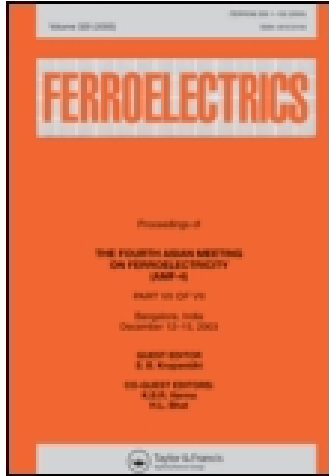


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# MECHANISMS OF THE FERROELECTRIC AND STRUCTURAL PHASE TRANSITIONS. STRUCTURAL DISTORTIONS IN PEROVSKITES

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The symmetry aspects of probable distortions in perovskite-like crystals are discussed. Four soft modes of the lattice which are condensed at different conditions lead to the distortions. The superpositions of the independent distortions (tilts and polar displacements) are considered and the symmetry of the phases is derived. The sequences of phase transitions in the  $ABX_3$ -crystals are analysed.

The first part of the invited lecture concerning the symmetry aspects of the structural phase transitions in perovskite-like crystals is published here. A number of papers dealing with the mechanisms of order-disorder transitions were (or will be) published in current literature.<sup>1-14</sup> Some new results will be reported at this meeting.<sup>14-18</sup>

It is well known that many oxides and halogenides of the general formula  $ABX_3$  belong to the perovskite-like structure which is slightly distorted by cation displacements or by tilts of  $BX_6$ -octahedra as compared with the ideal cubic structure. The nature of the distortions is connected with the instability of lattice in respect to one or several (soft) modes of vibrations. The distorted structures can be considered as the ideal lattice with the "frozen-in" displacements of atoms taking part in the soft modes. This process of a soft mode condensation results in the stabilization of the distorted structure in the definite conditions.

As it was shown earlier<sup>19</sup> the distorted phases of ferroelectric oxides in some cases could not be described as the result of the polar ( $\Gamma_{15}$ ) soft mode condensation. Thorough investigations of the successive phases in  $NaNbO_3$ <sup>20</sup> led to the conclusion that other normal vibrations describing the tilts of  $BX_6$ -octahedra should be taken into consideration. These are  $M_3$  and  $R_{25}$  modes which belong to  $M$ - and  $R$ -points of the Brillouin zone (below we call them tilting modes). Later it was shown that the successive phase transitions determined by the tilting modes condensation often occur in other oxides and halogenides  $ABX_3$ .<sup>21,68</sup>

There is the third distortion due to the (antipolar)  $M'_3(M')$  mode that belongs to  $M$ -point of the zone. Its condensation leads to antipolar displacements of B-ions (and one of X-ions) in the neighbour cells. As an example, the tetragonal phase of  $WO_3$ <sup>65</sup> may serve.

Thus four soft modes:  $\Gamma_{15}$ ,  $M_3$ ,  $R_{25}$  and  $M'$  were found in perovskites by the modern experimental means. Other modes take part in the structure distortions as the secondary phenomena due to anharmonicity of a lattice.<sup>22</sup>

## 1 SYMMETRY OF DISTORTED PHASES

The simplest distortions of structure due to the modes listed above, are shown schematically in Figure 1. The polar and antipolar modes condensation result in the  $C_{4v}^1$  ( $c \simeq a \simeq a_0$ ) and  $D_{4h}^7$  ( $c \simeq a_0$ ,  $a \simeq \sqrt{2}a_0$ ) space groups correspondingly (Figures 1a and 1b). The tilting modes ( $M_3$  and  $R_{25}$ ) condensation (Figures 1c and 1d) result in different but similar distortions. In the first case there are the columns of octahedra along the axes of rotation which are tilted in the same direction ( $D_{4h}^5$ ,  $c \simeq a_0$ ,  $a \simeq \sqrt{2}a_0$ ). In another case every octahedron is surrounded by the six neighbours tilted in the opposite direction ( $D_{4h}^{18}$ ,  $c \simeq 2a_0$ ,  $a \simeq \sqrt{2}a_0$ ).

