct ones labelled by index s . In order for the phase transition to occur, consistent with assumed homogeneity of the crystal system before and after transition, and with stability (identical absence of a cubic term $f^{(3)}$ by virtue of symmetry prohibiting construction of a third degree invariant) the order parameters $\{c^j\}$ must obey Selection Rules.

Stability requires absence of $f^{(3)}$ or:

$$D_{(3)}^j \not\subset D^1 \quad (I)$$

Spatial Homogeneity requires absence of terms:

$$(c_\alpha^j \partial c_\beta^j / \partial x - c_\beta^j \partial c_\alpha^j / \partial x)$$

and permutation ($x \rightarrow y \rightarrow z \rightarrow x$). Thus using the notation of the previous paper⁴

$$D_{[2]}^j \otimes D^V \not\subset D^1 \quad (II)$$

where $[2]$ means antisymmetrized square, D^V is the polar vector representation in D^V , D^1 is the trivial representation, all referring to G_0 .

If a set of order parameters $\{c_\alpha^j\}$ obey these Selection Rules, and correspond to a physical quantity (or field) relevant to the transition in the particular crystal and substance then $\{c^j\}$ is an active set of parameters.

3. Subduction and Symmetry Breaking

The Landau program involves solution of the ℓ_j simultaneous equations

$$\partial \Phi / \partial c_\alpha^j = 0 \quad \alpha = 1, \dots, \ell_j$$

where $\ell_j = \dim D^j$. This is a difficult, and often tedious algebraic procedure involving solution of ℓ_j simultaneous cubic equations (if the highest degree G_0 -invariant polynomial kept is $f^{(4)}$) or even higher degree. When the extremizing sets $\{\bar{c}_\alpha^j\}$ are determined, these are

substituted into

$$\delta\rho = \sum_{\alpha} \bar{c}_{\alpha}^j \phi_{\alpha}^j(\vec{r})$$

The isotropy group G' of $\delta\rho(\{\bar{c}_{\alpha}^j\})$ is the subgroup corresponding to symmetry breaking $G_0 \rightarrow G'$. Different extremizing sets of $\{\bar{c}_{\alpha}^j\}$ may arise (not equivalent to each other) and give different subgroups.

I introduced the subduction criterion as a procedure to avoid this algebra. Evidently if

$$D^j \text{ of } G_0 \nrightarrow D^1 \text{ of } G' \quad (\text{III})$$

then $G_0 \rightarrow G'$ can occur via the order parameters $\{c_{\alpha}^j\}$. Thus any extremizing set $\{\bar{c}_{\alpha}^j\}$ must be a subset of the full $\{c_{\alpha}^j\}$ which satisfies the subduction property (III). Subduction has been conjectured to be sufficient as well as necessary but this is unproven, although no valid counterexamples have yet been brought to my attention.

Further extensions of subduction was produced by Goldrich, and Jarić working with me⁵. The chain subduction eliminates subgroups of subgroups. Let $G'' \subset G' \subset G_0$ and let

$$D^j \text{ of } G_0 \nrightarrow D^1 \text{ of } G' \quad (c \text{ times})$$

and

(IV)

$$D^j \text{ of } G_0 \nrightarrow D^1 \text{ of } G'' \quad (c \text{ times})$$

Then G'' is eliminated. That is the actual (maximum) isotropy group of $\delta\rho$ is G' which of course implies that $\delta\rho$ is invariant under any subgroup of G' .

The Selection Rules (I), (II), and the subduction criteria (III), (IV), together with the evident group - subgroup condition

$$G' \subset G_0 \quad (\text{V})$$

permit investigation of symmetry breaking within the domain of the Landau Theory. No particular attention is given here to problems of critical exponents.

Another procedure eliminating need for algebraic extremization of Φ (Landau-Higgs polynomials) has been given by Michel and Mozrzymas⁶ using Morse Theory. Although elegant, it seems restricted to $l_j \leq 3$ at present.

Then, the thermodynamic Landau Theory can be viewed as a theory of symmetry breaking continuous phase transitions in which the following questions can be investigated:

- A) The transition $G_0 \rightarrow G'$ occurs: determine mechanism;
- B) The group G_0 is known, predict possible subgroups G', \dots , and for each group - subgroup transition determine the mechanism;
- C) Transition to G' occurred; determine the possible parent groups G_0 and for each the mechanism.

In the above the term "mechanism" is used to denote the symmetry D^j of active representation, and the bases $\{c_\alpha^j\}$ which are physically significant order parameters.

4. Physical Order Parameters

In order to clarify the physical content of the term "order parameter" which indeed refers to the physical agency responsible for the phase transition some illustrations may be helpful. In each case note that the set of order parameters $\{c_\alpha^j\}$ is assumed to be a basis for irreducible representation D^j of G_0 . In any particular system, the choice of relevant order parameter is made depending on the physics.

