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Some remarks on the 'family tree' of Bärnighausen.

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Some comments are made on a recent paper of Bärnighausen [*Acta Cryst.* (1975), A**31**, S3]. A few improvements are suggested; these include a more detailed partial synopsis in relation to Landau theory, and a comparison between sequences of subgroups and physical transitions in real compounds.

A short paper on the 'family tree' of perovskite-like structures has been published (Bärnighausen, 1975). Bärnighausen has built up a diagrammatic set of sequences of maximal subgroups of *Pm3m* from the tables of Neubüser & Wondratschek (1966*a*,*b*) and has arranged structures which are topologically equivalent to the perovskite structure according to the group–subgroup relations of their space groups. His paper is very interesting because it rationalizes the structural relationship between real chemical compounds; I think that this process should be systematically extended to other families of chemical compounds. The paper of Bärnighausen is also fruitful because it suggests new questions for research. For instance, his synopsis clearly shows subgroups of *Pm3m* which are either attached or not attached to real derivative structures of the perovskite structure: is there a theoretical reason for a specific subgroup not to be associated with a real derivative structure? The 'family tree' exhibits, from the viewpoint of symmetry, the relations which exist between different forms of the same real compound: is there a theoretical reason why this compound possesses these precise forms? I have given some partial answers to these questions elsewhere (Billiet, 1977).

In the present paper, I only wish to make some comments and suggest a few improvements. Bärnighausen has limited his synopsis to the subgroups which are significant for 17 selected crystal structures. The synopsis has not pointed out all the subgroups of *Pm3m* and it can certainly be extended to other perovskite-like structures. Let me remark that subgroups are infinite in number; theoretically, the table must continue indefinitely downwards; moreover, all the maximal subgroups of any group of the table have not been indicated. For example, we have tabulated the *translationengleich* maximal subgroups (Table 1) and the *klassengleich* maximal subgroups (Table 2) of *Pm3m*; these maximal subgroups are finite in number. Furthermore, there are special *klassengleich* maximal subgroups of the space group *Pm3m* with ideal perovskite structure which have the same space-group symbol *Pm3m*; the vectors of the conventional cubic unit cell of these isosymbolic maximal subgroups are obtained when those of the ideal perovskite are multiplied by prime odd integers k. For each value k, there are k^3 conjugated isosymbolic maximal subgroups (index k^3) with different settings (origin in $[p,q,r]$ with reference to the setting of ideal perovskite; p,q,r are integers with the conditions: $0 \leq p < k$, $0 \leq q < k$, $0 \leq r < k$) (Billiet, 1978). Therefore the isosymbolic maximal subgroups are infinite in number. The synopsis has not shown all the group–subgroup *relations*; some groups can be maximal subgroups of several other groups as indicated in Fig. 1(*a*). Moreover, Bärnighausen has reassembled in one single box all the subgroups which belong to the same index and to the same space-group symbol. A more detailed presentation (Fig. 1*b*) of the synopsis shows that there are two non-conjugated subgroups *Fm3c*, four conjugated subgroups $R\bar{3}m$, two classes of four conjugated subgroups $R\bar{3}c$, four conjugated subgroups *R3m* and four conjugated subgroups *R3c*. Equivalent derivative structures (*i.e.* twin and antiphase domains of the same transition) correspond to conjugated subgroups (*i.e.* subgroups g and g' of *Pm3m*, such as $g' = tgt^{-1}$, with t an element of *Pm3m*); the number of these equivalent derivative structures is given by the index of their subgroups with reference to *Pm3m* (Billiet, 1969). Derivative structures connected with non-conjugated subgroups are not equivalent (Table 3). Particularly, it should be noted that the *choice* of the origin of the subgroups is of great importance at the level of equivalent positions (Table 3) (Billiet, 1978). Furthermore, it can be

Table 1. *Translationengleich maximal subgroups of Pm3m*

The index of the subgroup is given within the first set of parentheses. The vectors of the conventional unit cell of the subgroup are given within the next set with respect to the vectors (**A**,**B**,**C**) of the conventional unit cell of *Pm3m*. The origin of any subgroup is confused with that of *Pm3m*. Subgroups in square brackets are conjugated.

[*P4/mmm* (3) (**A**,**B**,**C**); *P4/mmm* (3) (**B**,**C**,**A**); *P4/mmm* (3) (**C**,**A**,**B**)]; [$R\bar{3}m$ (4) (**A**,**B**,**C**); $R\bar{3}m$ (4) (**A**,−**B**,−**C**); $R\bar{3}m$ (4) (−**A**,**B**,−**C**); $R\bar{3}m$ (4) (−**A**,−**B**,**C**)]; *Pm3* (2) (**A**,**B**,**C**); *P432* (2) (**A**,**B**,**C**); *P43m* (2) (**A**,**B**,**C**).

