ROLE OF PARTICULAR MAXIMAL SUBGROUPS
IN CONTINUOUS PHASE TRANSITIONS

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It is shown how to determine (without differential calculus) the possible symmetries in a ferroelectric transition, the number and the types of domains, and the preferential directions.

The purpose of this letter is to indicate a simple method of determining the symmetries in continuous phase transitions. To illustrate the method, ferroelectric transitions will be considered, but the method does work, with obvious changes, also in other cases. The method will be discussed in greater detail and other examples will be considered elsewhere.*.

It is known that in a continuous transition, the symmetry group of the crystal on one side of the transition is a subgroup of that on the other side. However, all possible subgroups do not appear. Examination of experimental results has confirmed the idea that only some particular maximal subgroups play a role. Thus, a simple method of determining the possible symmetries, preferential directions, and domain configurations can be devised.

In the present case, the method is based on the following simple rule: The symmetry group of a phase that arises in a ferroelectric transition is a maximal polar subgroup of the group of the high-temperature phase. By polar subgroup, I mean a subgroup that permits the existence of an invariant polarization vector. A maximal polar subgroup is a polar subgroup that is not contained in any other polar subgroup. The condition of maximality is plausible for energetic reasons: it ensures the.formation of a minimum number of domain walls. So far I have not been able to find any exception to this proposition [2].

* The method has been used by the author for two years already. The first four paragraphs and the two figures are extracted from a talk given at Philips Research Laboratories, Eindhoven, on October 19, 1964. The appearance of a recent paper [1] indicates that the publication of the present method may be of general interest.

a) As first example, let us take $BaTiO_3$. The high-temperature space group is O_h^1. Let us look at the subgroups (see fig. 1) [3]. The maximal polar subgroups are C_{4v}^1, C_{2v}^{14}, and C_{3v}^5. These are exactly the symmetries of the three ferroelectric phases of $BaTiO_3$.

If we know the maximal polar subgroups, we also know the possible directions of polarization. For this, it suffices to consider the point groups. It is necessary, however, to take into account how many times a given point group occurs as subgroup of a given group [4]. This point has been neglected in the example of $BaTiO_3$ (see fig. 2). This scheme is not complete; only the relevant point groups are shown. O_h has 4 subgroups C_{3v}, which are not shown in the figure, 3 subgroups C_{4v}, and 12 subgroups C_{2v}. Of these latter 12, only 6 are maximal polar subgroups. To each maximal polar subgroup, there corresponds a definite direction of polarization. To the 4 groups C_{3v} correspond the 4 [111]-directions, to the 3 groups C_{4v} correspond the 3 [100]-directions, to the 6 maximal polar subgroups C_{2v} correspond the 6 [110]-directions. The other 6 groups C_{2v} that are not maximal polar would give rise to polarization in the 3 [100]-directions with two types of domain for each direction. These latter groups are eliminated by our condition, and indeed they do not occur in the orthorhombic phase of $BaTiO_3$.