Lattice displacements (motion of the ions or atoms comprising the crystal) are often the mechanism for structural phase transitions. The normal modes may become "soft" in the sense that the frequency $\omega(\vec{k}j)$ decreases $T \rightarrow T_c$, thus producing the transition. Normal mode symmetries were discussed in ref (4).

Magnetization can be an order parameter for magnetic transitions in which a spontaneous magnetic moment (ferromagnetism or antiferromagnetism) develops in the system. Local moments (intrinsic atomic spin moments) may cooperate to produce a self-consistent spontaneous magnetic field in which the moments align. The order parameters can be the components of the total magnetization which are like an axial vector, or sublattice magnetizations which have more complex structures. Normal magnetic modes can be constructed by superposition of the atomic moments - these transform as irreducible representations D^j of G_0 .

A tensor order parameter for transitions can be constructed by taking the Kronecker product of local atomic spin moment and displacement⁷.

An electronic order parameter or charge density wave can be created from electronic eigenfunctions⁴ (Bloch functions $\psi^{\vec{k}j}$) which produce a total order parameter with the symmetry $D^{*\vec{k}j}$.

Spin density wave or continuous spin density distribution can be an order parameter.

The spontaneous electrical polarization of a ferroelectric crystal can be an order parameter - usually this is a special case of "soft mode" lattice displacement or normal mode. The appearance of a non-zero electrical polarization: $\langle \vec{P} \rangle \neq 0$ then implies $\langle Q_{\alpha}^j \rangle \neq 0$ where Q_{α}^j is a normal mode.

In the normal \rightarrow superconducting transition of certain metal or alloy systems, the disordered state (higher symmetry) corresponds to "no Cooper electron pairing": it is the normal metal. The state with finite number of electron pairs (Cooper pairing of time-reversed occupied states: \vec{k} spin up with $-\vec{k}$ spin down) is ordered. The order parameter in superconductivity is the number of pairs $\langle \hat{N} \rangle$. Actually this can be viewed as breaking of continuous symmetry since, in the normal state $[\hat{H}, \hat{N}]_- = 0$ where \hat{H} is the Hamiltonian operator and \hat{N} the (conserved) electron density. The resultant symmetry is the gauge symmetry $U(1)$. In the superconducting state $[\hat{H}, \hat{N}]_- = 0$ and gauge group symmetry is broken in the ordered state.

A final example of an order parameter is related to surface adsorption of "ad-atoms" on a solid surface to produce an ordered superlattice. The density of coverage can be taken as an order parameter.

Many other examples of physical order parameters could be given - a discussion of this is given in a useful form in the recent book by Boccara [8].

5. Illustrations of Symmetry Breaking

If a general physical theory is to have merit, it should be capable of correctly predicting specific physical phenomena. In the form of the symmetry rules (I)-(V) given previously the theory is capable of analysing questions A,B,C, of Section 3.

For illustration we cite two of the space groups for which this program has been carried out: the space group O_h^3 -Pm3n (No. 223) or A-15 type; and the perovskite space group O_h^1 -Pm3m (No. 221)

a) Structural Transitions in High Temperature Superconductors O_h^3 -Pm3n.

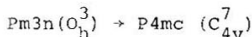
The A-15 type crystal structure has been of great physical interest⁹ owing to the occurrence of high temperature superconductivity in alloys (Nb_3Sn , V_3Si) with this structure. At temperatures close to the superconducting temperature a structural phase transition occurs from the cubic (O_h^3) structure to a tetragonal structure space group. The belief is that the two transitions are closely interconnected and that understanding the detailed mechanism of the structural phase transition may provide important understanding of the mechanism of superconductivity¹⁰.

Since there are two molecules/cell ($2 A_3B$) there are 12 branches of normal modes (3r) at each wave vector. As usual the sets of normal modes are decomposed into irreducible subsets which span irreducible representations D^{*k_m} , as described in ref 4 Section 6. The program of analyzing active order parameters in this structure has been carried out¹⁰ for wave-vector stars Γ, \vec{R}, \vec{X} and reference should be made there for details. Some results will be cited for these stars: giving star, set of normal mode irreducible representations, and activity. We only give the results for the optic modes ($\omega^2(\vec{k}_m) \neq 0$) if $\vec{k} \rightarrow 0$. Notation is taken from the original papers. At

$$\begin{aligned} \vec{\Gamma}: & A_{2g} \oplus F_{1g} \oplus F_{2g} \quad (\text{all inactive}), \text{ plus} \\ & 2F_{1u} \oplus 2F_{2u} \quad (\text{active}) \end{aligned}$$

All the inactive representations fail to satisfy the stability condition (II). We did not use the homogeneity condition (I) in this work.

As an example of a predicted group - subgroup phase transition which may occur in this structure, we find



Active order parameter $\text{F}_{1\text{u}}$.

