

References

- ALEXANDROV, K. S., ANISTRATOV, A. T., BESNOSIKOV, B. V. & FEDOSEEVA, N. V. (1981). *Phase Transitions in Crystals of Haloid Compounds*. Novosibirsk (USSR): Nauka.
- CHRISTENSEN, A. N. & RASMUSSEN, S. E. (1965). *Acta Chem. Scand.* **19**, 421-428.
- COMES, R., LAMBERT, M. & GUINIER, A. (1970). *Acta Cryst.* **A26**, 244-254.
- FONTANA, M. D., KUGEL, G. E. & CARABATOS, C. (1981). *J. Phys. (Paris) Suppl.* **42**, C6-749-C6-751.
- FRANCOMBE, M. H. & LEWIS, B. (1958). *Acta Cryst.* **11**, 175-178.
- HARADA, J. & HONJO, G. (1967). *J. Phys. Soc. Jpn.* **22**, 45-57.
- JONA, F. & SHIRANE, G. (1962). *Ferroelectric Crystals*. Oxford: Pergamon Press.
- KANIA, A., ROLEDER, K. & LUKASZEWSKI, M. (1984). *Ferroelectrics*, **52**, 265-269.
- KASSAN-OGLY, F. A. & NAISH, V. E. (1986a). *Acta Cryst.* **B42**, 297-306.
- KASSAN-OGLY, F. A. & NAISH, V. E. (1986b). *Acta Cryst.* **B42**, 307-313.
- KAY, H. F. & VOUSDEN, P. (1949). *Philos. Mag.* **40**, 1019-1040.
- KLEEMANN, W., SCHAFFER, F. J. & FONTANA, M. D. (1984). *Phys. Rev. B*, **30**, 1148-1154.
- KUGEL, G. E., VOGT, H., KRESS, W. & RYTZ, D. (1984). *Phys. Rev. B*, **30**, 985-991.
- LINES, M. E. & GLASS, A. M. (1977). *Principles and Application of Ferroelectrics and Related Materials*. Oxford: Clarendon Press.
- LUKASZEWSKI, M., PAWELCZYK, M., HANDERER, J. & KANIA, A. (1983). *Phase Transitions*, **3**, 247-258.
- MERZ, W. J. (1949). *Phys. Rev.* **76**, 1221-1225.
- MERZ, W. J. (1953). *Phys. Rev.* **91**, 513-517.
- REMEIKA, J. P. & GLASS, A. M. (1970). *Mater. Res. Bull.* **5**, 37-45.
- RYTZ, D., HOCHLI, U. T. & BILZ, H. (1980). *Phys. Rev. B*, **22**, 359-364.
- RYTZ, D. & SCHEEL, H. J. (1982). *J. Cryst. Growth*, **59**, 468-484.
- TRIEBWASSER, S. (1956). *Phys. Rev.* **101**, 993-997.
- TRIEBWASSER, S. (1959). *Phys. Rev.* **114**, 63-70.

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The Immanent Chaotization of Crystal Structures and the Resulting Diffuse Scattering. IV. Diffuse Scattering in Perovskites with Two-Dimensional Movable Objects (Tilting)

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Abstract

This paper is devoted to the calculation of the diffuse-scattering picture and its temperature evolution in cubic perovskites, the loose packing of which at high temperatures is connected with the existence of two-dimensional movable objects. The freezing of these objects as temperature decreases leads to structural phase transitions in consecutive order to pseudotetragonal, pseudoorthorhombic and pseudo-rhombohedral, accompanied by the vanishing of relrod families of diffuse scattering and by the appearance of diffuse (superstructure) reflections. Depending upon the values of the ionic radii crystals with different numbers of phase transitions are possible. The temperature dependence of the order parameters, lattice constants, superstructure reflections, and tilting (antitilting) angles are calculated and compared with experimental data.

Introduction

The present paper immediately follows parts I, II and III (Kassan-Ogly & Naish, 1986a, b, c).

In II we constructed the diagram (Fig. 8 in II) for the existence and stability of ABX_3 compounds based

upon the ionic radii, and perovskites were classified as loose-packing types (I), (II) and (III). In the present paper we shall deal with just the perovskites from region (II) of the diagram (tilting).