Table 2. *Klassengleich maximal subgroups of Pm3m*

The index of the subgroup is given within the first set of parentheses. The coordinates of the origin of the subgroup are given within the next set with reference to the conventional setting of *Pm3m*. The vectors of any subgroup are twice those of *Pm3m*. Subgroups between square brackets are conjugated.

Fm3m (2) (0,0,0); *Fm3m* (2) ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$); *Fm3c* (2) (0,0,0); *Fm3c* (2) ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$); [*Im3m* (4) (0,0,0); *Im3m* (4) (0,1,1); *Im3m* (4) (1,0,1); *Im3m* (4) (1,1,0)]; [*Im3m* (4) ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$); *Im3m* (4) ($\frac{1}{2},-\frac{1}{2},-\frac{1}{2}$); *Im3m* (4) ($-\frac{1}{2},\frac{1}{2},-\frac{1}{2}$); *Im3m* (4) ($-\frac{1}{2},-\frac{1}{2},\frac{1}{2}$)].

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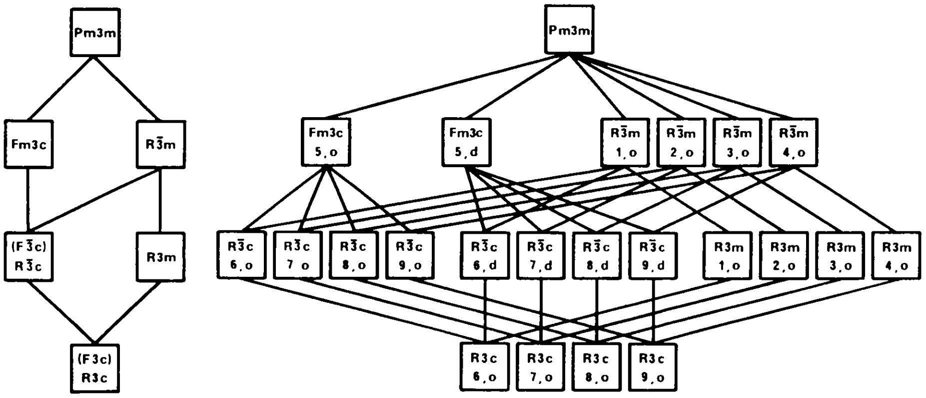
† For eight years (1 October 1969–30 September 1977) the author has worked in the Tunisian education system (Faculty of Mathematical, Physical and Natural Sciences, Tunis; Faculty of Sciences and Technology, Sfax). He is happy to dedicate the present paper to the Tunisian people for their hospitality, kindness and pacifism.



(*a*) (*b*)

Fig. 1. (*a*) A condensed part of the set of subgroups of *Pm*3*m*. The non-conventional symbol of Bärnighausen is given in parentheses. (*b*) A detailed view of the part given in (*a*). The conventional settings are given with reference to the conventional setting of *Pm*3*m*: (1) (**A**,**B**,**C**), (2) (**A**,−**B**,−**C**), (3) (−**A**,**B**,−**C**), (4) (−**A**,−**B**,**C**), (5) (2**A**,2**B**,2**C**), (6) (**A** + **B**, **B** + **C**, **A** + **C**), (7) (**A** − **B**, −**B** − **C**, **A** − **C**), (8) (−**A** + **B**, **B** − **C**, −**A** − **C**), (9) (−**A** − **B**, −**B** + **C**, −**A** + **C**). *o*: origin at (0,0,0); *d*: origin at ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$). Rhombohedral axes for space groups $R\bar{3}m$, $R\bar{3}c$, $R3m$, $R3c$.