Since the active order parameter is at wave vector $\vec{\Gamma} = (0,0,0)$ the space group is "Zellengleich": no loss of translational symmetry. The chain subduction criterion simply eliminates sub-subspace groups from consideration. This predicted transition has not yet been observed. If it were, one could have a case of a "ferroelectric" metal since the resultant space group is "polar", and consistent with a spontaneous electric moment (polarization) parallel to the crystal c or z axis, as noted by Anderson and Blount (see Ref 10).

The transition which does seem to be identified is: $\text{Pm}3\text{n} (\text{O}_h^3) \rightarrow \text{P}4/\text{mmc} (\text{D}_{4\text{h}}^9)$ in Nb_3Sn which is produced by a uniform strain of symmetry $\text{A}_{2\text{g}}$. Since this order parameter violates the stability criterion the transition cannot be continuous. It is in fact weakly first order.

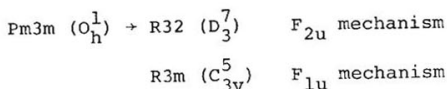
Other examples in this structure are given at $\vec{*X}$ and $\vec{*R}$ in ref 10 involving cell doubling or multiplication in one or more direction. In view of the great physical interest in these systems work on them is actively in progress and the literature should be consulted.

b) Structural Transitions in Perovskite Ferroelectrics - $\text{O}_h^1\text{-Pm}3\text{m}$

The "perovskite" structure $\text{O}_h^1\text{-Pm}3\text{m}$ is occupied by many important prototype ferroelectric crystals: SrTiO_3 , BaTiO_3 have been used in applications to switching devices, electronic controls, etc. The high temperature structure is $\text{Pm}3\text{m}$, but as temperature is lowered one finds structural transition such as: cubic \rightarrow polar ferroelectric crystal type. The polar type may be in rhombohedral (trigonal), tetragonal, orthogonal, ... , class. In the work of Goldrich and myself⁵ we gave an analysis of possible Zellengleich structural transitions. At $\vec{\Gamma}$ the optic modes are

$$\Gamma: 3F_{1u} \oplus F_{2u}$$

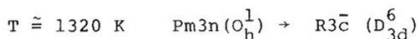
and both symmetry types are active. Examples of some predicted zellengleich continuous transitions are



Again note the criterion (II) was not employed.

The report at this Symposium by Prof. Bärninghausen¹¹ has given very many examples of transitions in a "family tree" originating from prototype $\text{Pm}3\text{m} (\text{O}_h^1)$ structure - some zellengleich, some not. At the time of writing the present report we have not yet completed an investigation in progress to compare the theory and experiments. Not all the transitions cited by Prof. Bärninghausen seem to have been classified in terms of first or second order of transition.

I want to turn to another system in the perovskite class which has been the subject of very recent investigations.¹² In PrAlO_3 the prototype high temperature structure is $\text{Pm}3\text{m}-\text{O}_h^1$ for $T > 1320$ K. As the temperature is decreased, a sequence of transitions occur.¹³ At



via $\vec{R}25^-$ phonon.

Now the normal mode $\vec{R}25^-$ in this structure has symmetry of an allowable projective (ray) representation of $G(\vec{R})/T = \text{O}_h$ i.e. the full cubic point group. The triply degenerate representation has 3 bases corresponding to x,y,z displacements of the 6 oxygen atoms comprising first neighbors of the Al atom at the center of the cube. In Fig. 1 (on the following page) we illustrate the edges of the octahedron at whose corner are the 6 oxygen atoms in question: left side of Figure labelled "cubic". We consider the cartesian displacements of these oxygens: recall that wave vector \vec{R} brings phase factors $\exp i\vec{R} \cdot \vec{t} = -1$ for translation from one primitive cell to the nearest adjacent one

$[\vec{R} = \frac{\pi}{a} (1,1,1); \vec{t}_L = a(1,0,0) \text{ etc}]$. Corresponding atoms in adjacent cells are thus displaced out of phase to each other. Taking these factors into account it can be established that the "effective order parameter" for this transition composed from the $\bar{R}25$ - symmetry displacements is a "rigid" rotation of the octahedral cage of oxygens. The direction of the axis of rotation \hat{n} and the angle of rotation about that axis θ are effective order parameters. Experiment shows^{12,13} that in the succession of transitions to be discussed θ is the same magnitude of about 9° and we can thus suppress it for our purposes.

Then the phase transition to $R\bar{3}c$ is driven by rotation of the octahedron about the $[111]$ direction. This is illustrated in Fig.1 Trigonal Structure. This transition is second order (continuous) as shown by (2). The ordered trigonal state is characterized by appearance of a non-zero rotation $\langle \hat{n} \rangle \neq 0$.