Let us briefly discuss some other examples:
b) $PbZrO_3$. As seen from fig. 1, the low-temperature space group C_{2v}^8 is not a subgroup of the high-temperature space group O_h^1, so that the transition cannot be of second order.
c) Rochelle salt: C_2^2 (low temperature) is a maximal polar subgroup of D_2^3 (high-temperature); there is another such subgroup, C_2^1. Potassium dihydrogen phosphate: C_{2v}^{19} (low-temperature) is
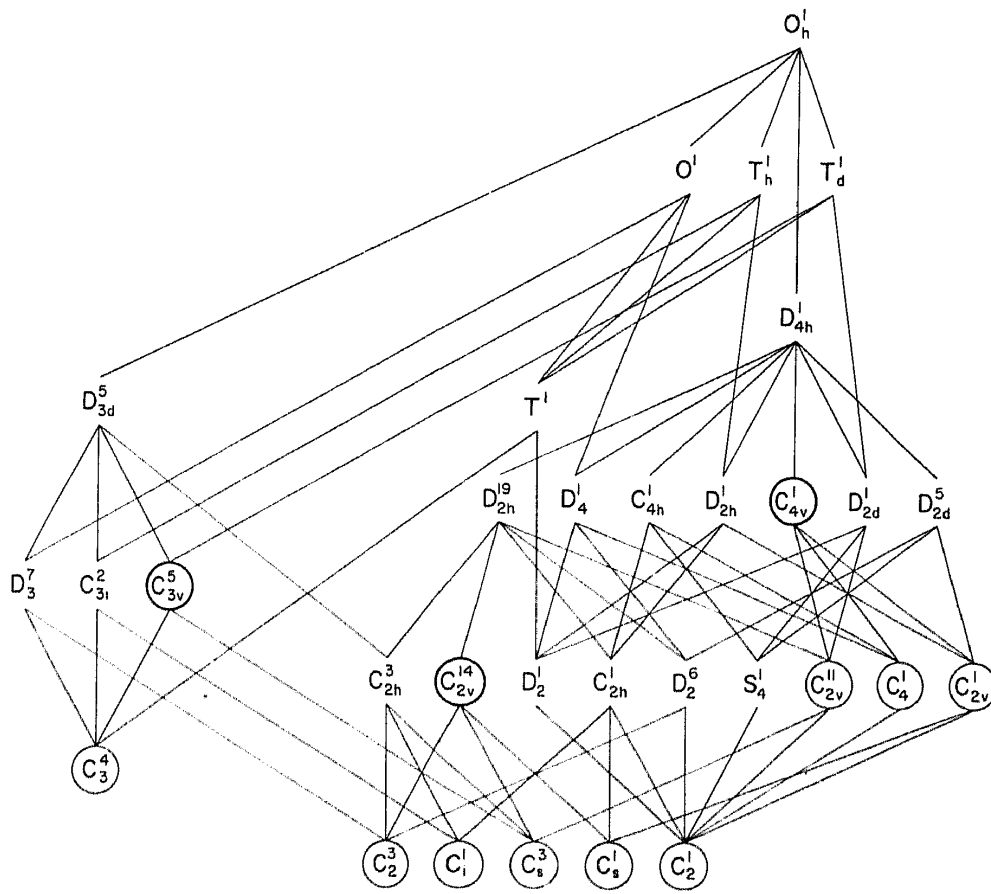
Fig. 1. Maximal polar subgroups of O_h^1 (BaTiO$_3$).

$$a = \begin{bmatrix} 0 1 1 \end{bmatrix} \quad b = \begin{bmatrix} 0 1 \bar{1} \end{bmatrix} \quad c = \begin{bmatrix} 1 0 1 \end{bmatrix} \quad d = \begin{bmatrix} 1 0 \bar{1} \end{bmatrix} \quad e = \begin{bmatrix} 1 1 0 \end{bmatrix} \quad f = \begin{bmatrix} \bar{1} 1 0 \end{bmatrix}$$
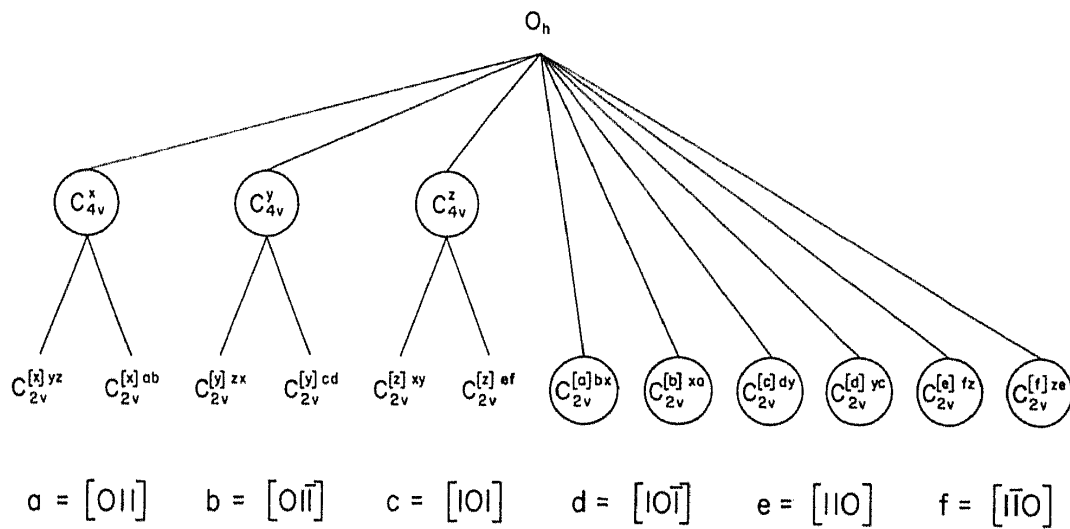
Fig. 2. Domain structure in the tetragonal and orthorhombic phases of BaTiO$_3$.