shown (Fig. 1*b*) that *all* the conjugated subgroups $R3m$ of $Pm3m$ are not subgroups of *all* the conjugated subgroups $R\bar{3}m$ of $Pm3m$ but that *each* subgroup $R3m$ is a subgroup of only *one* subgroup $R\bar{3}m$. This is very important from the thermodynamical point of view of the phase-transition theory of Landau: since the index is equal to 2, a transition from a group $R\bar{3}m$ to *its* subgroups $R3m$ can be second-order (one phase at the transition point) while transitions to *other* (non-subgroup) groups $R3m$ are necessarily first-order (two phases at the transition point). Is the Landau theory significant with an induced transformation in a sample from a subgroup $R\bar{3}m$ to another subgroup $R\bar{3}m$ (ferroic transformations)? Finally, for a given chemical compound with several perovskite-like structures, it would be desirable to have its sequence of physical transitions assembled together with its set of group–subgroup relations. Therefore, in Fig. 2 (after Wood, Miller & Remeika, 1962; Lefkowitz, Lukaszewicz & Megaw, 1966; Athee, Glazer & Megaw, 1972; Glazer & Megaw, 1972; Ishida & Honjo, 1973) it can be seen that some transitions in $NaNbO_3$ are associated with group–subgroup steps while some others are connected with

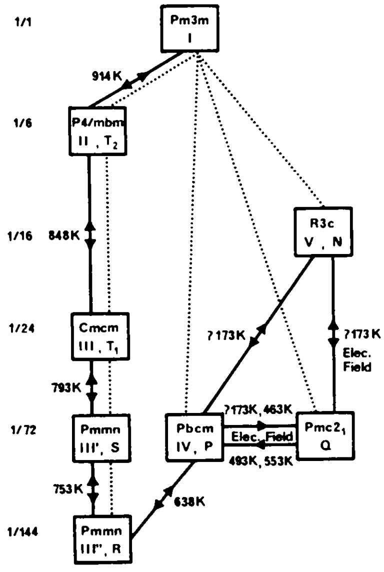


Fig. 2. Symmetry relations and physical transitions in $NaNbO_3$. Each dotted line represents in condensed form several sequences of subgroups such as in Fig. 1(*b*). Physical transitions are represented by thick lines together with the temperatures of transition. On the left is the degree of preserved symmetry (inverse of the index of the subgroup). Unit cells of subgroups are given with reference to *Pm*3*m*: (II) *P*4/*mbm* (**A** + **B**, −**A** + **B**, **C**) (III) *Cmcm* (2**A**,2**B**,2**C**), (III′) *Pmmn* (2**A**,2**B**,2**C**), (III″) *Pmmn* (2**A**,2**B**,6**C**), (IV) *Pbcm* (**A** + **B**, − **A** + **B**, 4**C**), (V) *R*3*c* (rhombohedral axes: **A** + **B**, **B** + **C**, **A** + **C**), (*Q*) $Pmc2_1$ (2**C**, **A** + **B**, −**A** + **B**). The antiferroelectric form (IV) can be changed into the ferroelectric form *Q* by the application of an electric field.

Table 3. *Two non-equivalent derivative structures belonging to two non-conjugated subgroups Fm*3*m*

Ideal perovskite structures

O	3(*d*)	4/*mmm*	$\frac{1}{2}$,0,0; 0,$\frac{1}{2}$,0; 0,0,$\frac{1}{2}$
A	1(*b*)	*m*3*m*	$\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$
B	1(*a*)	*m*3*m*	0,0,0

NaCl order on octahedral sites *B* in perovskite structure: *Fm*3*m* (the vectors of the conventional unit cell are twice those of *Pm*3*m*; the origin is the same as that in *Pm*3*m*)

(0,0,0; 0,$\frac{1}{2}$,$\frac{1}{2}$; $\frac{1}{2}$,0,$\frac{1}{2}$; $\frac{1}{2}$,$\frac{1}{2}$,0) +

O	24(*e*)	4*mm*	x,0,0; 0,x,0; 0,0,x; $\bar{x}$,0,0; 0,$\bar{x}$,0; 0,0,$\bar{x}$ ($x \simeq \frac{1}{4}$).
A	8(*c*)	$\bar{4}3m$	$\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$; $\frac{3}{4}$,$\frac{3}{4}$,$\frac{3}{4}$
B″	4(*b*)	*m*3*m*	$\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$
B′	4(*a*)	*m*3*m*	0,0,0

NaCl order on cuboctahedral sites *A* in perovskite structure: *Fm*3*m* (the vectors of the conventional unit cell are twice those of *Pm*3*m*; the origin of *Fm*3*m* is at the centre of the unit cell of *Pm*3*m*)

(0,0,0; 0,$\frac{1}{2}$,$\frac{1}{2}$; $\frac{1}{2}$,0,$\frac{1}{2}$; $\frac{1}{2}$,$\frac{1}{2}$,0) +