In such perovskites unit-cell sizes are determined by the contact of B and X ions (Fig. 3 in II). Here B ions are immobile, A ions have three degrees of freedom, and each X ion has two degrees of freedom and, depending on the ionic-radii ratio, is able to meet in its motion either an X ion from the neighbouring cell or A ions from its own cell. This type of loose packing determines, as we shall see later on, the peculiarities of diffuse scattering in perovskites from the tilting region.

The majority of cubic perovskites are found just in this region [see, for example, Alexandrov, Anistratov, Besnosikov & Fedoseeva (1981) and Fesenko (1972)]. However, X-ray patterns in the mono-Laue method have been obtained for only two crystals: $KMnF_3$ (Comes, Denoyer, Deschamps & Lambert, 1971) and $NaNbO_3$ (Denoyer, Comes & Lambert, 1971; Ishida & Honjo, 1973). For only one of these ($NaNbO_3$) has the temperature evolution (although fragmentary) of diffuse scattering been traced, as was done by Comes, Lamber & Guinier (1970) for $KNbO_3$ (a crystal of shifting type). The appearance of three families of

diffuse spots created by the intersection of Ewald's sphere with three families of mutually perpendicular equidistant 'shining' relrods is the distinguishing feature of these X-ray patterns. In addition, the specific diffuse streaks traced by the 'shining' replanes are also observed in NaNbO_3 .

In the present paper, using the ideas of parts I, II and III, we shall describe the whole picture and the temperature evolution of diffuse scattering in perovskites from the tilting region as well as the temperature dependence of the lattice constants and the tilting angles. As one will see later on the mechanism and types of phase transitions occurring in these crystals differ substantially from those in shifting perovskites. This will necessarily require a discussion of some traditional concepts.

Tilting model

In the literature devoted to cubic perovskites the concept 'tilting' is used very often and is often called 'octahedra rotation' but various authors retain the meaning with some variations. For example, some authors imply that the octahedra are rigid, others imply they are deformable, some consider only pure rotation, others consider rotation accompanied by inclination of the octahedra, and so on [see, for example, Alexandrov *et al.* (1981), Megaw (1973), Lines & Glass (1977)]. Møller (1959) was apparently the first to advance a 'tilting' model (even two different models). Later on this was extensively developed by Rousseau, Gesland, Juillard, Nouet, Zarembowitch & Zarembowitch (1975), Rousseau (1979), Bulou, Ridou, Rousseau & Nouet (1980), Bulou, Nouet, Hewat & Shafer (1980) and Ridou, Rousseau & Bouillot (1981). Here we develop this model.*

Let us formulate the rigorous notions: paratiling, tilting and antitilting. Fig. 1 shows the xy plane normal to the z axis and crossing the centres of the unit cells of perovskite. Solid lines correspond to the intersection of this plane and the side faces of the unit cells, dots are the centres of squares - B -ion positions,

* The 'tilting' problem from the viewpoint of lattice dynamics was considered by Stirling (1972), Boyer & Hardy (1981), and Flocken, Guenther, Hardy & Boyer (1985).

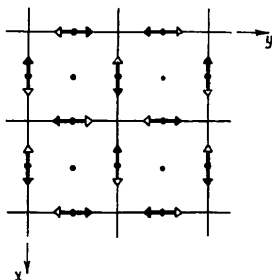


Fig. 1. z paratiling in one plane.

dots on lines - X -ion equilibrium positions, light arrows correspond to the positions of all X ions in one state (configuration), dark arrows - the other state. The synchronous oscillations of all X ions from one state to another and the same oscillations in all the remaining equivalent xy planes occurring without any correlation between planes will be called paratiling along the z axis or simply z -paratiling. These oscillations occurring in different planes in phase will be called z -tilting and oscillations in neighbouring planes in antiphase will be called z -antitilting.

It should be noted that the X -ion octahedra in z -paratiling are not rigid, they are incessantly contracting and stretching in a plane normal to the z axis keeping their size along the z axis. Nevertheless there are rigid movable two-dimensional objects. In this case there are four planar sublattices in the xy plane (the ions belonging to one of these sublattices are marked by '1' in Fig. 2). Owing to cubic symmetry similar considerations are valid for the x and y axes so that it is intuitively clear that paratiling, tilting and antitilting in different directions are independent and equal in value.