At

$$T \cong 205 \text{ K} \quad R\bar{3}c (D_{3d}^6) \rightarrow C2/m (C_{2h}^3)$$

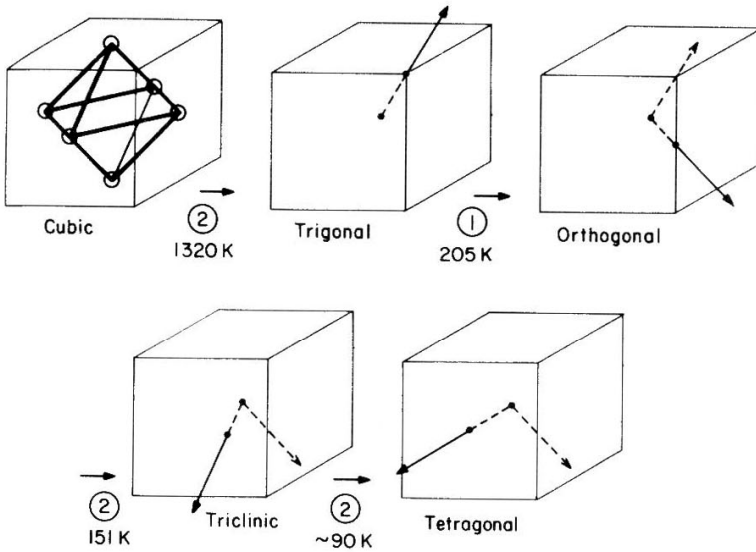


Figure: Unit cell of perovskite structure. The top left figure shows the octahedral "cage" of 6 oxygen atoms: at corners is Pr^{3+} ion, at the body center is Al^{3+} (these ions are not shown). The succeeding figures (left to right) show the development of non-zero order parameter $\langle c \rangle \neq 0$ where c stands for the direction of the axis \hat{n} as temperature is lowered. Numbers encircled indicate if transition is first or second order; transition temperature is given beneath this number.

This transition occurs when the direction of \hat{n} changes from [111] to [110] as shown in the Figure. The transition is first order since $C2/m$ is not a subgroup of $R\bar{3}C$, thus condition (V) is violated.

Next, beginning at

$$T \sim 151K \quad C2/m (C_{2h}^3) \rightarrow C\bar{1}(C_i^1)$$

the order parameter rotates from [110] to $[\cos\xi, \sin\xi, 0]$, $\xi \leq \pi/4$. As T decreases, $\xi \rightarrow 0$. This transition is second order and in Fig. 1 is labelled Triclinic.

It has been reported^{12a,14} that another transition occurs at

$$T \sim 118K \quad C\bar{1}(C_i^1) \rightarrow ?.$$

The order parameter continues to approach [1,0,0] but motion of $\langle \hat{n} \rangle$ occurs giving it an out-of-plane z component. This transition has not yet been fully understood^{12a}, and seems to involve coupling of the rotation with other parameters. (Not shown in the Figure).

Finally at

$$T \leq 90K \quad C\bar{1}(C_i^1) ? \rightarrow F4/mmc(D_{4h}^{18})$$

This transition is produced when the axis of rotation points in [1,0,0] direction where it remains as $T \rightarrow 0K$. The transition to this tetragonal space group is second order.

In the cases just presented of second order transition it can be verified that the order parameter - referenced with respect to the higher symmetry phase of the pair involved in symmetry breaking or restoration - satisfies the Selection Rules (I)-(IV).

An interesting matter concerns the final transition at $T \sim 90K$ when the symmetry increases at the lower temperature transition.

6. Some Developments of the Theory

In this section I shall review two recent developments of the thermodynamically based Landau theory.

Let us return to the expansion of the Free Energy Φ of the system given II in Section 2. Recall that the wave vectors \vec{k} are a quasi-continuous array in the Reduced Brillouin Zone. Then the selection of a single irreducible representation D^j or D^{*km} opens the possibility that nearby irreducible representations (almost infinitesimally close) can be mixed in to the expansion of Φ . The reason the restriction to a single irreducible representation arose in the initial formulation of the theory now needs to be recalled. Each physically irreducible inequivalent representation of G_0 (i.e. either real or the direct sum of two conjugate complex irreducible representations) corresponds to one distinct single bilinear G_0 -invariant

$$f^{(2)}(\{c_\alpha^j\}) = \sum_{\alpha} (c_\alpha^j)^2$$

If more than one such $f^{(2)}$ appeared in the expansion of Φ then at the transition more than one "A" coefficient would vanish:

$$A_j(T, P) = A_{j_1}(T, P) = \dots = 0$$

This would overdetermine the phase transition point. However, suppose we allow for possible slow spatial variation of the order parameter - which nonetheless satisfies condition (II) on homogeneity in lowest order. Then we may permit the occurrence in the expansion of Φ of terms involving spatial gradients. The expansion is now of form

$$\begin{aligned} \Phi - \Phi^0 &= A_0(T, P) f^{(2)} + \sum_Y D_Y f_Y^{(4)} + \\ &\sum_V [(\alpha(\vec{\nabla} c_V^j)^2) + \beta(\vec{\nabla}^2 c_V^j)^2 + \dots] \end{aligned}$$