The displacements of ions at the displacive-type transitions in perovskites are fairly small and the transitions are nearly continuous. The group theoretical analysis of the probable second-order transitions from the space group  $O_h^1$  was made

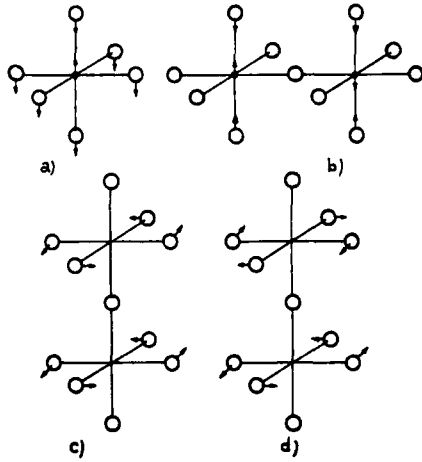


FIGURE 1 Displacements of atoms taking part in the soft modes of perovskites (a) Slater mode ( $\Gamma_{15}$ ), (b) antipolar mode  $M'_3$ , (c) tilting mode  $M_3$ , (d) tilting mode  $R_{25}$ .

earlier.<sup>23</sup> Its results permit us to enumerate the distorted phases due to the condensation of a single mode. It should be mentioned here that the irreducible representations corresponding to  $\Gamma_{15}$  and  $R_{25}$  modes are three-dimensional.  $M_3$  and  $M'$  modes are non-degenerated, but full representations in the last cases are three-dimensional too (the  $M$ -star consists of three vectors).

Successive phase transitions due to condensation of one, two or three components of all four modes are possible.<sup>23</sup> The following sequences of the transitions may be found

$$(\Gamma_{15}) \quad O_h^1 \longrightarrow C_{4v}^1 \longrightarrow C_{2v}^{14} \longrightarrow C_{3v}^5 \quad (1)$$

(000) (00p) (pp0) (ppp)

$$(M^1) \quad O_h^1 \longrightarrow D_{4h}^7 \longrightarrow D_{4h}^{18} \longrightarrow T_d^3 \quad (2)$$

(000) (00a) (aa0) (aaa)

$$(M_3) \quad O_h^1 \longrightarrow D_{4h}^5 \longrightarrow D_{4h}^{17} \longrightarrow T_h^5 \quad (3)$$

(000) (00ψ) (ψψ0) (ψψψ)

$$(R_{25}) \quad O_h^1 \longrightarrow D_{4h}^{18} \longrightarrow D_{2h}^{28} \longrightarrow D_{3d}^6 \quad (4)$$

(000) (00φ) (φφ0) (φφφ)

It seems convenient to introduce “ $p$ ” and “ $a$ ” notations (polar and antipolar) for the  $\Gamma_{15}$  and  $M'$  distortions and maintain  $\psi$  and  $\phi$  for the  $M_3$  and  $R_{25}$  tilts.<sup>25</sup> Then the distortion in Figure 1 will be (00p), (00a), (00ψ), (00φ). These notations were used in Eqs. (1)–(4). They carry information about the orientations of displacements (tilts) relative to the initial cubic axes.

There is the possibility for the degenerated modes to condense simultaneously three or two components of distortions. Instead of Eqs. (1) and (4) we have, in that case, the following sequences of transitions:

$$O_h^1 \longrightarrow C_{3v}^5 \longrightarrow C_{2v}^{14} \longrightarrow C_{4v}^1 \quad (1a)$$

(000) (ppp) (pp0) (00p)

$$O_h^1 \longrightarrow D_{3d}^6 \longrightarrow D_{2h}^{28} \longrightarrow D_{4h}^{18} \quad (4a)$$

(000) (φφφ) (φφ0) (00φ)

In Eqs. (1)–(4) we did not take into consideration the relative stability of phases. For multi-dimensional representations the more complex distortions such as  $(\psi_1\psi_20)$ ,  $(p_1p_2p_3)$  etc. are possible too.<sup>23,25</sup> These phases in our opinion should be preferable for nondegenerated modes.

