Ferroelectrics

The sequences of structural phase transitions in perovskites

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THE SEQUENCES OF STRUCTURAL PHASE TRANSITIONS IN PEROVSKITES

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A classification of the octahedral tilt systems in perovskites is given, based on the work of Glazer[1] but extending it and using a new notation; this leads to a simple description of the sequences of phase transitions, and shows how they are related to the soft modes M_3 and R_{25}. Examples from the literature are discussed.

The perovskite structure is very commonly found in oxides and halogenides of the general formula ABX_3. Many of these materials have a structure which is slightly distorted as compared with the ideal cubic structure, either by cation displacements (as in ferro- and antiferroelectrics) or by the tilting of BX_6 octahedra. A classification of octahedral tilt systems in perovskites and a derivation of the symmetry of distorted phases was made some years ago by Glazer.[1] The results were used successfully in the structure analysis of sodium niobate and sodium-potassium niobate solid solutions.[2-5] In the papers cited it was assumed as a working approximation that (a) the tilts around different cubic axes are mutually independent, (b) the octahedra are regular throughout, (c) A-cation displacements do not change the symmetry of the distorted phase. These assumptions will be accepted in this paper. The symmetry of distorted structures[1] will be re-examined, and we shall make an attempt to determine the most probable sequences of phase transitions in relation to octahedral tilting, and to compare the theoretical predictions with the experimental evidence.

In all displacive-type transitions in crystals, displacements of ions from their equilibrium positions are fairly small compared with the interionic distances. Transitions of this type are nearly continuous (of second order or nearly so). This allows us to take advantage of the results of group-theoretical analysis of space group O_h^1 [6,7] from which the possible second-order transitions to subgroups were tabulated. Among irreducible representations of this space group there are two which correspond to modes of the perovskite lattice associated with octahedral tilting only. These modes, M_3 and R_{25}, both belong to boundary points,

M and R, of the Brillouin zone. If either or both become soft modes of the lattice, a phase transition of the type we are discussing will arise.

When one octahedron in the perovskite structure is tilted about any axis, say [001], it causes tilting of neighbouring octahedra in the layer normal to the axis of tilt;[1] the distortion of the whole layer is uniquely defined by the first tilt. For successive layers along the tilt axis, there is however freedom of choice. If they have the *same* sense of tilt, the structure will be tetragonal, with space group D_{4h}^5, $z = 2$, $a = b \simeq \sqrt{2}a_0$, $c \simeq a_0$, where a_0 is the ideal cubic cell parameter. This distortion is due to condensation of the M_3 mode, and will be given the symbol (00ψ). On the other hand, if successive layers along [001] have *opposite* senses of tilt, the distortion corresponds to condensation of the R_{25} mode, the structure is still tetragonal, but with space group D_{4h}^{18}, $z = 4$, $a \simeq b \simeq \sqrt{2}a_0$, $c \simeq 2a_0$; it is given the symbol (00ϕ). In both symbols, the positional sequence within the brackets indicates that the tilt is about the c-axis, [001]. The notation thus carries information about the orientation relative to the axial directions [100], [010], and [001]; in this it resembles the Hermann-Mauguin notation for space groups, and differs from that of Schoenflies.

With further condensation of M_3 and R_{25} modes about different axial directions, more complex distortions can arise. Here we note that the magnitudes of tilts about two axes, or all three, may be equal or independent. Restricting ourselves for the moment to systems each involving only one species of tilt, we have, for the M_3 mode, $(\psi\psi 0)$, $(\psi\psi\psi)$, $(\psi_1\psi_2 0)$, $(\psi_1\psi_2\psi_2)$, and $(\psi_1\psi_2\psi_3)$; and for the R_{25} mode, $(\phi\phi 0)$, $(\phi\phi\phi)$, $(\phi_1\phi_2 0)$, $(\phi_1\phi_2\phi_2)$, and $(\phi_1\phi_2\phi_3)$. The

symmetry and unit-cell dimensions of these phases are shown in Table I (see also references[6,7]), with Glazer's notation[1] included for comparison.

