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SYMMETRY CHANGES IN CONTINUOUS TRANSITIONS. A SIMPLIFIED THEORY APPLIED TO V_3Si

E. ASCHER
Battelle Institute, Advanced Studies Center, Geneva, Switzerland

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A simplified theory of continuous phase transitions is outlined, commented, and applied to the V_3Si transition. The necessity of taking into account time-reversal symmetry is stressed. The Shubnikov space group of the tetragonal phase of V_3Si is found to be either $P4_2/m'mc$ or $P4_2/n'mc$.

Continuous transitions

By a continuous transition we mean a transition in which the state of the system changes continuously (as a function of a scalar parameter), whereas the symmetry (at a critical value of that parameter) undergoes a sudden change to a lower symmetry. The existence of (Weiss-) domains is immanently related to this type of transition. At the critical value of the parameter the system is split into domains of lower symmetry in such a way that the totality of the subsystems still has the original symmetry. This notion of continuous transitions is by no means limited to phase transitions. Here, however, we shall be concerned only with continuous phase transitions.

Four methods

The oldest theory of symmetry changes in such transitions is probably that related to the determination of the directions of easy magnetization, although the separate steps mentioned below had not been viewed as a whole. The free energy of the crystal in the state of higher symmetry (symmetry group G) is written down as a sum of invariant products of the components of the magnetization vector. The free energy is then minimized with respect to these components, and the possible directions of easy magnetization are thus found. The superposition of each of these (uniform) vector fields and of the original symmetry gives a symmetry group G_i that may arise in a transition from the original symmetry to one compatible with ferromagnetism. The symmetry groups G_i thus determined are necessarily subgroups of the original symmetry group G.

The next method is that of Landau and Lifshitz [1]. First the subgroup condition is derived. Then a choice is made among the subgroups by considering the representations of the group G. The procedure has been described in several publications (see bibliography in [2]). Here we want only to stress that it includes again the minimization of a thermodynamic potential. Recently Birman [2], working with representations, has shown that the minimalization can be avoided.

Anteriorly, however, a further simplification had been proposed which avoids the explicit utilization of representations and the minimization procedure [3-5]. We want to discuss here how this theory applies to the phase transition in V_3Si and to superconduction in general.

The subgroup condition

The requirement that the symmetry groups G_i of the possible phases in continuous phase transitions be subgroups of the symmetry group of the original phase of course remains. A further restriction should however be introduced, namely that the subgroups should have the same translational part as the original group. This restriction had actually been made in most cases, although perhaps unintentionally. Let us illustrate this with the group $Pm3n\text{-}O_h^3$, the high-temperature symmetry group of V_3Si. The subgroups of O_h^3 belonging to the tetragonal system are listed in table 1 [6]. Among these, the subgroups having the same translational part are

$P4_2/mmc\text{-}D_{4h}^9$, $P\bar{4}2c\text{-}D_{2d}^2$, $P\bar{4}m2\text{-}D_{2d}^5$, $P4_2mc\text{-}C_{4v}^7$,

$P4_222\text{-}D_4^5$, $P4_2/m\text{-}C_{4h}^2$, $P\bar{4}\text{-}S_4^1$, and $P4_2\text{-}C_4^3$.

(In [2] only five of these groups are given.)

Choice among the subgroups

Among the subgroups thus found, a further choice is made, viz. only those that are maximal with respect to the property of leaving invariant

Table 1
Subgroups of O_h^3 belonging to the tetragonal system (only the lowest index of each subgroup is indicated).

Index							
3	D_{4h}^9						
6	$D_{4h}^{10}, D_{4h}^{12}, D_{4h}^{14}, D_{4h}^{16}$	D_{2d}^2, D_{2d}^5	C_{4v}^7	D_4^5	C_{4h}^2		
12	$D_{4h}^{13}, D_{4h}^{19}, D_{4h}^{20}$	$D_{2d}^1, D_{2d}^3, D_{2d}^6, D_{2d}^8, D_{2d}^{11}$	C_{4v}^3, C_{4v}^4	$D_4^3, D_4^6, D_4^7, D_4^{10}$	C_{4h}^4	S_4^1	C_4^3
24		$D_{2d}^4, D_{2d}^7, D_{2d}^9, D_{2d}^{10}, D_{2d}^{12}$	$C_{4v}^8, C_{4v}^{11}, C_{4v}^{12}$	D_4^4, D_4^8	C_{4h}^6		C_4^2, C_4^4, C_4^6
48						S_4^2	

a vector V of appropriate type. These subgroups are called maximal V-subgroups. It can be seen that they are closely related to little groups.