Henceforth, as in part III, we first idealize the sublattices assuming them to be rigid and infinite, oscillating at high temperatures and freezing as temperature decreases with displacement (*spontaneous tilting*) relative to their equilibrium positions (frozen optical soft phonon). Secondly, we introduce interaction parameters between oscillations in neighbouring layers assuming (from cubic symmetry) all three interaction parameters J^x, J^y, J^z to be equal, positive in the tilting case and negative in the antitilting case. Thirdly, from simple geometrical considerations of ion displacements during freezing we introduce coupling parameters between the amplitudes of the sublattice oscillations and the structural distortions of a crystal. Fourthly we describe the sublattice oscillations in a symmetrical double-well potential approximately using the Ising model, precisely, by three mutually perpendicular one-dimensional Ising models (one-dimensionality of the model is the consequence of the two-dimensionality of rigid objects - see part I).

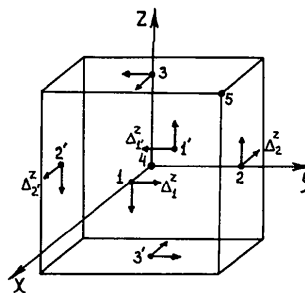


Fig. 2. Degrees of freedom of the X ion and their participation in tiltings of different orientations.

Problem formulation

The elastic X-ray scattering intensity has the form:

$$I(\boldsymbol{\kappa}) = \frac{1}{N} \sum_{nn'} f_n f_n^* \exp[-i\boldsymbol{\kappa}(\mathbf{R}_n - \mathbf{R}_{n'})], \quad (1)$$

where N is the number of atoms, f_n the X-ray form factor, $\boldsymbol{\kappa}$ the scattering vector, and \mathbf{R}_n the radius vector of the ion n .

In our model all A and B atoms are immobile (despite the fact that the A ion has three degrees of freedom, its motion does not contribute to the concerted motion of rigid extended objects and the individual motions of the A ions are of no interest to us since they give only the diffuse background), and each X ion is able to occupy four positions which are symmetrical with respect to a face centre so that each X ion participates in two paratiltings not leaving its own face. For example, X ion 3 in Fig. 2 is oscillating in the xy plane in the x direction participating in y -paratilting and at the same time is oscillating in the y direction participating in x -paratilting.

In so far as the interaction time of a separate X-ray quantum with a crystal is less than the time during which X ions change their positions so the scattering intensity would be obtained as an ensemble of elementary scattering acts on all possible crystal configurations.

To derive the initial formula for the scattering intensity we make use of formula (2) from paper III, valid for the general case when each ion can occupy two positions participating in various oscillations:

$$I(\boldsymbol{\kappa}) = \frac{1}{LN} \sum_{nn'} \sum_{ll'} f_l f_l^* \exp[-i\boldsymbol{\kappa}(\mathbf{R}_{nl} - \mathbf{R}_{n'l'})] \times \sum_{\{\sigma\}} p_\sigma \exp[-i\boldsymbol{\kappa}(\Delta_{nl}^\alpha \sigma_{nl}^\alpha - \Delta_{n'l'}^\alpha \sigma_{n'l'}^\alpha)]. \quad (2)$$

In our model of three paratiltings formula (2) adopts the form:

$$I(\boldsymbol{\kappa}) = \left\{ \frac{1}{LN} \sum_{nn'} \sum_{ll'} f_l f_l^* \exp[-i\boldsymbol{\kappa}(\mathbf{R}_{nl} - \mathbf{R}_{n'l'})] \times \sum_{\{\sigma\}} \exp\{-i\boldsymbol{\kappa}[(\Delta_{nl}^x \sigma_x^x - \Delta_{n'l'}^x \sigma_{x'}^x) + (\Delta_{nl}^y \sigma_y^y - \Delta_{n'l'}^y \sigma_{y'}^y) + (\Delta_{nl}^z \sigma_z^z - \Delta_{n'l'}^z \sigma_{z'}^z)]\} \right\} \times \sum_{\{\sigma\}} \exp(-\beta\mathcal{H}) \quad (3)$$