Some of the sequences in Eqs. (1)–(4) were observed in real crystals. These are the well known ferroelectric transitions in  $\text{BaTiO}_3$  and  $\text{KNbO}_3$ , recently determined distortions in  $\text{PrAlO}_3$ <sup>26</sup> and solid solutions  $\text{Na}_x\text{WO}_3$  that will be discussed at the meeting.<sup>27</sup>

The cases mentioned above do not settle the matter about the distortions of perovskites. For the determination of all possible cases of symmetry changes it should be supposed that several soft modes take part in the distortions and condense successively at different temperatures (pressures). There are theoretical and experimental foundations for the conclusions.<sup>28–30</sup>

We will discuss below the possible symmetry changes in perovskites due to condensation of two or more soft modes. The distortion, as it was used in earlier papers,<sup>31,25</sup> will be considered as independent ones, so the symmetry of distorted phases can be derived as a superposition of the distortions shown in Figure 1. The whole problem in some respect is illustrated in Figure 2. The successive transitions (Eqs. 1–4) in this figure are located on the inclined edges of a half-octahedron. The distortions due to two modes should be located on the inclined sides and on vertical sections, the distortion due to three or four modes—in the volume of the figure.

The space groups of phases due to superposition of  $M_3$  and  $R_{25}$  distortions were determined by Glazer.<sup>31</sup> The same problem was reconsidered later<sup>25</sup> in connection with the probable sequences of the phase transitions. Two points should be mentioned here. In the paper cited it was proposed that as a rule the structure distortions increase with decreasing temperature (increasing external pressure). The

crystal of CsPbCl<sub>3</sub> is an example of such a sequence:

$$O_h^1 \rightarrow D_{4h}^5 \rightarrow D_{2h}^{17} \rightarrow C_{2h}^2$$

$$(000) \quad (00\psi) \quad (0\phi\psi) \quad (\phi_1\phi_2\psi) \quad (5)$$

The softening of the proper modes could be observed preferably near the transition points where the mode is condensed for the first time (see Figure in Ref. 25).

In our paper<sup>25</sup> a new type of distortion was deduced. If the axis of the  $\psi$  and  $\phi$  tilts of octahedra coincide the neighbouring octahedra in the columns along the axis would rotate at the angles  $\psi + \phi$  and  $\psi - \phi$ . The notation of the distortion (00 $\Delta$ ) was proposed (sp. group  $D_{4h}^5$ ,  $c \approx 2a_0$ ,  $a \approx \sqrt{2}a_0$ ). It was observed independently in KMnF<sub>3</sub> below 90°K.<sup>33</sup>

The symmetry of distorted phases due to  $M_3$  and  $\Gamma_{15}$ ,  $R_{25}$  and  $\Gamma_{15}$ ,  $M_3 + R_{25}$  and  $\Gamma_{15}$  modes can be determined easily. We can use the tables of distorted phases due to  $M_3$  and  $R_{25}$  modes (see Refs. 25 and 31b) and the results of Ref. 56 were the transitions between the nonpolar space groups and their polar subgroups were tabulated. All results of such procedure are too bulky to be presented here, some of them are shown in Table I. It is worthwhile to mention that the volume changes of the distorted phases are determined by the tilting modes. This data is also included in Table I. The distortions presented here should be located on the planes  $OGR$ ,  $O\Gamma M$  and partially in the volume of Figure 2. The symmetry changes due to several distortions where the antipolar mode  $M'$  takes part were partially deduced too. This data will be published later.

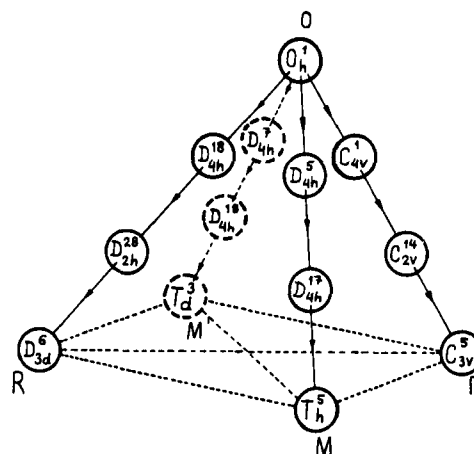


FIGURE 2 Diagram of successive transitions in perovskites. Transitions with single mode condensation are located on the edges of the figure; with two modes—on the planes  $ORM$ ,  $O\Gamma M$  etc. The diagram of successive transitions due to  $M_3$  and  $R_{25}$  modes ( $ORM$ -plane) was published (see Ref. 25).