To find the probable sequence of phase transitions, we use two familiar principles:

i) According to thermodynamical theory, successive transitions are possible when each of the phases concerned is described by one of the irreducible representations of the cubic phase, or, if this is multidimensional, by one or more of its components.

ii) distortions of the structure increase with decreasing temperature (increasing external pressure).

The ferroelectric transitions in $BaTiO_3$ and $KNbO_3$ are examples of sequences obeying these principles.

Here, however, we introduce the idea of transitions associated with tilts. The irreducible representations involved are the M_3 and R_{25} representations, which are 1-dimensional and 3-dimensional respectively. If a phase is described by the two representations M_3 and R_{25} simultaneously, the distorted structure is a combination of ψ and ϕ tilts.

Transitions due to either the M_3 or the R_{25} modes form sequences analogous to those in $BaTiO_3$, (000) → (00ϕ) → (0$\phi\phi$) → ($\phi\phi\phi$) and (000) → (00ψ) → (0$\psi\psi$) → ($\psi\psi\psi$) respectively. We note here that only the highest transition in each sequence is second-order

TABLE I

Tilts systems and crystallographic data

Symbols		Space group	Unit cell in unit a_0			Z
This paper:	Glazer[1]		a	b	c	
000	$a^0a^0a^0$	$O_h^1 = Pm3m$	1	1	1	1
00ψ	$a^0a^0c^+$	$D_{4h}^5 = P4/mbm$	$\sqrt{2}$	$\sqrt{2}$	1	2
$\psi\psi$0	$a^+a^+c^0$	$D_{4h}^{17} = I4/mmm^b$	2	2	2	8
$\psi\psi\psi$	$a^+a^+a^+$	$T_h^5 = Im3$	2	2	2	8
0$\psi_1\psi_2$	$a^0b^+c^+$	$D_{2h}^{25} = Immm$	2	2	2	8
$\psi_1\psi_1\psi_2$	$a^+a^+b^+$	$D_{2h}^{25} = Immm$	2	2	2	8
$\psi_1\psi_2\psi_3$	$a^+b^+c^+$	$D_{2h}^{25} = Immm$	2	2	2	8
00ϕ	a^0a^0c	$D_{4h}^{18} = I4/mcm$	$\sqrt{2}$	$\sqrt{2}$	2	4
$\phi\phi$0	$a^-a^-c^0$	$D_{2h}^{28} = Imam$	$\sqrt{2}$	$\sqrt{2}$	2	4
$\phi\phi\phi$	$a^-a^-a^-$	$D_{3d}^6 = R\bar{3}c$	$\sqrt{2}$	$\sqrt{2}$	$\sqrt{2}$	2
$\phi_1$0ϕ_2	$a^-b^0c^-$	$C_{2h}^3 = I2/m$	$\sqrt{2}$	2	$\sqrt{2}$	4
$\phi_1\phi_1\phi_2$	$a^-a^-c^-$	$C_{2h}^6 = I2/c$	$\sqrt{2}$	$\sqrt{2}$	2	4
$\phi_1\phi_2\phi_3$	$a^-b^-c^-$	$C_i^1 = I\bar{1}$	$\sqrt{2}$	2	$\sqrt{2}$	4
0$\phi\psi$	$a^0b^-c^+$	$D_{2h}^{17} = Cmcm$	2	2	2	8
00Δ^a	—	$D_{4h}^5 = P4/mbm$	$\sqrt{2}$	$\sqrt{2}$	2	4
$\phi\phi\psi$	$a^-a^-c^+$	$D_{2h}^{16} = Pnam$	$\sqrt{2}$	$\sqrt{2}$	2	4
$\psi\psi\phi$	$a^+a^+c^-$	$D_{2h}^{13} = Pmmm$	2	2	2	8
$\psi_1\psi_2\phi$	$a^+b^+c^-$					
0$\psi\Delta$	—					
$\psi\psi\Delta$	—					
$\psi_1\psi_2\Delta$	—					
$\phi_1\psi\phi_2$	$a^-b^+c^-$	$C_{2h}^2 = P2_1/m$	$\sqrt{2}$	2	$\sqrt{2}$	4
ϕ0Δ	—	$C_{2h}^3 = C2/m$	2	2	2	8
$\phi\psi\Delta$	—	$C_{2h}^2 = P2_1/m$	2	2	2	8
$\phi\phi\Delta$	—	$C_{2h}^5 = P2_1/a$	$\sqrt{2}$	$\sqrt{2}$	2	4
$\phi_1\phi_2\Delta$	—	$C_i^1 = P\bar{1}$	$\sqrt{2}$	$\sqrt{2}$	2	4