The terms permitting spatial fluctuations can be rewritten if we recall that for the space groups the c^j are of Bloch form

$$c_v^j \sim e^{i\vec{k} \cdot \vec{r}} u(\vec{k}\vec{r})$$

and thus approximately (in long wave length approximation)

$$\vec{v}c_v^j \sim \vec{k} c_v^j$$

Using these last results we can reassemble all fluctuation terms into the bilinear $f^{(2)}(\{c^j\})$ by redefining the effective A coefficient:

$$A(T, P, \vec{k}) \equiv A_0 + \alpha k^2 + \beta k^4 \dots$$

Then, the condition for second order transition is that $A(T, P, \vec{k})$ for fixed (T, P) shall be a minimum in \vec{k} : $A_{\text{MIN}}(T, P, \vec{k}_0)$. Clearly if

$$\alpha > 0; A_{\text{MIN}} = A_0: (\vec{k}=0)$$

$$\alpha < 0; A_{\text{MIN}} = A(T, P, \vec{k}_0): \vec{k}_0 = (-\alpha/\beta)^{1/2}$$

Thus if $\alpha > 0$, $\beta > 0$ the usual condition $A_0(T, P) = 0$ determines a line of second order phase transitions. However a new type of phase transition occurs when

$$\alpha(T, P) = 0, \quad \beta > 0$$

The last condition determines a line which separates a region in the (T, P) plane where $\alpha > 0$ and the usual condition $A_0 = 0$ applies, from a region where $\alpha < 0$ and thermodynamic equilibrium is achieved for finite $\vec{k}_0 \neq 0$. The latter region corresponds to "helical" (spiral) modulated structures since \vec{k}_0 will generally be irrational. If the line $A_0(T, P) = 0$, and the line $\alpha(T, P) = 0$ intersect, they do so at a point L which is a higher order critical point.

The point L is now known as the Lifschitz Point and the phenomenon associated with occurrence of these temperature-dependent finite wave-vector effects are Lifschitz phenomena. The equilibrium value of \vec{k}_0

is temperature dependent since α and β will generally depend on T . The Lifschitz phenomena are evidently connected (at least in some generic fashion) with a "quasi-failure" of selection rule (II) on spatial homogeneity. Reference should be made to the literature: original work of Lifschitz, Dimmock, Dzaloshinsky; more recently especially in connection with the prediction of the Lifschitz point by Hornreich, Shtrikman, Mukamel; and elaboration of the relevant thermodynamic theory by Michaelson¹⁵.

A second topic which we mention briefly is the use of subgroup methods in the thermodynamic theory¹⁶. The motivation of this work is that the usual theory (as presented in Section 2-4) may not take account adequately of crystal substructures. In a non-symmorphic space group where the interaction between certain distinct sublattices may be the major mechanism for the phase transition, the usual procedure of working with the entire space group G_0 and its irreducible representations may obscure the essential physics. Consider a subspace group of G_0 denoted G'_0 ; where G'_0 is a group describing the space symmetry of (for example) a substructure in the crystal obtained by considering together several equivalent sublattices. This group G'_0 can be a subgroup of G_0 and a "supergroup" of the ultimate subgroup of G' achieved by the phase transition. Now we may index the order parameter "effectively" with respect to G'_0 . As an example, consider atom site displacement as a local order parameter, which when induced from the site to the intermediate group G'_0 can be indexed according to irreducible representations $D^{j'}$ of G'_0 . We may then use the subduction criterion referring to

$$G_0 \rightarrow G'_0$$

For the thermodynamic calculations we consider the total Free Energy Φ as:

$$\Phi - \Phi_0 = \sum_{S.L.} \Phi_{S.L.} + \sum \Phi_{INT} \sim \sum_{S.L.} \Phi_{S.L.}$$

where we isolate the sublattice contribution and assume the inter-sublattice contribution is small.

Then $(\phi - \phi_0)$ can be expanded in G'_0 -invariant polynomials.

Carrying the theory through it is possible to find an order parameter which induced from site to irreducible representations of G'_0 is active in giving second order continuous phase transition, while the same site order parameter induced to G_0 would give an inactive or first order prediction. In this case we assert that the interaction terms ϕ_{INT} will produce a "weakly" first order transition - or "nearly second order".

This approach was applied to the phase transition in A-15 alloys mentioned above. Here G'_0 is the symmetry group of the three sublattices of "one dimensional" chains considered as a single structural entity - for example the atoms in V_3Si , and is $P4_2/mmc(D_{4h}^9)$. The site symmetry group (at the V atoms) is $2mm(C_{2v})$. When atomic displacement order parameters are simulated by taking $\ell=2$ spherical tensor harmonics, at the atom sites as variables, the representations are $\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$ (referenced on $2mm$) which boost to $\Gamma_3 \sim (e_{xx} - e_{yy})$ on the group G'_0 : $P4_2/mmc$. (This order parameter is only part of the usual strain parameter.) Continuing using rules (I)-(V) on subgroups it is found that a transition $Pm3n(O_h^3) \rightarrow P4_222(D_4^5)$ can occur as second order. But the same transition using full strain parameter $[2e_{zz} - e_{xx} - e_{yy}]$ of the full G_0 group gives a first order transition. We conclude

$$Pm3n(O_h^3) \rightarrow P4_222(D_4^5)$$

is "nearly second order".