## 2. EXPERIMENTAL DATA ON THE SUCCESSIVE TRANSITIONS

During the recent decade the systematic investigations of the sequences of phase transitions in several perovskites were carried out in many countries. The exhaustive structural work on some oxide systems was made at Cavendish Laboratory. Our group was mostly interested in

TABLE I

Volume in $a_0^3$	tilts		polar displacements						
	Space group	Symbol	(00p)	(0p0)	(p00)	(pp0)	(p0p)	(0pp)	(ppp)
$\sqrt{2} \cdot \sqrt{2} \cdot 1$	$D_{4h}^5 = P4/m\bar{3}m$	$oo\psi$	$P4/m$	$Pmc$	$Pmc$	$Amm$	$Pc$	$Pc$	$P1$
$2 \cdot 2 \cdot 2$	$D_{4h}^{17} = I4/mmm$	$\psi\psi\psi$	$I4/m$	$Imm$	$Imm$	$Fmm$	$Cm$	$Cm$	$P1$
$2 \cdot 2 \cdot 2$	$T_h^3 = Im\bar{3}$	$\psi\psi\psi$	$Imm$	$Imm$	$Imm$	$Cm$	$Cm$	$Cm$	$R\bar{3}$
$2 \cdot 2 \cdot 2$	$D_{4h}^{25} = Immm$	$\psi_1 \psi_2 \psi_3^*$	$Imm$	$Imm$	$Imm$	$Cm$	$Cm$	$Cm$	$P1$
$\sqrt{2} \cdot \sqrt{2} \cdot 2$	$D_{4h}^{18} = I4/mcm$	$oo\phi$	$I4/m$	$Ima$	$Ima$	$Fmm$	$Cc$	$Cc$	$P1$
$\sqrt{2} \cdot \sqrt{2} \cdot 2$	$D_{2h}^{28} = Imam$	$\phi\phi\phi$	$Ima$	$Imm$	$Ima$	$Cm$	$Cc$	$Cm$	$P1$
$\sqrt{2} \cdot \sqrt{2} \cdot 2$	$D_{3d}^5 = R\bar{3}c$	$\phi\phi\phi$	$C2$	$C2$	$C2$	$P1$	$P1$	$P1$	$R\bar{3}m$
$2 \cdot 2 \cdot 2$	$C_{2h}^3 = C2/m$	$\phi_1 \phi_2$	$Cm$	$C2$	$Cm$	$P1$	$Cm$	$P1$	$P1$
$2 \cdot 2 \cdot 2$	$D_{2h}^{17} = Cmcm$	$o\phi\phi$	$Cmc$	$Amm$	$Ama$	$Pm$	$Cc$	$Cm$	$P1$
$\sqrt{2} \cdot \sqrt{2} \cdot 2$	$D_{4h}^5 = P4/m\bar{3}m$	$oo\phi$	$P4/m$	$Pmc$	$Pmc$	$Amm$	$Pc$	$Pc$	$P1$
$\sqrt{2} \cdot \sqrt{2} \cdot 2$	$D_{2h}^{16} = Pnma$	$\phi\phi\phi$	$Pmn$	$Pna$	$Pmc$	$Pc$	$Pm$	$Pc$	$P1$
$2 \cdot 2 \cdot 2$	$D_{2h}^{13} = Pmmn$	$\psi_1 \psi_2 \phi^*$	$Pmn$	$Pmn$	$Pmc$	$Pc$	$Pm$	$Pm$	$P'$
$2 \cdot 2 \cdot 2$	$C_{2h}^2 = P2_1/m$	$\phi_1 \psi \phi_2$	$Pm$	$P2_1$	$Pm$	$P1$	$Pm$	$P1$	$P1$

\* Some other tilt systems correspond to the space groups  $D_{2h}^{25}$  and  $D_{2h}^{13}$  [25].