where: n is the joint index (x, y, z) running over all unit cells of a crystal; the lower indices $x = \{0, 1, 2, \dots, N_x\}$, $y = \{0, 1, 2, \dots, N_y\}$, $z = \{0, 1, 2, \dots, N_z\}$ are the three-dimensional coordinates of the cell centres; l is the ion number within a cell; the upper indices of magnitudes Δ, σ and J merely denote a type (orientation) of paratilting; N is the number of unit cells; $L = 5$ (the number of ions in the perovskite cell); $\mathbf{R}_{nl} = \mathbf{R}_n + \mathbf{r}_l$, where \mathbf{R}_n is the radius vector

of the cell centre, and \mathbf{r}_l the radius vector of the equilibrium state of ion l in a cell; Δ_{nl}^α is the displacement vector of ion nl at its participation in α paratilting; Δ_l^α is the same for all cells and is the displacement amplitude (modulus of the Δ_{nl}^α vector) of ion l at its participation in α -paratilting; σ is an operator accepting values of $+1$ and -1 at random. The operator σ_x^x , for example, determines one of two states (light or dark arrows in Fig. 1) in which all X ions in a plane crossing the centres of cells with number x' are found. \mathcal{H} is the Hamiltonian of our model:

$$\mathcal{H} = -V \left[\sum_{ij} \Delta_{ij}^\alpha \sigma_{ij}^\alpha \Delta_{i+1,j}^\alpha \sigma_{i+1,j}^\alpha + \sum_{ij} \Delta_{ij}^\alpha \sigma_{ij}^\alpha \Delta_{i,j+1}^\alpha \sigma_{i,j+1}^\alpha \right]. \quad (4)$$

Quite similarly to formulas (9) of part III one has:

$$J^x = \frac{V}{kT} \Delta_x^x \Delta_{x+1}^x, \quad J^y = \frac{V}{kT} \Delta_y^y \Delta_{y+1}^y, \quad (5)$$

$$J^z = \frac{V}{kT} \Delta_z^z \Delta_{z+1}^z,$$

where, for example, Δ_z^z and Δ_{z+1}^z are the displacement amplitudes of X ions found beneath one another in neighbouring xy planes, and J^α is 'the exchange' interaction parameter between elementary paratiltings. We take into account, for the sake of simplicity, only the interactions between nearest planes. V in formula (5), as against formula (5) in part III, has a far simpler structure since ions of only one species (X) are involved in tilting. Finally, we do not use the mean-field approximation since the Ising model here is one-dimensional for which the exact solution was obtained in part I.

Calculation of the diffuse-scattering picture

For the first stage on using formula (3) let us take the sum over $+1$ and -1 values of all σ operators. For this purpose we are able to use the mathematical scheme developed in part I. More precisely, we must use the procedure for the exact solution of the scattering problem in the one-dimensional Ising model three times. After rather cumbersome calculations we obtain:

$$I(\boldsymbol{\kappa}) = \frac{1}{LN} \sum_{nn'} \sum_{ll'} f_l f_l^* \exp[-i\boldsymbol{\kappa}(\mathbf{R}_{nl} - \mathbf{R}_{n'l'})] \times \{\cos \boldsymbol{\kappa} \Delta_{nl}^x \cos \boldsymbol{\kappa} \Delta_{n'l'}^x + \delta_{xx'} \sin \boldsymbol{\kappa} \Delta_{nl}^x \sin \boldsymbol{\kappa} \Delta_{n'l'}^x \times [(1 - \tanh^2 J^x)/(1 - 2 \tanh J^x \cos \boldsymbol{\kappa} a + \tanh^2 J^x)]\} \times \{\cos \boldsymbol{\kappa} \Delta_{nl}^y \cos \boldsymbol{\kappa} \Delta_{n'l'}^y$$

$$\begin{aligned}
& + \delta_{yy'} \sin \kappa \Delta_{nl}^y \sin \kappa \Delta_{n'l'}^y \\
& \times [(1 - \tanh^2 J^y)/(1 - 2 \tanh J^y \cos \kappa^y a \\
& + \tanh^2 J^y)] \\
& \times \{ \cos \kappa \Delta_{nl}^z \cos \kappa \Delta_{n'l'}^z \\
& + \delta_{zz'} \sin \kappa \Delta_{nl}^z \sin \kappa \Delta_{n'l'}^z \\
& \times [(1 - \tanh^2 J^z)/(1 - 2 \tanh J^z \cos \kappa^z a \\
& + \tanh^2 J^z)] \}. \quad (6)
\end{aligned}$$