the only maximal polar subgroup of D_{2h}^{12} (high-temperature). SbSI: C_{2v}^9 (low-temperature) is a maximal polar subgroup of D_{2h}^{16} (high-temperature). The other maximal polar subgroup is C_{2v}^2. Thiourea, $SC(NH_2)_2$, has a ferroelectric transition $D_{2h}^{16} \rightarrow C_{2v}^2$.

d) $NH_4H_2PO_4$: D_2^4 (low-temperature) is *not* a subgroup of D_{2d}^{12} (high-temperature), therefore the antiferroelectric transition cannot be of second order.

e) NH_4HSO_4: C_s^2 (low-temperature) is a maximal polar subgroup of C_{2h}^5 (high-temperature); C_1^1 (stable below -119°C) is not. The other maximal polar subgroup of C_{2h}^5 is C_2^2. The ferroelectric transition $C_{2h}^5 \rightarrow C_s^2$ occurs also in di-glycine nitrate, and rubidium bisulfate; $C_{2h}^5 \rightarrow C_2^2$ takes place in colemanite.

f) MASD, $NH_3CH_3Al(SO_4)_2.12H_2O$: as strange as it may appear, C_2^2 (low-temperature) is a maximal polar subgroup of T^4 (high temperature) (C_3^4 is the other one). The other possible space group assignment for MASD could be T_h^6 (the space goup of the cubic alumns); however, C_2^2 is not maximal polar in T_h^6; therefore, the transition $T_h^6 \rightarrow C_2^2$ could not be ferroelectric.

Concerning the most general expansion of the free energy in terms of polarization - and /or magnetization, stress, etc. - it is clear that an expansion having the symmetry of the paraelectric state can be found by making use of the point group of the paraelectric state; it is not necessary to consider the space group; for antiferroelectricity and antiferromagnetism, a knowledge of the space group is necessary. The same expansion is also valid for the sum over all possible domain orientations in the ferroelectric state, but it is certainly not valid for a ferroelectric, monodomain single crystal. The terms of the expansion, and generally all tensors characterizing a crystal, may be found, without any group theoretical operation, by simple inspection, once the way in which the components of the three types of vector (electrical polarization, magnetization, and current density) transform [5]. Thus, is is very easy to settle the question of invariants of third order [6] once and for all. (As is known, there should be no such invariants in second order transitions.) It is worthwhile pointing out that, at any rate for the examples given in this letter, the possible ferroelectric phases for a given paraelectric phase, instead of being found by the old method of minimizing the free energy [7], may be determined without differential calculus. The application of these considerations to magnetic anisotropy and magnetic domains will be treated elsewhere.

References

1. C. Haas, Phys. Rev. 1404 (1965) 863.
2. Similar results have been obtained partially by Željudev and Šuvalov, Izv. Akad. Nauk SSSR 21 (1957) 264, in a less straightforward manner.
3. D. K. Fadeev, Tablicy osnovnih unitarnyh predstavlennij fedorovskih grupp (Izdatelstvo AN SSSR 1961, English translation, Pergamon Press, 1964) gives the maximal subgroups for each space group. Graphs giving this information are contained in a BMI-technical report of the author, available on request.
4. E. Ascher and A. Janner, Acta Cryst. 18 (1965) 325.
5. Tables giving this information are available in a BMI-technical report.
6. V. L. Indenbom, Kristallografiya 5 (1960) 115, and Izv. Akad. Nauk SSSR 24 (1960) 1180.
7. V. L. Ginzburg, Usp. Fiz. Nauk 38 (1949) 490.

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