Necessity of considering time reversal

That the vector V should be the electrical polarization $\boldsymbol{P}$, in the case of ferro-electric transitions, and the magnetization $\boldsymbol{M}$, in the case of ferromagnetic transitions, is commonly admitted although not always consistently used. These vectors behave differently under space-inversion and time-reversal; they belong to two different non-trivial irreducible representations of the (crystallographic) group $\bar{1}1'$ generated by the space-inversion $\bar{1}$ and the time-reversal $1'$. There is a third non-trivial irreducible representation of that group, and the quantity in Maxwell's equations that transforms according to that representation is the current density $\boldsymbol{j}$ (or the vector potential A). Three important types of continuous phase transition are distinguished by these three types of vector. If time-reversal were disregarded, the type $\boldsymbol{P}$ and the type $\boldsymbol{j}$ would be undistinguishable.

The type of the superconductive transition

In [3] the hypothesis has been put forth, that phase-transitions from a non-superconducting phase to a superconducting one are always of the type $\boldsymbol{j}$. A connexion between this hypothesis and the microscopic theory will be developed elsewhere. Here we shall show how simply it permits to make precise predictions of the symmetries that may occur in phase transition to the superconductive state.

Symmetry predictions for V_3Si

We shall derive the possible Shubnikov space groups for the superconducting phase of V_3Si. Shubnikov space groups are the space groups that one obtains when time-reversal is included into the list of possible symmetry operations [7, 8]. We shall arrive at our final result in three steps. First we shall determine the possible ordinary space groups for the superconducting phase, then we shall find the possible Shubnikov point groups, and a combination of the two results will yield the possible Shubnikov space groups.

Maximal $\boldsymbol{j}$*-subgroups of* $Pmn3$.

Fig. 1 shows the lattice of subgroups of the ordinary space group $Pmn3$-O_h^3 [9]. The maximal $\boldsymbol{P}$-, $\boldsymbol{M}$-, and $\boldsymbol{j}$-subgroups are singled out. The maximal $\boldsymbol{j}$-subgroups are

$$P4_2mc - C_{4v}^7,\ Ama2 - C_{2v}^{16} \text{ and } R3c - C_{3v}^6.$$

These are also maximal $\boldsymbol{P}$-subgroups. The first of these space groups belongs to the tetragonal system. (It is one of the two groups proposed in [2].)

Domain structure

Note the multiplicity and the index of the subgroup. The group C_{4v}^7, e.g., occurs three times (the fourfold axes being in the three [100]-directions) and has index 6. This means that we have three types of domain. The characteristic vector $\boldsymbol{j}$ (or $\boldsymbol{P}$) is directed in each domain along a [100]-direction in either of both antiparallel ways. This kind of reasoning holds for the three types of vector; quantitatively, there is however a significant difference; in general, the electrical polarization $\boldsymbol{P}$ is bound strongly to the preferential direction determined by the symmetry of the crystal; this bond is weaker for $\boldsymbol{M}$, and seems to be very weak for $\boldsymbol{j}$. In other words the anisotropy energy diminishes as one goes from $\boldsymbol{P}$ to $\boldsymbol{M}$ and to $\boldsymbol{j}$. The anisotropy energy is experimentally most interesting in the magnetic case since then it is of the same order of magnitude as the energies that can be produced by application of external fields. In the case of ferroelectricity, the anisotropy energy is generally too high; in the case of superconductivity, it is generally too low.