Analogously, the component $\Gamma_4 \sim e_{xy}$ referenced re G'_0 gives second order transition to $P4mc(C_{4v}^7)$. Again we observe this as a first order transition for the full group G_0 , so we conclude

$$Pm3n(O_h^3) \rightarrow P4mc(C_{4v}^7)$$

is "nearly second order".

As remarked earlier, the transitions in Nb_3Sn has been studied. It has been identified by Shirane and Axe¹⁷ as producing the lower symmetry space group $G' = P4_2/mmc(D_{4h}^9)$ - our G'_0 , by a weakly first order transition. But our examination of the data, plus a conver-

sation with Shirane indicates that the tetragonal phase could indeed be labelled $P4_222 (D_4^5)$ in this structure. For further details of this subgroup approach reference should be made to the paper of Agyei and myself.¹⁶

7. Renormalization Transformations and Symmetry

We now turn to give a very brief account of some symmetry aspects of the renormalization transformation method in phase transitions.

For given system, with symmetry group G_0 , we proceed as with the thermodynamically based Landau theory to identify acceptable order parameters by investigating whether or not the Selection Rules (I) and (II) are obeyed. We shall now consider the bases of the acceptable irreducible representation D^j (recall $j \rightarrow (*k)m$) to be position dependent fields $\psi_\alpha^j(\vec{r})$, $\alpha = 1, \dots, \ell_j$. We construct the Hamiltonian $H[\psi]$, which is a functional of the field order parameters. We write it as

$$H[\psi] = -1/2 \int d^d x \vec{\nabla} \psi_\alpha \cdot \vec{\nabla} \psi_\alpha^j - \sum_\gamma \sum_s \int d^d x I_\gamma^{(s)} u_\gamma^s$$

In this expression the spatial integral is over a "d-dimensional" configuration space; the $\vec{\nabla}$ is a spatial derivative; $I_\gamma^{(s)} ([\psi^j(\vec{r})])$ is a G_0 -invariant of s^{th} degree, γ labels the distinct invariants of s^{th} degree. Generally in practice such an expansion of $H[\psi]$ is only carried out to $s=4$, and of course includes the quadratic term $s=2$, as well as the bilinear fluctuation term shown in the first line. The u_γ^s are parameters, one from the bilinear u_1^2 , and $(r-1)$ from the quadri-linear u_γ^4 : a total of r . A renormalization-scaling transformation R replaces $H[\psi]$ by $RH[\psi] \equiv H_R[\psi]$. The exact form of R will not concern us here - it is in fact not "uniquely" determined but the result of a sequence of procedures which have become canonical in the last few years: Fourier transformation of $H[\psi]$; integration of large momenta down to some irrelevant cut-off; regrouping of terms to recover the initial form of $H[\psi]$ as in the previous equation with the discarding of higher order terms; then repeat the previous steps.

(See ref. [2] for details.) For our purposes the most important aspect of R is the fact that it maps $H[\psi]$ upon itself, keeping the form invariant at each stage, but changing the r parameters. Conventionally keeping terms up to fourth degree, $H[\psi]$ can be represented as a point in an r dimensional parameter space Π . The initial $H[\psi]$ is then some point \vec{u} with coordinates (u^2, u_1^4, \dots) . After R is applied, one finds the new point \vec{u}_R with coordinates (u_R^2, u_{1R}^4, \dots) . Repeated application of R is viewed as mapping Π on itself (by the conventions just given). The point \vec{u} changes to \vec{u}_R then \vec{u}_{RR}, \dots . If, after repeated applications of R the sequence

$$\vec{u}, \vec{u}_R, \vec{u}_{RR}, \dots, \vec{u}^*, \dots$$

converges to a vector with property

$$\vec{u}_R^* = \vec{u}^*$$

then u^* is called a fixed point,

$$\vec{u}^* = (u^{2*}, u_1^{4*}, \dots)$$

where u_Y^{s*} is the fixed-point value of u_Y^s . The fixed point \vec{u}^* corresponds to a fixed Hamiltonian $H^*[\psi]$, with functional form preserved (according to the structure of the calculation) as prescribed initially but with new coefficients. From $H^*[\psi]$ critical exponents can be determined from $Z[H^*[\psi]]$ for this Hamiltonian.