The factor before the square brackets in (6) is the three-dimensional δ function. On multiplying the three brackets in (6) one obtains eight terms of three types: the first term without any Kronecker's δ symbols describes *Bragg reflections* in relspace; three terms of the same type with one δ symbol describe *the diffuse shining relrods* (Kronecker's δ symbol reduces the dimensionality of the three-dimensional δ function to two dimensions); three other terms with two δ symbols correspond to *the diffuse shining replanes* (one-dimensional δ function); the last term with three δ symbols corresponds to the continuous *background* in relspace (no δ functions). Let us introduce for convenience the notation of all eight terms:

$$\begin{aligned}
I(\boldsymbol{\kappa}) = & I_{\text{Br}}(\boldsymbol{\kappa}) + [I^x(\boldsymbol{\kappa}) + I^y(\boldsymbol{\kappa}) + I^z(\boldsymbol{\kappa})] \\
& + [I^{xy}(\boldsymbol{\kappa}) + I^{yz}(\boldsymbol{\kappa}) + I^{zx}(\boldsymbol{\kappa})] + I_{\text{bg}}(\boldsymbol{\kappa}). \quad (7)
\end{aligned}$$

For the further analysis we shall need the ultimate expressions for vectors Δ_{nl}^α and \mathbf{r}_l which can be easily obtained from Figs. 1 and 2:

$$\begin{aligned}
\Delta_{n2}^x &= (00\Delta^x) \exp[-i(\pi/a)(R_y + R_z)], \\
\Delta_{n3}^x &= -(0\Delta^x 0) \exp[-i(\pi/a)(R_y + R_z)], \\
\Delta_{n1}^y &= -(00\Delta^y) \exp[-i(\pi/a)(R_x + R_z)], \\
\Delta_{n3}^y &= (\Delta^y 00) \exp[-i(\pi/a)(R_x + R_y)], \\
\Delta_{n1}^z &= (0\Delta^z 0) \exp[-i(\pi/a)(R_x + R_y)], \\
\Delta_{n2}^z &= -(\Delta^z 00) \exp[-i(\pi/a)(R_x + R_y)], \\
\Delta_{n1}^x &= \Delta_{n2}^y = \Delta_{n3}^z = \Delta_{n4}^\alpha = \Delta_{n5}^\alpha = 0, \quad (9)
\end{aligned}$$

$$\begin{aligned}
\mathbf{r}_1 &= \frac{a}{2}(100), \quad \mathbf{r}_2 = \frac{a}{2}(010), \quad \mathbf{r}_3 = \frac{a}{2}(001), \\
\mathbf{r}_4 &= 0, \quad \mathbf{r}_5 = \frac{a}{2}(111), \quad (10)
\end{aligned}$$

$$f_1 = f_2 = f_3 = f_X, \quad f_4 = f_B, \quad f_5 = f_A. \quad (11)$$

R_x , R_y and R_z are the coordinates of the cell centres.

Let us consider the expression for the intensity of the Bragg reflections:

$$\begin{aligned}
I_{\text{Br}}(\boldsymbol{\kappa}) &= \frac{1}{N} \sum_{nn'} \sum_{ll'} f_l f_l^* \exp[-i\boldsymbol{\kappa}(\mathbf{R}_{nl} - \mathbf{R}_{n'l'})] \\
& \times \cos \kappa \Delta_{nl}^x \cos \kappa \Delta_{n'l'}^x \cos \kappa \Delta_{nl}^y \\
& \times \cos \kappa \Delta_{n'l'}^y \cos \kappa \Delta_{nl}^z \cos \kappa \Delta_{n'l'}^z. \quad (12)
\end{aligned}$$