O	24(*d*)	*mmm*	0,$\frac{1}{4}$,$\frac{1}{4}$; $\frac{1}{4}$,0,$\frac{1}{4}$; $\frac{1}{4}$,$\frac{1}{4}$,0; 0,$\frac{1}{4}$,$\frac{3}{4}$; $\frac{3}{4}$,0,$\frac{1}{4}$; $\frac{1}{4}$,$\frac{3}{4}$,0
B	8(*c*)	$\bar{4}3m$	$\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$; $\frac{3}{4}$,$\frac{3}{4}$,$\frac{3}{4}$
A″	4(*b*)	*m*3*m*	$\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$
A′	4(*a*)	*m*3*m*	0,0,0

non-comparable group steps. The former may be second-order – provided that Landau theory authorizes it – while the latter are obligatory first-order. Contrary to a generally accepted opinion, it can be seen that here the symmetry does not necessarily decrease when the temperature is lowered.

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On 'non-stoichiometric phases' in thin films of rare-earth oxides.

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Kaul & Saxena [*Acta Cryst.* (1977), A33, 992–996] have reported the existence of long-range and short-range order in a non-stoichiometric phase 'LnO$_x$' (Ln = rare earth). It is shown that the experiments they are describing are indeed the oxidation of the rare-earth hydride LnH$_2$ into the rare-earth cubic *C*-type sesquioxide. The interpretation they give of their experiments is to be discarded entirely.

Kaul & Saxena (1977) recently published a paper on rare-earth metal-oxide thin crystals which contains an interpretation of the experimental data considerably at variance with the results of other workers in this field. Some of the interpretations suggested for the chemical composition of the thin films and for the diffraction data have been published before and have been criticized by several teams of investigators (Gasgnier, Ghys, Schiffmacher, Henry la Blanchetais, Caro & Boulesteix, 1974; Gasgnier, Henry la Blanchetais & Caro, 1976; Curzon & Singh, 1975*a*,*b*, 1977*a*,*b*; Surplice, 1976; Cadim & Al-Bassam, 1977; Safrai, Buckwald & Hirsch, 1976). We should like to point out once again some of the errors involved.

The stability of rare-earth monoxides in the solid state

Kaul & Saxena (1977) suggest the existence in thin films of the monoxide 'LnO' (Ln = rare earth) as a f.c.c. phase. They claim that this material is 'reasonably well understood'. They give as evidence the old paper by Eick, Baenziger & Eyring (1956) but they choose to ignore more recent papers of two of these authors (Felmlee & Eyring, 1968; Work & Eick, 1972), which criticize their first paper, and they also ignore the work of McCarthy & White (1970) as well as that of Brauer, Bärnighausen & Schultz (1967).

Felmlee & Eyring (1968) have shown that for Sm the compounds called 'SmO' and 'Sm$_2$O' are in fact SmN$_{1-x}$O$_x$ and SmH$_2$ respectively, and that the cation is always in the trivalent state.

Work & Eick (1972) have shown that it is thermodynamically impossible to prepare 'ScO' and that the material elaborated by Dufeck, Bronzek & Petrie (1969) is, in fact, an oxynitride ScO$_x$N$_y$.

McCarthy & White were unable to prepare 'SmO' by oxidation–reduction (the technique for the preparation of EuO). They describe several unsuccessful attempts to obtain the monoxide. Brauer *et al.* (1967) have shown that it is impossible to obtain 'SmO' by reaction of the metal with the sesquioxide.

It is well known from the work of Johnson (1969) that the reducibility order of the rare earths is: Eu, Yb, Sm, Tm, Pm, Dy, Nd, Ho, Er, Pr, Tb, Ce, Gd and La. It is possible to obtain divalent cations down to Nd in halide systems but in chemical systems involving O, it is possible to reduce only Eu^{3+} and possibly Yb^{3+}.

Kaul & Saxena (1977) suggest that their 'LnO$_x$' f.c.c. phase may also have a value of x larger than 1·5 tending to the LnO$_2$, CaF$_2$-type phase. Such a phase is known only for Ln = Ce, Pr, Tb (Kunzmann & Eyring, 1975) and for the last two rare earths this phase is stable only at a high pressure of oxygen. It is highly improbable, if not completely impossible, that a phase with $x > 1{\cdot}5$, especially for Er and Dy, will be prepared under a 10^{-6} torr vacuum.

The f.c.c. phase

Kaul & Saxena (1977) claim, after several of their coworkers and Semiletov, Imanov & Ragimli (1974, 1976), that in thin films the 'LnO' phase exhibits an f.c.c. electron diffraction pattern. They add that 'the oxygen content in