TABLE II  
Structure distortions due to the tilting modes

Crystal	$T_1, ^\circ K$	$G_1$	$T_2, ^\circ K$	$G_2$	$T_3, ^\circ K$	$G_3$	$T_4, ^\circ K$	$G_4$	References
SrTiO <sub>3</sub>	110	$oo\phi$	-	-	-	-	-	-	35
LaAlO <sub>3</sub>	700	$\phi\phi\phi$	-	-	-	-	-	-	36, 37
SmAlO <sub>3</sub>	2100	$\phi\phi\phi$	1100	$\phi\phi\phi$	-	-	-	-	37
PrAlO <sub>3</sub>	1320	$\phi\phi\phi$	205	$\phi\phi\phi$	151	$\phi_1 \phi_2$	116	?	26, 36
NaTaO <sub>3</sub>						$\phi\phi\phi$			39
CaTiO <sub>3</sub>						$\phi\phi\phi$			40
Na <sub>0.81</sub> WO <sub>3</sub>	433	$oo\psi$	343	$\psi\psi\psi$	290	$\psi\psi\psi$	-	-	27
SrZrO <sub>3</sub>	1440	$D_{4h}$	1130	$D_{2h}$	1000	$\phi\phi\phi$	-	-	41, 42
KMnF <sub>3</sub>	185	$oo\phi$	91	$oo\phi$	-	-	-	-	44, 45, 33
NaMgF <sub>3</sub>	1170	$D_{4h}$	1030	$\phi\phi\phi$	-	-	-	-	43
RbCaF <sub>3</sub>	198	$oo\phi$	45	$\phi\phi\phi$	7	?	-	-	46-48
RbCdF <sub>3</sub>	124	$oo\phi$	-	-	-	-	-	-	49
TiCdF <sub>3</sub>	191	$oo\phi$	-	-	-	-	-	-	49
CsSrF <sub>3</sub>	247	$D_{4h}$	-	-	-	-	-	-	66
CsPbF <sub>3</sub>	295	$D_{4h}$	-	-	-	-	-	-	68
CsPbCl <sub>3</sub>	320	$oo\psi$	314	$\phi\phi\phi$	310	$\phi_1 \phi_2 \psi$	-	-	51
CsSrCl <sub>3</sub>	386	$D_{4h}$	375	$D_{2h}$	363	$C_{2h}$	-	-	52, 53
TiMnCl <sub>3</sub>	296	$oo\phi$	276	$\phi\phi\phi$	235	$D_{2h}$	-	-	54
RbCdCl <sub>3</sub>	387	$oo\phi$	363	$(D_{2h})$	340	$(D_{2h})$	-	-	55
CsCaCl <sub>3</sub>	95	$D_{4h}$	-70	?	-	-	-	-	24, 66
CsPbBr <sub>3</sub>	403	$oo\phi$	361	$\phi\phi\phi$	-	-	-	-	57

chlorides.<sup>21,24,25,32,45,50,52-54</sup> The available experimental data was collected in Table II. The structural distortions due to  $M_3$  and  $R_{25}$  modes are presented here. In respect to the previous paper<sup>25</sup> this summary was enriched to a greater extent.

It should be mentioned at first that the paths of successive distortions in real crystals correspond to the most probable versions deduced in Ref. 25. It could be seen that the first mode distorting the cubic lattice is  $R_{25}$ -mode in the majority of oxides and fluorides (exceptions:  $\text{NaNbO}_3$ , see Table III, and  $\text{NaWO}_3$ ). But this is  $M_3$ -mode which condenses in all chlorides investigated exhaustively.

The crystals  $\text{CaTiO}_3$  and  $\text{NaTaO}_3$  were included in Table II without indication of transition points. It was stated by the reliable structural investigations<sup>39,40</sup> that the space group of both

TABLE III

Distortion types in the solid solutions of  $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$  [58-62].