Substituting (8)–(11) into (12) one obtains:

$$\begin{aligned}
I_{\text{Br}}(\boldsymbol{\kappa}) &= \frac{1}{N} \sum_{nn'} \exp[-i\boldsymbol{\kappa}(\mathbf{R}_n - \mathbf{R}_{n'})] \\
& \times \frac{1}{L} \sum_{ll'} f_l f_l^* \exp[-i\boldsymbol{\kappa}(\mathbf{r}_l - \mathbf{r}_{l'})] \\
& \times \cos \kappa \Delta_l^x \cos \kappa \Delta_l^y \cos \kappa \Delta_l^z \\
& \times \cos \kappa \Delta_{l'}^y \cos \kappa \Delta_{l'}^z \cos \kappa \Delta_{l'}^x, \quad (13)
\end{aligned}$$

where the notations Δ_l^x differ from the corresponding notations Δ_{nl}^x in (8) by the absence of exponential factors.

The first factor in (13)

$$\frac{1}{N} \sum_{nn'} \exp[-i\boldsymbol{\kappa}(\mathbf{R}_n - \mathbf{R}_{n'})] = \sum_{\mathbf{b}} \delta(\boldsymbol{\kappa} - \mathbf{b}) \quad (14)$$

merely determines the positions of the perovskite Bragg reflections and the remaining factors in (13) correspond to the perovskite structural factor modulated by typical Bragg reducing factors of $\cos \kappa \Delta$ type (see part I) so that in the particular limiting case $\Delta = 0$ the modulation factor becomes equal to unity, *i.e.* the modulation vanishes.

Let us now consider the expression for the intensity of the diffuse background $I_{\text{bg}}(\boldsymbol{\kappa})$. Using only the relations (9) it is easy to show that this expression is precisely equal to zero. In other words the diffuse background is absent. This fact is not surprising since *in the accepted model* no single ion possesses three degrees of freedom. It should be noted that in the perovskite KNbO_3 the diffuse background was present and its intensity was determined solely by the niobium atoms that did possess three degrees of freedom (see part III).

Let us now consider the diffuse shining replanes, for example, (110):

$$\begin{aligned}
I^{xy}(\boldsymbol{\kappa}) &= \frac{1}{LN} \sum_{nn'} \delta_{xx'} \delta_{yy'} \sum_{ll'} f_l f_l^* \\
& \times \exp[-i\boldsymbol{\kappa}(\mathbf{R}_{nl} - \mathbf{R}_{n'l'})] \\
& \times \cos \kappa \Delta_{nl}^z \cos \kappa \Delta_{n'l'}^z \sin \kappa \Delta_{nl}^x \\
& \times \sin \kappa \Delta_{n'l'}^x \sin \kappa \Delta_{nl}^y \sin \kappa \Delta_{n'l'}^y \\
& \times [(1 - \tanh^2 J^x)/(1 - 2 \tanh J^x \cos \kappa^x a \\
& + \tanh^2 J^x) \\
& \times (1 - \tanh^2 J^y)/(1 - 2 \tanh J^y \cos \kappa^y a \\
& + \tanh^2 J^y)]. \quad (15)
\end{aligned}$$

Substituting (8)–(11) into (15) one obtains:

$$\begin{aligned}
I^{xy}(\boldsymbol{\kappa}) &= \frac{1}{N_z} \sum_{zz'} \exp[-i\boldsymbol{\kappa}^z(R_z - R_{z'})] \\
& \times \frac{1}{5} f_X f_X^* \sin^2 \kappa^x \Delta^y \sin^2 \kappa^y \Delta^x
\end{aligned}$$

$$\begin{aligned} & \times [(1 - \tanh^2 J^x)/(1 - 2 \tanh J^x \cos \kappa^x a \\ & + \tanh^2 J^x)] \\ & \times [(1 - \tanh^2 J^y)/(1 - 2 \tanh J^y \cos \kappa^y a \\ & + \tanh^2 J^y)]. \end{aligned} \quad (16)$$

The first factor in (16),

$$\frac{1}{N_z} \sum_{zz'} \exp[-i\kappa^z(R_z - R_{z'})] = \sum_{b^z} \delta(\kappa^z - b^z), \quad (17)$$

determines the positions of the equivalent relplanes perpendicular to the z axis and crossing the perovskite Bragg reflections. The factors of the kind $\sin^2 \kappa \Delta$ are typical diffuse factors (see part I) leading to the vanishing of diffuse scattering in the formal limiting case $\Delta = 0$. Quite similarly the expressions for $I^{y^2}(\kappa)$ and $I^{z^2}(\kappa)$ can be obtained.