a $\Delta = \psi \pm \phi$.

b Wrongly given in [1]; corrected by Glazer (Acta Cryst. A31, p. 758, 1975).

(or nearly so), associated with a soft mode detectable above and below the transition; the other transitions are first-order.

We now consider what happens when the two kinds of soft modes are both present, each set of tilts being about a different axis. The resultant symmetry can be derived from a superposition of their separate distortions. For small tilt angles, the result is independent of the sequence of operators. Thus, the symmetry represented by $(0\phi\psi)$ corresponds to the space group $D_{2h}^{17} = Cmcm$, with $z = 8$, $a \simeq b \simeq c \simeq 2a_0$, and this phase could appear in either of the two sequences

$$\left.\begin{array}{ccc} (000) & \rightleftarrows (00\psi) & \rightleftarrows (0\phi\psi) \\ O_h^1 & D_{4h}^5 & D_{2h}^{17} \end{array}\right\} \tag{1a}$$

or

$$\left.\begin{array}{ccc} (000) & \rightleftarrows (0\phi0) & \rightleftarrows (0\phi\psi) \\ O_h^1 & D_{4h}^{18} & D_{2h}^{17} \end{array}\right\} \tag{1b}$$

Other combinations of ϕ and ψ tilts can be formed in the same way; the resulting tilt systems are included in Table I.

We must also consider the possibility that tilts of type ϕ and ψ may occur together about *the same* tilt axis. The resulting tilts in adjacent layers of octahedra are $\psi + \phi$, $\psi - \phi$. We write this system as (00Δ), where $\Delta = \psi \pm \phi$. It has the same space group D_{4h}^5 as (00ψ), but, unlike the latter, shows doubling of the c-axis; on the other hand, its space group is lower than that, D_{4h}^{18}, possessed by (00ϕ) which resembles it in the doubling of the c axis. These Δ^- tilts have not been considered by Glazer.[1] Combinations with ϕ or ψ tilts about other pseudocubic axes are possible, and are listed, together with (00Δ), in Table I. Combinations involving Δ tilts about more than one pseudocubic axis are also possible, e.g. $(\phi\Delta\Delta)$, $(\psi\Delta\Delta)$, but are not considered in this paper. When the paper was first drafted, there were no published observations of Δ tilts, but one has now been reported[8] and will be discussed below. We think it likely that others may be found in ordered structures such as $A_2(B_1B_2)X_6$, or other complex ones.

It is known that in the distorted phases of $KMnF_3$, $SrTiO_3$, and other ABX_3 perovskites with a single tilt system, only the X ions are displaced; these are the ions which take part in the soft mode vibration. In several cases listed in Table I, the same space group corresponds to two or more tilt systems. In these cases the X ions are located in general positions, and can be given additional displacements without changing the space group. If, however, the symmetry group

is orthorhombic or lower, the point symmetry of the A-ion site is lowered, and the A ion are displaced. In such crystals, the structure is essentially determined by the minimum of potential energy, and only roughly fits the theoretical situation described by condensation of the soft modes. That is the reason why it is not safe to reverse the argument and attempt to determine the symmetry of the soft modes from the ionic displacements in low-temperature phases,[9] a method which could result in overestimation of the number of modes condensed at the phase transition.