Phases	Components of distortion		Full distortion	space group	volume in $a_0$
	tilts	displacements			
	space group	symbol	symbol		
$T_1$	$D_{4h}^5$	00 $\phi$	000	$D_{4h}^5$	$\sqrt{2}\cdot\sqrt{2}\cdot 1$
$T_2$	$D_{2h}^{17}$	$\phi$ 0 $\phi$	000	$D_{2h}^{17}$	2·2·2
S	$D_{2h}^{13}$	$\phi\psi_1\psi_2$	000	$D_{2h}^{13}$	2·2·2
G	$D_{2h}^{13}$	$\phi\psi_1\psi_2$	p00	$C_{2v}^1$	2·2·2
Q	$C_{2h}^2$	$\phi_1\psi_1\phi_2$	$p_1\psi_1p_2$	$C_s^1$	$\sqrt{2}\cdot 2\cdot\sqrt{2}$
F	$D_{2h}^{25}$	$\psi_1\psi_2$	oop	$C_{2v}^{20}$	2·2·2
K	$D_{2h}^{17}$	0 $\phi\phi$	$p_1p_2$ 0	$C_s^1$	2·2·2
H	$D_{4h}^5$	00 $\phi$	oop	$C_{4v}^2$	$\sqrt{2}\cdot\sqrt{2}\cdot 1$
L	$C_{2h}^5$	0 $\psi$ 0	$p_1\psi_1p_2$	$C_s^1$	$\sqrt{2}\cdot 1\cdot\sqrt{2}$
J	$O_h^1$	000	oop	$C_{4v}^1$	1·1·1
M	$O_h^1$	000	oop	$C_{2v}^4$	1·1·1

crystals is  $D_{2h}^{16}$ . These room temperature phases were ascribed conditionally to  $G_3$ -phases meaning that the distorted crystals should transform to cubic phase  $G_0$  at elevated temperatures via one of the phases  $G_1$  at least. The same type of distortion has been observed recently for  $G_3$ -phase of  $\text{SrZrO}_3$ .<sup>42</sup>  $\text{NaMgF}_3$  is another example of the distortion. The structure of tetragonal phase of the crystal was not solved. The investigations of  $\text{Na}_{1-x}\text{K}_x\text{MgF}_3$  solid solutions were carried out in Ref. 68. The temperatures of  $G_0 \rightarrow G_1$  and  $G_1 \rightarrow G_2$  phase transitions are lowered monotonously with  $K$ -content and no other phases were observed. The probable sequence of transitions is  $O_h^1 \rightarrow D_{4h}^5 \rightarrow D_{2h}^{16}$ , that is the same as for  $\text{CsPbBr}_3$ , but in this case  $\text{NaMgF}_3$  would be the single example among fluorides with  $M_3$ -type distortion of the cubic phase.

The  $R_{25}$ -type distortion has been recently found for  $G_1$ -phase of  $\text{RbCaF}_3$ ,  $\text{RbCdF}_3$  and  $\text{RbTlF}_3$ .<sup>46-49</sup> The Raman-spectra have led to either  $(0\psi\phi)$  or  $(00\Delta)$  distortions of  $G_2$ -phase in  $\text{RbCaF}_3$  below 45°K. The single crystals of  $\text{CsPbF}_3$  have been grown at this laboratory.<sup>68</sup> The crystal has the high ionic mobility<sup>50</sup> and is transformed to a tetragonal phase ( $c > a$ ) below 255°K. The transition temperature to a great extent depends on the growth conditions. The similar transition was detected optically at 247°K in  $\text{CsSrF}_3$ .<sup>68</sup>

The sequence of transitions in  $\text{CsSrCl}_3$  was published earlier.<sup>32,52,53</sup> We believed there that the sequence is similar to Eq. (5). This supposition was examined recently by EPR-method on the crystals with  $\text{Mn}^{2+}$  and  $\text{Dy}^{3+}$  additions.<sup>69</sup> The value to tilt angle ( $\sim 6^\circ$ ) in  $G_1$ -phase was confirmed here, but the tilt angles in the  $G_2$ -phase are much lower than angles evaluated from the lattice constants.<sup>32</sup> It may correspond to other type of  $G_2$ -distortion— $\psi\psi\phi$  and the sequence of phases for the crystal, except Eq. (5), may be

$$(000) \rightarrow (00\phi) \rightarrow (\psi\psi\phi) \rightarrow (\psi\Delta\phi) \quad (6)$$

The NQR-spectra on  $\text{Rb}^{87}$  and  $\text{Cl}^{35}$  nuclei in  $\text{RbCdCl}_3$  crystal<sup>55</sup> permitted to conclude that the symmetry of  $G_1$ -phase is  $D_{4h}^5$ . We would like to pay attention to the difference of  $\text{Cl}^{35}$  spectrum splittings for this crystal and  $\text{CsPbCl}_3$ . The structure of the phase would be worthwhile to solve.