Instead of this conventional view of the R transformation as a mapping in the parameter space Π , my conjecture is that the significant mapping is rather in "Space of Invariants": \mathcal{I} . We propose to consider the mapping R as producing a mapping in the space \mathcal{I} . Because of the conventions adopted in defining R , the mapping is restricted to be from \mathcal{I} onto \mathcal{I} .

Dr. M. Jarić investigated some of these mappings [18]. (An earlier report related to this is the work of Korzhenevski [18]. Jarić observed that if $V \in O(\ell_j)$ is some orthogonal $\ell_j \times \ell_j$ matrix, the partition function of the crystal defined as a functional integral

$$Z \equiv \int D\psi \exp H[\psi]$$

is invariant under

$$\{\psi_{\alpha}^j\} \rightarrow \{V\psi_{\alpha}^j\}$$

The physical properties of the system (correlation functions, critical exponents, etc) are directly calculable from Z , and are unchanged by this gauge transformation. However under a general $V \in O(\ell_j)$ the invariants I_Y^S will be mapped onto a larger space - in general outside of \mathcal{Q} , and outside $H[\psi]$. Only a subset of V will preserve the functional form of $H[\psi]$. The subset forms a group denoted G_g :

$$G_g = \{T; T^{-1} R T = R\}$$

This group may be considered to produce new linear combinations of the basic set I_Y^S . The group G_T determines the structure of the R transformation.

Jarić showed that the transformations V , which work on the bases $\{\psi_{\alpha}^j\}$ commute with R and hence belong to G_T . In fact the original matrices D^j realize transformations of the $\{\psi_{\alpha}^j\}$ which leave each I_Y^S invariant and consequently D^j as a subgroup of G_g produces the identity representation in G_T .

Various other observations help in the construction of groups G_T . Thus let \bar{D} be a "maximal" group which leaves each I_Y^S invariant. Then \bar{D} is a normal subgroup of G_g . Hence G_g can be found as a normalizer of \bar{D} in $O(\ell_j)$:

$$G_g = \{V; V \in O(\ell_j), V^{-1} \bar{D} V = \bar{D}\}$$

In his investigation Jarić restricted attention to $s=4$. Then, by reducing the symmetrized fourth power of the matrices V in G_g we restrict attention (selection rule) to those V with property

$$V_{(4)} + \bar{D}$$

This produces G_T .

In a few concrete calculations the matrices V were found by a brute force method. Given the set of I_Y^4 , $\alpha = 1, \dots, (r-1)$, an arbitrary $\ell_j \times \ell_j$ orthogonal matrix was constructed, whose elements depended on certain parameters

$$V(\theta_1, \dots, \theta_p)_{\alpha\beta}$$

Requiring that

$$I_Y^4(V(\psi_\beta^j)) = \sum_Y D(V)_{YY'} I_Y^4(\{\psi_\beta^j\})$$

gives a set of $(r-1)$ fourth degree equations for the p parameters. In favorable cases a solution can be obtained ($p \leq (r-1)$), and the groups G_g and G_T determined.

The procedure given results in some systemization or classification of the sets of fixed points which can arise. Evidently repeated application of R , per hypothesis, either leaves the structure of $H[\psi]$ form-invariant, and thus conserves the symmetry G_g of $H[\psi]$, or (if some $u_Y^{s*} = 0$) will increase the symmetry since the fewer the invariants the higher is the symmetry (example if all $u_Y^4 = 0$, and the only remaining term u_1^2 , the symmetry group of the Gaussian $H[\psi]$ is the full $O(\ell_j)$). Thus the space Π of the parameters $\{\vec{u}\}$, or the space \mathcal{U} of invariants I_Y^s can be decomposed into a disjoint sequence of $H^*[\psi]$. These may be considered to begin at $O(\ell_j)$ and proceed through a chain of subgroups:

$$O(\ell) \supset \dots \supset D' \supset \dots \supset \bar{D}$$

terminating in the "identity" group \bar{D} whose action maps each I_Y^s onto itself. To each group corresponds a subspace (or a fixed point) in Π (or \mathcal{U}) and this decomposition can reveal the structure of sets of equivalent arrays of fixed points, and the structure of regions in Π related by transformation G_T .

Since this investigation is still continuing we summarize by remarking that the results so far obtained indicate the considerable merit in the use of group theory combined with Renormalization Scaling Methods. Jarić's work illustrated the use of the symmetry groups G_g and G_T in: decomposing the parameter space Π into subspaces according to symmetry; finding sets of equivalent fixed points; analyzing the "flow" of the Hamiltonian under R by use of G_T .

