

SYMMETRIES AND PHASE TRANSITION

E. Ascher

Département de Physique Théorique

Université de Genève

1211 Genève 4, Suisse

1. This is a shortened version of a talk given (April 1979) at the University of Louvaine. It should have served also as basis for a similar talk at the conference held in Bielefeld (September 1979), which, however, because of my inability to attend, finally was not given.

The aim of this paper is to explore what can be said about phase transitions on the basis of symmetry considerations alone. This cannot exhaust the theory of symmetry changes in phase transitions. Group theory does not contain a theory of phase transitions, but it helps. It helps a lot. To see this, we shall discuss the consequences of two almost trivial, but - as it seems - unavoidable principles.

The main question here concerns the relation, if any, between two phases, connected by a phase transition.

It is necessary to make more precise the term of "connection". We shall do this by somewhat restricting our problem to phase transitions which may be described by using an order parameter. Two phases connected by a transition will then be a disordered phase and one of the phases arising from it by some ordering. We know since L. Landau (in fact already since P. Curie) that the symmetry group L of the ordered phase is a subgroup of that, H , of the disordered one. Two ordered phases belonging to the same ordered phase are not necessarily in a relation of group and subgroup.

If presented with two groups connected by phase transition that do not display such a relation, it is always possible - and sometimes useful - to construct a group that contains the two as subgroups. If the subgroup describing the ordered phase is the trivial group (so that the ordered phase then has no symmetry) it is usually worthwhile to

consider that the symmetry groups at hand represent the "true" symmetries of the phases only modulo some hidden symmetry; in the same way the translational symmetries are hidden in the macroscopic properties of a crystal.

Our investigation then is restricted to two phases that are in a group-subgroup relation. A second restriction is that to subgroups of finite index. We limit ourselves to these because we do not want to eclipse the main ideas by the mathematical safeguards needed in the case of infinite index. What does this restriction amount to ? This depends of course on the type of symmetry group we want to consider. If e.g. the symmetry group of the disordered phase is a space group, a subgroup of finite index is a space group of the same dimension. It is clear, however, that subgroups of infinite index are important in connection e.g. with crystallization and incommensurable phases.

2. The first of the two principles we want to investigate is the following : The group and subgroup (corresponding to a disordered and ordered phase that arises from it) determine an irreducible representation of the symmetry group of the ordered phase. This is an important part of Landau's theory. Two additional features : The stability condition (which is a necessary condition for the transition to be continuous) and the homogeneity condition are not considered here.

Given a group H and a subgroup L , how can they determine irreducible representations of H . Well, they first determine the permutation representation π_L of H afforded by L . This is obtained by associating to $h \in H$ the permutation that it induces (by multiplication on the left, e.g.) on the cosets of L in H . Because L is of finite index (say n), the kernel of this representation (also termed the core of L) is also of finite index. Thus the quotient $H/K = G$ is a finite group of order $|G|$.

The projection $p: H \rightarrow G$ of H onto G establishes a one-to-one correspondence between those subgroups of H that contain K and all subgroups of G . Therefore the permutation representation $\pi_L: H \rightarrow S_n$ may be factored as $\pi_L = \pi_J \circ p$ where π_J is the faithful permutation representation $\pi_J: G \rightarrow S_n$ of the finite group G afforded by its subgroup $J = L/K$ of index n .

With the permutation representation π_L there is associated a linear representation τ of degree n which for simplicity's sake, we also term permutation representation (τ permutes the n basis vectors of a vector space as π_L permutes the cosets). This representation is in fact the representation I_L^H induced in H by the 1-representation I_L of L . It is clear that I_L^H can be factored: $I_L^H = I_J^G \circ \rho$ (where I_J^G is faithful). Now obviously $I_L^H(H)$ and $I_J^G(G)$ denote the same group of linear transformations of a n -dimensional complex (for definiteness) vector space M . Furthermore if $J \neq G$ then I_J^G - and hence I_L^H too - is always reducible.

We can now state the following permutation condition: An irreducible representation associated with the pair $L < H$ is an irreducible representation contained in I_L^H . (If we want to generalize to reducible representations, then these too should be contained in the permutation representation).

Introducing the inner product of two class functions and on G by

$$\langle a|b \rangle_G = \frac{1}{|G|} \sum_g a(g)^* b(g)$$

and using a special case of Frobenius reciprocity theorem, we find

$$\langle I_J^G | \chi_i \rangle_G = \langle I_J | \text{Res}_J \chi_i \rangle_J$$

(here $\text{Res}_J \chi_i$ is the character of the representation τ_i of G restricted to $J < G$ and I_J^G the character of I_J^G . If the permutation condition is fulfilled, then the left hand side is different from zero, say equal to n_i . From the right hand side we then conclude that n_i is the dimension of the subspace U of the representation space M_i of τ_i (which is also the representation space of $T_i = \tau_i \circ \rho$ of H) on which the subgroup J of G acts trivially. We may thus take as order parameter of a transition from H to L a generic element of M . Indeed, in the phase with symmetry H the invariant component is zero, in the phase with symmetry L , the ordered phase, there are n_i invariant components.