Applying the principles enunciated above, we can now determine the sequences of phase transitions between the tilt systems listed in Table I. They are shown in Figure 1 for the most important distorted phases. We distinguish between transitions that can be
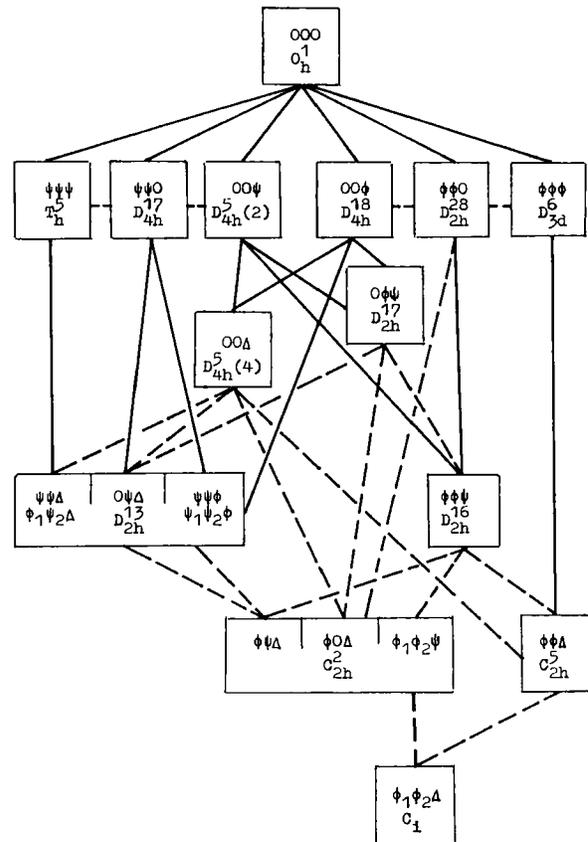

FIGURE 1 The probable sequences of phase transitions and of tilts in perovskites. Full lines correspond to second-order transitions; the soft modes M_3 or R_{25} are first condensed at these points. Dashed lines correspond to the first-order transitions. The number of ϕ or ψ-tilt components are changed at these points. The groups $(\phi_1\phi_20)$, $(\phi_1\phi_1\phi_2)$ ..., $(\psi_1\psi_20)$ ... are omitted for sake of clarity (see Table I). Positional order within the symbol is disregarded in this Figure.

continuous (though they are not necessarily so) and those that can not; the former, shown by full lines, are associated with the points of condensation of a soft mode, while the latter, shown by dashed lines, are first-order transitions. The number of components of ϕ- or ψ-tilts are changed at these points and no soft mode should be observable. For example, the transition between tilt systems (00ϕ) and $(\phi 0\phi)$ cannot be continuous, because a second tilt equal in magnitude to the first must appear at the transition point. A sequence of continuous transitions is possible only *via* the lower-symmetry phase $(0\phi_1\phi_2)$.

A search of the literature has revealed many crystals with tilt systems of the kinds discussed here. Of these, all that are reported to undergo two or more transitions are listed in Table II. Table IIa contains those where detailed studies leading to a knowledge of all the tilt systems have been made; for substances in Table IIb the information is incomplete.

We note that all the phases in Table IIa can be described in terms of tilts of the kinds postulated.

In the compounds $NaNbO_3$, $CsPbCl_3$, $CsPbBr_3$, and $KMnF_3$, the first two transitions are connected with the condensation of a single soft mode in each case—with different sequences in the different materials—as shown by the full-line joins in Figure 1. They are therefore capable of being second-order transitions. In fact, most of them are experimentally known to be continuous or to have only very small discontinuities, but this is not invariably the case: the $(00\psi) \to (\phi\psi\phi)$ transition in $CsPbBr_3$, for example, shows more obvious discontinuities. Particular attention may be called to $KMnF_3$,[8] where the lowest phase provides the first known example of

the (00Δ) tilt, with the magnitudes of ψ and ϕ equal in this case. Before this was directly established, it could have been predicted from the earlier experimental work[12] that the probable tilt system for this G_2 phase was either $(\psi 0\phi)$, $(\psi_1\psi_2\phi)$, or (00Δ).