The investigations of  $\text{Cs}(\text{Sr}_{1-x}\text{Ca}_x)\text{Cl}_3$  ( $x = 0 \div 1$ ) single crystals have been performed lately.<sup>24,68</sup> The phase transition  $G_0 \rightarrow G_1$  is monotonously lowered with the calcium-content. The twinning of the pure  $\text{CsCaCl}_3$  was observed below 95°K, second phase transition probably takes place below 70°K.

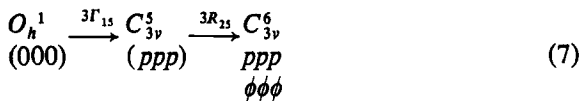
There are only several examples of structural distortions in perovskites where the participation of polar (antipolar) and tilting modes was reliably confirmed. These are  $\text{NaNbO}_3$  and  $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$  solid solutions,  $\text{Pb}(\text{Ti}_{0.1}\text{Zr}_{0.9})\text{O}_3$  and  $\text{WO}_3$ . A number of distorted phases exist in sodium-potassium niobate solid solutions which have been thoroughly examined recently.<sup>58-62</sup> The identified distorted phases were included in Table III. The phases exist in the definite ranges of temperatures and of concentrations (see the phase diagram in Ref. 62). It is clearly seen from Table III that in all cases the superpositions of displacements and of tilts correspond to groups listed in Table I. An exception is L-phase where the group and the reported type of polar distortions was not included in Table I.

In the pure  $\text{NaNbO}_3$  there are three soft modes which condense with temperature lowering. Only  $\Gamma_{15}$  mode condenses in pure  $\text{KNbO}_3$ . The  $M_3$ -mode condensation exist up to 50% potassium content (one of the morphotropic boundaries), the influence of  $R_{25}$ -mode spreads up to the boundary at 32.5 mol.% K. The situation with the third boundary (17.5 mol.% K) is less clear. The number of tilt components changes here at the temperature range up to 200°C, but the rearrangement of tilt system takes place at higher temperatures (phases  $G \rightarrow Q, F \rightarrow K$ ) together with the  $p$ -components changes. It means that in some cases tilts and displacements are mutually dependent.

Two very complex structures  $R$  and  $P$  exist in the system. The tilt systems are non-homogeneous here and consist of two types of differently tilted layers orthogonal to axis which is fourfold increased. The antipolar displacements take place simultaneously. These unusual distortions have not had any reasonable explanation up to now. The tilt systems such as  $\phi\Delta\psi$  and  $\phi\Delta\phi$  (see Ref. 25) would be worthwhile to use as the trial models if the structures of the phases were somewhat redetermined.

The notations introduced above (" $p$ ", " $a$ ",  $\psi$  and  $\phi$ ) are as suitable as Glazer's ones<sup>31</sup> when it is necessary to designate the distortion type determined by tilts or displacements only. When the combination of different distortions takes place it is necessary to use symbols ( $a^+$ ,  $a^-$  etc.) for tilts and vertical, inclined or double arrows for polar and antipolar displacements, as was shown in Ref. 62. It may be more preferable to use a matrix notation, for example,  $\begin{matrix} p & 0 & 0 \\ \phi & \psi_1 & \psi_1 \end{matrix}$  for the  $G$ -phase in Table III, where the first line is related to displacements and the second one to tilts. In this case we can see immediately the directions of all distortions in the structure.