8. Integrity Basis and Invariant Space

" G_0 -invariant" polynomials play a very important role in the two approaches to symmetry breaking just discussed. Hence we briefly review some pertinent matters. First a clarification. The term " G_0 -invariant" refers to the matrix group D^j which in general is a non-faithful (homomorphic) image of G_0 . Hence the invariant polynomials f_Y^S , or I_Y^S refer always to invariance with respect to the transformations of the bases $\{c_\alpha^j\}$ or $\{\psi_\alpha^j(\vec{r})\}$ respectively under irreducible representation D^j . According to a "classical" theorem of Hilbert if G_0 is a finite group there exists a finite set of basic invariants known as the integrity bases. Call the members of the integrity basis for irreducible representation D^j of G_0 :

$$\theta_1, \theta_2, \dots, \theta_m$$

where each θ_μ is a function of the $\{c_\alpha^j\}$, and $m \leq |G_0|$. The set θ_μ generate the algebra of invariants in the sense that the most general invariant in the $\{c_\alpha^j\}$, $I(\{c_\alpha^j\})$ can be written as a rational integral polynomial in the set $\{\theta_\mu\}$:

$$I(\{c_\alpha^j\}) = P(\theta_1, \theta_2, \dots, \theta_m)$$

If the (matrix) group D^j representing G_0 is a Coxeter group (group generated by reflexions) or a generalized Coexter group (unitary group generated by reflexions) some strong results can be proved. The number of basic invariants, or order of the integrity basis is denoted m . Let the algebraic degree (in c_α^j) of the polynomial θ_μ be d_μ . Then for (generalized) Coexter groups

$$\Pi(d_\mu) = |G_0|$$

$$\sum_{\mu=1}^m (d_{\mu} - 1) = r$$

where r is the total number of (pseudo) reflections in G_0 . Note that a (generalized) Coxeter group is a matrix group every one of whose elements g can be written as an ordered product of powers of generators

$$g = g_1^{p_1} g_2^{p_2} \dots$$

where each (matrix) generator g_{α} has all but one eigenvalue unity, and one single eigenvalue $e^{i\lambda}$ where $\lambda = (\pi/n)$ n an integer for generalized Coxeter group, or $\lambda = \pi$ for the case of Coxeter group. For (generalized) Coxeter groups of interest so far in condensed matter physics m is a small integer.

For groups G_0 which are normal subgroups with Abelian factor group of a (generalized) Coxeter group the structure of a general polynomial invariant is

$$I = P_0(\theta_1, \dots, \theta_m) + \sum_{i=1}^L \phi_i(c_{\alpha}^j, \dots) P_i(\theta_1, \dots, \theta_m)$$

The additional polynomial invariants $\phi_i(c_{\alpha}^j)$ occur linearly premultiplying the arbitrary polynomial P_i in the members of the integrity basis θ_i . [19]

The possible importance of using the invariant polynomials of the integrity basis to construct the free energy Φ for a thermodynamic theory of symmetry breaking was apparently first realized by Gufan and collaborators [20].

The simplest illustration for a Coxeter group is the cubic point group $m\bar{3}m:O_h$. The members of the integrity basis for the three dimensional faithful irreducible representation based on $\{c^j\} \equiv (x, y, z)$ are

$$\theta_1 = \sum_{\alpha=1}^3 (c_{\alpha}^j)^2; \theta_2 = \sum_{\alpha=1}^3 (c_{\alpha}^j)^4; \theta_3 = (c_1^j)^2 (c_2^j)^2 (c_3^j)^2$$

Since $m3m$ is a Coxeter group the dimension formulae are easily verified.

In constructing the G_0 -invariant objects Φ or $H[\psi]$ it is a natural to determine the number of distinct invariants of n^{th} degree. Molien [19] gave an algorithm for this by constructing a generating function for the multiplicity of the trivial irreducible representation in the symmetrized n^{th} Kronecker aproduct $D_{(n)}^j$. It is denoted $c_{n,1}$.

The Molien function is:

$$M(D^j, G_0; z) = \sum_n c_{n,1} z^n = \frac{1}{|G_0|} \sum_g (\det[1 - zD^j(g)])^{-1}$$

The sum is over the entire group. Jarić and I simplified this expression so that it could be easily applied to space group irreducible representations using only the character system [21]. Let

$$\chi(g) \equiv \text{Tr } D^j(g)$$

then

$$M(D^j, G_0; z) = \frac{1}{|G_0|} \sum_g \exp\left(\sum_m z^m \chi(g^m)/m\right)$$

In this form many Molien functions were computed for space group $Pm3n$ [21].

It is worth noting that for a (generalized) Coxeter group the Molien Function takes a particularly important form

$$M(D^j, G_0; z) = \prod (1/(1 - z^{d_\mu}))$$

which permits one to directly obtain the structure of the integrity basis, namely the set $\theta_1, \dots, \theta_m$ [19].

Using the Molien series we are able to construct Φ and $H[\psi]$ relatively easily, especially if we are prepared to truncate these " G_0 -invariant" physical quantities at terms of 4^{th} or 6^{th} degree, requiring only the coefficients $c_{4,1}$ and $c_{6,1}$.

Some very interesting questions remain concerning the relevance of the ring (algebra) of invariants to the mappings described in Section 7 of the present paper. These are under investigation at present.

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