If instead of "restriction" we use the term "subduction", we see that the permutation condition is just Birman's subduction criterion

(BIR66) which, according to his version of Landau's theory, "is necessary and sufficient in order that T_1 of H should be acceptable-active" (BIR78). Remember that the permutation condition arises quite naturally from the requirement that an irreducible representation be associated with a pair $L < H$.

3. It is now generally admitted, that the Landau-Birman subduction criterion is too permissive. For help we now turn to the Curie-principle.

In 1894 Curie wrote : "La symétrie caractéristique d'un phénomène est la symétrie maxima compatible avec le phénomène" and "Quand plusieurs phénomènes se superposent...,il ne reste plus alors comme éléments de symétrie que ceux communs à chaque phénomène pris séparément". In the fifties, the Russian crystallographers of the Shubnikov school have applied this principle to ferro-electric and ferromagnetic phase transitions, i.e. to transition where the order parameter is the electric polarization (ZHE 56, SON 59) or the magnetization. In these cases, the symmetry group L of the ordered phase is then the intersection of the crystallographic symmetry group of a crystal with the symmetry group of the order parameter; this group is of course the largest subgroup of the symmetry group of the disordered phase that leaves invariant a given orientation of the order parameter.

Taking into account what we have found (in Section 2) concerning the relation between order parameters and representation spaces of irreducible representations, we now state the general Curie principle : The subgroups L of any symmetry group H of a disordered phase that can possibly arise in phase transitions, are those that are maximal with respect to the property of acting trivially on a given (non-zero) subspace of the representation space of an irreducible representation of H . Equivalently this means that these groups are maximal with respect to the property that the permutation afforded by the subgroup contains an irreducible representation a given number of times. Birman's "chain subduction criterion" is the general Curie principle restricted to one-dimensional subspaces. The general Curie principle - applied to crystallographic point groups - is implicit in MEL 56, MCD 65 and MUR 75 (in relation with molecularphysics) and JAN 75 (in relation with macroscopic properties of crystals).

The results found so far can be summarized as follows (χ_i is the character of the irreducible representation T_i of H) :

permutation condition - subduction criterion

$$\langle 1_L^H | \chi_i \rangle \neq 0$$

chain-subduction criterion

maximality of L with respect to

$$\langle 1_L^H | \chi_i \rangle = 1$$

general Curie-principle

maximality of L with respect to

$$\langle 1_L^H | \chi_i \rangle = n_i > 0$$

4. Even the generalized Curie-principle seems to be permissive. Examining (ASC 66a, ASC 77) a great number of experimental results indicated that in all cases the subgroups obeyed a more restrictive criterion ("maximality principle") : Among the subgroups L obeying to the general Curie-principle, only the maximal ones were found. In other words, these subgroups are maximal with respect to the property

$$\langle 1_L^H | \chi_i \rangle \neq 0$$

Recently (CRA 76) cases have been exhibited where this more restrictive principle applies. In this interesting paper, the authors fail to distinguish between the Curie-principle and the maximality principle. Then they point out, that the Curie-principle admits subgroups that do not correspond to a minimum of the thermodynamic potential (i.e. the Curie-principle is too permissive). For transitions that have magnetization as order parameter, they then give a list of Shubnikov-point groups that do correspond to minima of the thermodynamic potentials. The results are exactly those that have been obtained by the maximality principle already, in ASC 66a and ASC 66b.

However, this is by no means a proof of the maximality principle. The thermodynamic potentials which one minimizes are (usually incomplete) Taylor-expansions up to terms of a given (low) order. To draw valid conclusions, one needs standard polynomials for the thermodynamic potentials. I think that equivariant catastrophe theory will provide such polynomials. In trying to determine such a polynomial for an elastic, magnetizable and polarizable crystal, one can see that it requires lengthy computation. One certainly will have to rely on good computer programs.

5. It seems that in many cases of phase transition, the maximality principle is obeyed. To my knowledge so far, no experimental counterexample has been found, nor has a proof been given which would show under what conditions this principle is valid.

REFERENCES

- ASC 66a Ascher E. : Phys. Lett. 20, 352 (1966).
ASC 66b Ascher E. : Helv. Phys. Acta 39, 466 (1966).
ASC 66c Ascher E. : Properties of Shubnikov point groups.
ASC 77 Ascher E. and Kobayashi : J. Phys. C. Solid State Phys. 10, 1349 (1977).
BIR 66 Birman J. : Phys. Rev. Lett. 17, 1216 (1966).
BIR 77 Birman J. : With International Colloquium on Group Theoretical Methods in Physics, 1977.
CRA 76 Cracknell A.P., Lorenc J. and Przystawa J.A. : J. Phys. C. Solid State Phys. 9, 1731 (1976).
JAN 75 Janovec V., Dvorak V. and Petzelt J. : Czech. J. Phys. B25, 1326 (1975).
MCD 65 McDowell R.S. : J. Molec. Spectrosc. 17, 365 (1965).
MEL 56 Melvin M.A. : Rev. Mod. Phys. 28, 18 (1956).
MUR 75 Murray-Rust P., Burgi H.B. and Dunnitz J. : 1975.
SON 59 Sonin A.S. and Zhéludev I.S. : Kristallogr. 4, 487 (1959).
ZHE 56 Zhéludev I.S. and Shuvalov L.A. : Kristallogr. 1, 681 (1956).