In all the above-mentioned materials, the observed transitions are in agreement with the assumption of the onset of additional tilt distortions as the temperature decreases. This is not true for $PrAlO_3$ and $SmAlO_3$. In $PrAlO_3$, after the first transition, $(000) \to (\phi\phi\phi)$, the number of tilt components decreases, and in $SmAlO_3$ the tilt system is reconstructed at the second transition, $(\phi\phi\phi) \to (\phi\psi\phi)$. The reasons for this are unknown.

For substances in Table IIb, neither the space group nor the tilt system has been established with certainty for more than one phase; indeed, for $SrZrO_3$[19] and $NaMgF_3$[20] even the point groups indicated in the table are subject to some doubt. We may make some predictions.

i) For $TlMnCl_3$[18] and $CsSrCl_3$[17], the tilt systems for phases G_1 and G_2 are likely to be (00ψ) and (space group D_{4h}^5) and $(0\phi\psi)$ (space group D_{2h}^{17}) as for $CsPbCl_3$[10].

ii) For $NaMgF_3$[20] and many other crystals with a G_2 phase $(\phi\psi\phi)$ (space group D_{2h}^{16}) the G_1 phase is likely to be (00ψ) (space group D_{4h}^5) rather than $(0\psi\psi)$ as suggested by Glazer,[1] because the sequence $(000) \to (0\psi 0) \to (\phi\psi\phi)$ seems more natural than $(000) \to (0\psi\psi) \to (\phi\psi\phi)$. The possibility is not excluded that in some of these crystals the orthorhombic phase $(\phi 0\psi)$ (space group D_{2h}^{17}) found in $NaNbO_3$ and

TABLE II

Substance	Transition temperatures, tilt systems or point groups						Reference, methods
	T_1, °K	G_1	T_2, °K	G_2	T_3, °K	G_3	
(a)							
$NaNbO_3$	914	(00ψ)	848	$(\phi 0\psi)$	793	$(\phi\psi_1\psi_2)$	2–5[a]
$CsPbCl_3$	320	(00ψ)	314	$(\phi 0\psi)$	310	$(\phi_1\phi_2\psi)$	10[a]
$CsPbBr_3$	403	(00ψ)	361	$(\phi\psi\phi)$	–	–	11[a]
$KMnF_3$	185	(00ϕ)	91	(00Δ)	–	–	8, 12[a]
$PrAlO_3$	1320	$(\phi\phi\phi)$	205	$(\phi 0\phi)$	151	$(\phi_1 0\phi_2)$	13, 14[a,b]
$SmAlO_3$	2100	$(\phi\phi\phi)$	1100	$(\phi\psi\phi)$	–	–	15, 16[c,a]
(b)							
$CsSrCl_3$	386	D_{4h}	375	D_{2h}	363	D_{2h}	17[c]
$TlMnCl_3$	296	D_{4h}	276	D_{2h}	235	D_{2h}	18[c]
$SrZrO_3$	1440	D_{4h}	1130	D_{4h}	1000	D_{2h}	19[c]
$NaMgF_3$	1170	D_{4h}	1030	$(\phi\psi\phi)$	–	–	20[c,a]

[a] Direct structural methods.
[b] Indirect methods (radiospectroscopical etc.).
[c] Macroscopical methods and X-ray analysis of powders.

$CsPbCl_3$ may occur as an intermediate phase, giving the sequence $(000) \rightarrow (00\psi) \rightarrow (\phi 0\psi) \rightarrow (\phi\phi\psi)$.

We believe that Figure 1 will be of use in the structure determination of distorted perovskite phases, investigations of soft modes, and other related problems. As more detailed structural information becomes available, it will provide further checks on the assumptions about the sequence of phase transitions on which this paper was founded.

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