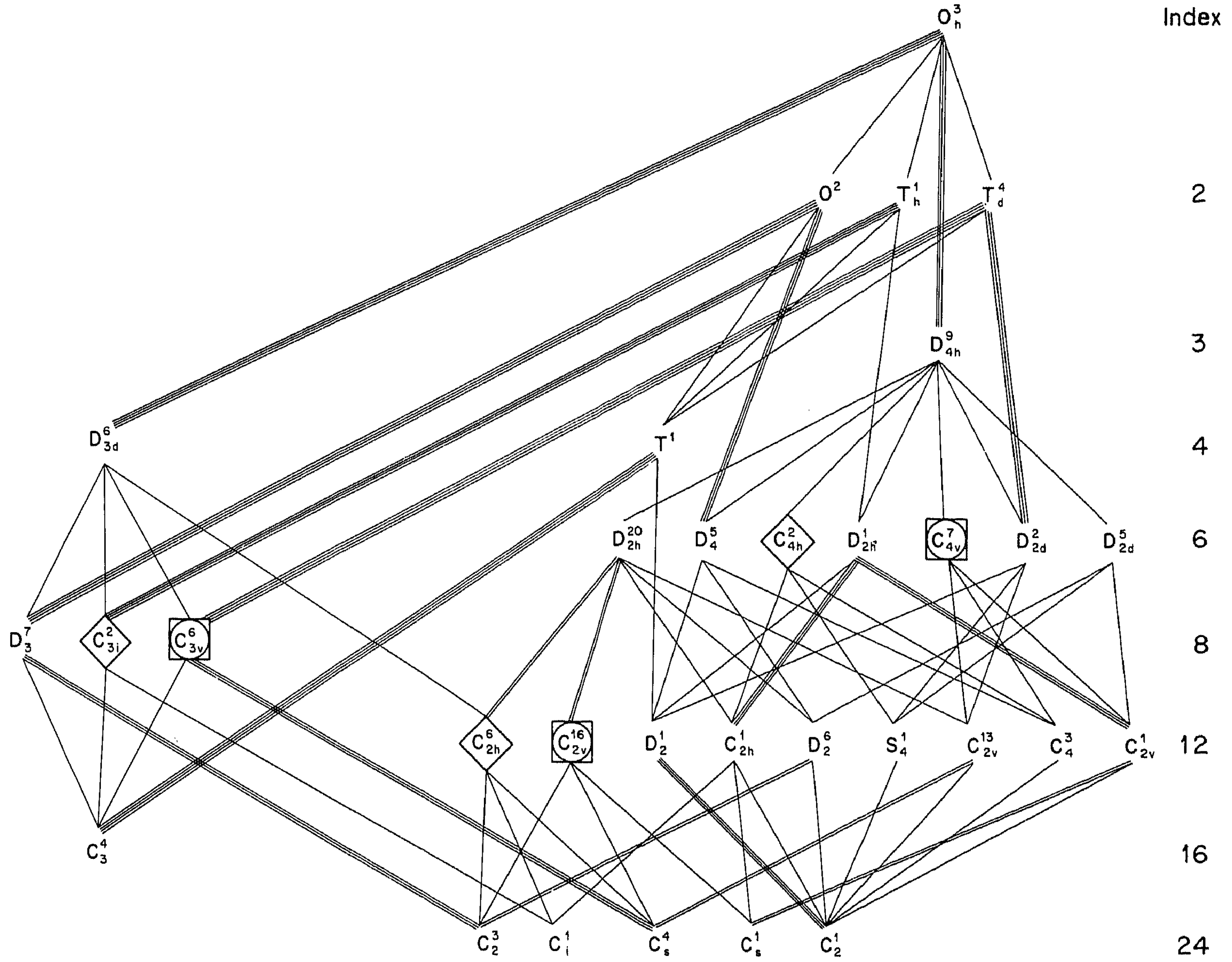

Fig. 1. Lattice of subgroups (with same translational part) of $Pmn3$ - O_h^3.
□ maximal ***P***-subgroups; ◇ maximal ***M***-subgroups; o maximal *j*-subgroups.

Maximal j-subgroups of $m3m1'$.

We now consider the Shubnikov point group of paramagnetic V_3Si, viz. $m3m1'$. Its maximal *j*-subgroups are [10, 11]

group	multiplicity	index
$4/m'mm$ - D_{4h} (C_{4v})	3	6
mmm' - D_{2h} (C_{2v})	6	12
$\bar{3}'m$ - D_{3d} (C_{3v})	4	8

Here the index is always twice the multiplicity. This reflects the fact that the group $m3m1'$ is not "piezoconductive" [4], i.e., it contains elements that inverse *j*; these elements are $\bar{1}$ and $1'$.

Maximal j-subgroups of $Pm3n1'$.

From the knowledge of the possible space-groups and the possible Shubnikov point groups, the possible Shubnikov space-groups may be determined. Let us illustrate this for the tetragonal crystal system. We know that the Shubnikov space groups we look for contain as subgroup of index 2 the space group C_{4v}^7 and that they belong to the Shubnikov crystal class D_{4h} (C_{4v}). We thus have to look for space groups of crystal class D_{4h} containing C_{4v}^7 as subgroup of index 2. An inspection of the lattices of subgroups of space groups [9] shows that there are two possibilities for this to happen: C_{4v}^7 is contained as subgroup of index 2 in D_{4h}^9 and in D_{4h}^{15}. The Shubnikov space groups we are looking for are thus $D_{4h}^9(C_{4v}^7)$ or D_{4h}^{15} (C_{4v}^7). The international crystallographic notation is respectively

$$P4_2/m'mc \text{ and } P4_2/n'mc.$$

For the orthorhombic system, we find similarly

$$Cmcm' - D_{2h}^{17} (C_{2v}^{16}) \text{ and } Cccm' - D_{2h}^{20} (C_{2v}^{16})$$

whereas for the trigonal case there is a single possibility

$$R\bar{3}'c - D_{3d}^{6} (C_{3v}^{6}).$$

Note that the lattices corresponding to these Shubnikov space groups are trivial magnetic lattices, i.e., they do not contain translations followed by time-reversal; they contain only ordinary translations (this is the first case, $M = M_T$, in refs. [8] and [12]). Note that the above groups

Note that the above groups are not maximal **P**-subgroups.

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