Short Communications

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About sequences of maximal subgroups: a few answers to a question from Bertaut.

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To each subgroup g_i of the space group G does not necessarily correspond a derivative structure s_i (space group g_i) of the structure S (space group G). This paper discusses some symmetrical, geometrical and thermodynamical aspects which occur in the real existence of a derivative structure.

In drawing to a conclusion an interesting paper devoted to maximal subgroups of space groups, Bertaut (1976) emphasizes the potential importance of group–subgroup relations for classifying the related structures and predicting the nature of transitions (symmetry of derivative structures, first or second-order transitions). Bertaut (1976) raises a question concerning the transition of NbO_2 from the high-temperature form ($P4_2/mnm$) to the low-temperature form ($I4_1/a$); the question is whether each step of the sequence of maximal subgroups on going from $P4_2/mnm$ to $I4_1/a$ corresponds to a step of the transition. This question can be generalized. May each subgroup g_i of the space group G of the structure S be associated with any derivative structure s_i of S, relevant to space group g_i? One knows, at the present time, no complete and definitive answer to this question, but may invoke some general elements which are likely to occur in

If we consider that atoms are points with spherical atomic scattering factors, to each subgroup of a sequence of maximal subgroups does not necessarily correspond a model derivative structure. Let us examine the example of spinel structure; this structure is composed of the sets a,d,e of equivalent positions of the space group $Fd3m$. In the maximal subgroup $Fd3$ of index 2, the corresponding sets, of notation a,d,e too, have the same cubic setting as in $Fd3m$ and their coordinates with reference to this setting are utterly identical; as a matter of fact the true symmetry of the collection of sets a,d,e of $Fd3$ is actually $Fd3m$; the collection of a,d,e positions of $Fd3$ is called the false derivative structure of spinel structure (Billiet, 1969). Accordingly, if we consider atoms as points to obtain the very symmetry $Fd3$, it would be necessary to insert between the sets a,d,e at least one set of positions g of $Fd3$, that is to say, at least 96 atoms for one cubic unit-cell! Do we have the right to name a so-built structure as a derivative structure of the spinel structure? But, as a matter of fact, the atoms are not points, the extension of the electronic shell is such that sets of general positions are always occupied. From this viewpoint, to each subgroup of the sequence of maximal subgroups can correspond a derivative structure.

To take again the example of the spinel structure, sets of positions i of $Fd3m$ are occupied by the electronic shell; each set i of $Fd3m$ can split into two sets g of $Fd3$ with different electronic densities; then it is possible that a derivative structure relevant to $Fd3$ can exist but it is advisable to remark that the spatial symmetry would not be due to the symmetry of atomic positions but to the lower symmetry of electronic distribution in the crystal.

Another geometrical point of view restricts again the possibility of real derivative structures. Leaving out the positions of hydrogen atoms, numerous structures $AB(OH)_6$ are derivative structures of the ReO_3 structure ($Pm3m$); in terms of atomic positions, to each stage of the sequence through maximal subgroups $Pm3m(a) \rightarrow Im3m(2a) \rightarrow Pn3m(2a) \rightarrow Pn3(2a)$ corresponds a model derivative structure. Nevertheless, as far as we know, there exist no chemical compounds with intermediary structures $Im3m$ and $Pn3m$ between ReO_3 ($Pm3m$) and hexahydroxystannates ($Pn3$). There is a good reason for this. Diagonal reflexion planes of space groups $Im3m$ and $Pn3m$ would force the oxygen atoms to stay in the planes of type (x,x,z); by shifting towards the centres of cubo-octahedral holes, neighbouring oxygens would then have very unsatisfactory separations; some O–O distances would be able to become most short and have impossible experimental values (2 Å) and coordination octahedra would be very distorted. On the other hand, in hydroxystannates, the symmetry does not compel the oxygens to remain in diagonal planes (x,x,z); the oxygens move towards the holes but keep comparable interneighbour distances; these distances have normal experimental values and the coordination octahedra are almost regular (Levy-Clement & Billiet, 1976).

There are other factors limiting actual types of derivative structures. When such a structure is the result of ordering distinct ionic charges, the crystal keeps a high degree of preserved symmetry (weak value of subgroup index); furthermore the local equilibrium of electrical charges allows in reality the existence of only a small number of models. Thus, theoretical study of the simplest types of 1:1 ordering through the set of octahedral positions in spinel structure shows us that only types relevant to $Imma$ and $P4_122$–$P4_322$ have credible existence, in terms of preserved symmetry and local equilibrium (Billiet, Morgenstern-Badarau & Michel, 1967); the well-known ordered spinels belong to both of these types: $Fe^{III}(Fe^{II}Fe^{III})O_4$ ($Imma$) (Verwey & Haayman, 1941), $V^{V}(Li^{I}Cu^{II})O_4$ ($Imma$) (Joubert, Grenier & Durif, 1965), $Zn^{II}(Li^{I}Nb^{V})O_4$ ($P4_122$–$P4_322$) (Blasse, 1964*a*, *b*) and $Zn^{II}(Zn^{II}Ti^{IV})O_4$ ($P4_122$–$P4_322$) (Billiet, Morgenstern-Badarau, Poix & Michel, 1965).

Some thermodynamical aspects are very likely to occur which would explain the actual nature of experimental transitions. For the establishment in a spinel structure of a

1:1 ordering of type $P4_122$–$P4_322$ through octahedral positions, the phase-transition theory of Landau anticipates a first-order transition (Hass, 1965). In fact a first-order transition does occur in $Zn(ZnTi)O_4$: at equilibrium temperature (552 °C) one notices the presence of both the cubic disordered form (*C*) and tetragonal ordered form (*Q*). However, if zinc is replaced by another divalent ion, $Zn(Zn_{1-x}M_xTi)O_4$, the tetragonal form at low temperature is gradually disordered according to the increase in substitution rate *x*; the lengths of the edges of the pseudocubic tetragonal unit cell gradually become equal until the compound is indeed perfectly cubic anew; the transition is then continuous; at any time there is *one* phase only; so here indeed is a *second*-order transition (Delamoye, Billiet & Michel, 1970; Delamoye, Billiet, Morgenstern-Badarau & Michel, 1967). This might even be a paradox! Then there would be, as in some liquid–vapour diagrams, a miscibility gap and a critical point in the phase diagram of $Zn(Zn_{1-x}M_xTi)O_4$ (Fig. 1)? Would Landau's theory be inaccurate? There are other questions!

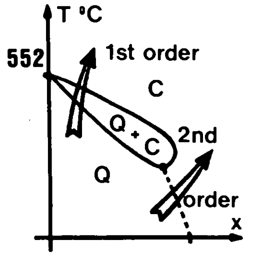

Fig. 1. Hypothetical phase diagram of $Zn(Zn_{1-x}M_xTi)O_4$.

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Use of matrix direct methods for low-resolution phase extension for tRNA: erratum.

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In Podjarny & Yonath [*Acta Cryst.* (1977). A**33**, 655–661] the matrix order in Table 1 and point T5(MODF) of Fig. 2 should read 100 instead of 226. The matrix order in points T3(MIR) and T3(MODF) of Fig. 2 should read 450 instead of 226. The MW value of predicted and MIR phases correlation in the whole 3 Å sphere in Table 1 should read 0·2 and not 0·85. Figs. 6(*c*) and 6(*d*) should be interchanged.

All information is given in the abstract.

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