Two other examples exist when displacements and tilts coexist. The first one is  $\text{Pb}(\text{Zr}_{0.9}\text{Ti}_{0.1})\text{O}_3$  crystal, where the sequence of phases:



corresponds to the successive condensation of polar and then of tilting modes.<sup>63,64</sup> This solid solution is the first of the lead zirconate family. The structure of  $\text{PbZrO}_3$  is very complex too. There are many reasons to suppose that other solid solutions on its basis will demonstrate a lot of different distorted

structures. The situations are probable where the points of condensation of the polar and tilting modes may be reversed, as it takes place in the case of  $(\text{Sr}_{1-x}\text{Ba}_x)\text{TiO}_3$  system.<sup>67</sup> Indirect indication on it exists (see Refs. 19, 20 and 71).

Successive distortions of  $\text{WO}_3$  structure according to Refs. 65 and 66 are the superpositions of antipolar  $M'$  and  $R_{25}$  tilt modes. Above 680°C the structure is distorted by  $M'$ -mode. Additional  $a$ - and  $\phi$ -distortions appear below this temperature. The symbols of distortions could not be presented here because the necessary structural data was inaccessible for us up to now.

### 3. CONCLUSION

The possible structure distortions which are determined by  $M_3$ ,  $R_{25}$  and  $\Gamma_{15}$  modes were considered above as a next step to an enumeration of possible distortions in perovskites (see Figure 2). The experimental data confirm the possible ways of the structure distortions discussed earlier.<sup>25</sup> The  $(\text{Na,K})\text{NbO}_3$  system is the brilliant example of the principle on which the diagram of successive transitions due to tilts was founded.<sup>25</sup> It was proposed there that the tilts of the structure increase with temperature lowering. It could be seen from the  $(\text{Na, K})\text{NbO}_3$ -system that this principle is valid in respect to the combinations of tilts and displacements also. The diagram of successive transitions due to  $M_3$ ,  $R_{25}$  and  $\Gamma_{15}$  modes could, of course, be built.

In our opinion the results of the paper would be useful in the structural analysis of perovskites especially for the selection of the trial models before the refinement procedure. The enumerated types of distortions could be used for the explanation of the phase transitions in other crystals, among them the elpasolite-like crystals of the general formula  $\text{A}_2\text{B}^{1+}\text{B}^{3+}\text{X}_6$  should be named. Many chlorides which belong to the structure are slightly distorted at room temperature and transformed to the cubic phase at elevated temperatures.<sup>68,70</sup> It is less clear to what extent the data could be applied in analysis of many other structures having the perovskite-like layers of  $\text{BX}_6$ -octahedra. These are the  $\text{ABX}_3$  politypes,<sup>72</sup> the crystals of  $(\text{AX})_n \cdot \text{ABX}_3$  ( $n = 1, \frac{1}{2}, \frac{1}{3}$ )<sup>73</sup> etc. The phase transition in  $\text{RbMnCl}_3$ , discovered recently,<sup>24,74</sup> belongs apparently to the martensite-like transitions. The sequence of transitions in  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$ <sup>75</sup> has been explained by the orientational ordering of methylammonium (MA) groups.

But at the same time the layer of  $BX_6$ -octahedra is distorted as  $(00\phi)$  at the transition  $D_{4h}^{17} \rightleftharpoons D_{2h}^{18}$  and the role of the lattice vibrations is not clear now.

It seems that the tilts in the perovskite structures are almost inevitable in  $ABX_3$  crystals with the proper alignments of ionic radii  $R_A$ ,  $R_B$ ,  $R_X$ . The detailed analysis of halogenides showed<sup>21,68</sup> that in crystals with  $t < 1$  ( $t$  is the tolerance-factor after Goldschmidt) the unit cell parameter in cubic phase ( $a_0$ ) is some percent less than  $R_B + R_X$ . The stronger the tension of the  $B-X$  bonds in these crystals the higher the temperature of the upper transition. We believe that the tension of  $B-X$ -bonds (when  $A-X$  distances are moderately longer than  $R_A + R_X$ ) and the tendency to lowering of the coordination number (when  $R_A$  is too small for  $Z = 12$ ) are the main crystal chemical reasons of tilting. It will be worthwhile to show more strictly that, for example, the excessive  $B-X$  repulsion leads to the lowering of proper mode frequency at proper points of the Brillouin zone.

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