As a result we obtained three mutually perpendicular families of diffuse replanes crossing Bragg reflections. It should be noted that these are the same replanes as in shifting perovskite (see part III) but now B atoms do not participate in the formation of these replanes [f_B is not present in formula (16)]. Let us now consider the diffuse relrods, for example, $I^x(\kappa)$. Using once again (8)–(11) we obtain:

$$\begin{aligned} I^x(\kappa) &= \frac{1}{N_y N_z} \sum_{yy'} \sum_{zz'} \exp \left[-i \left(\kappa^y + \frac{\pi}{a} \right) (R_y - R_{y'}) \right. \\ & \quad \left. - i \left(\kappa^z + \frac{\pi}{a} \right) (R_z - R_{z'}) \right] \\ & \times \frac{1}{5} f_x f_x^* [(1 - \tanh^2 J^x)/(1 \\ & - 2 \tanh J^x \cos \kappa^x a + \tanh^2 J^x)] \\ & \times [\sin^2 \kappa^y \Delta^x \cos^2 \kappa^x \Delta^y \\ & - 2 \cos(\kappa^y - \kappa^z) \frac{a}{2} \sin \kappa^y \Delta^x \\ & \times \sin \kappa^z \Delta^x \cos \kappa^x \Delta^y \cos \kappa^x \Delta^z \\ & + \sin^2 \kappa^z \Delta^x \cos^2 \kappa^x \Delta^z]. \end{aligned} \quad (18)$$

The first factor,

$$\begin{aligned} & \frac{1}{N_y N_z} \sum_{yy'} \sum_{zz'} \exp \left[-i \left(\kappa^y + \frac{\pi}{a} \right) (R_y - R_{y'}) \right. \\ & \quad \left. - i \left(\kappa^z + \frac{\pi}{a} \right) (R_z - R_{z'}) \right], \end{aligned}$$

determines the positions of the diffuse relrods parallel to the x axis crossing now not the Bragg reflections but the centres of the cells in the reciprocal lattice. It should be emphasized that the final square bracket in (18) becomes equal to zero at $\kappa^y = \kappa^z$ or, in other words, the intensity of the 'diagonal' relrods is equal to zero. In fact, this coincides with the extinction laws found in experiment [see, for example, Ishida & Honjo (1973) and Glazer & Megaw (1972)]. Quite

similarly the expressions for $I^y(\kappa)$ and $I^z(\kappa)$ can be obtained.

As a result we obtained the following picture of the scattering as a whole. In relspace there exist the reduced Bragg reflections, three families of equidistant mutually perpendicular diffuse relplanes crossing Bragg reflections, three families of equidistant diffuse relrods crossing the centres of cells in relspace; 'diagonal' relrods and diffuse background are absent.

Diffuse scattering temperature behaviour without account being taken of structural distortions

Examining the expressions for the intensity of the Bragg reflections (13), the diffuse relplanes (16) and the diffuse relrods (18) one can see that temperature is involved only in the J^x , J^y and J^z parameters and therefore $I_{Br}(\kappa)$ is completely temperature independent while for $I^{xy}(\kappa)$ and $I^x(\kappa)$ temperature dependence is determined only by factors of the following kind:

$$L^x(T) = \frac{1 - \tanh^2 J^x}{1 - 2 \tanh J^x \cos \kappa^x a + \tanh^2 J^x}. \quad (19)$$

Let us consider first the particular case when the 'exchange' interactions (5) are equal to zero. Then the factors $L^x(T)$, $L^y(T)$ and $L^z(T)$ become equal to unity and the whole picture of diffuse scattering in this case does not depend upon temperature.

Up to now, despite the fact that in expression (5) the x , y and z indices at oscillation amplitudes Δ were kept, these amplitudes in different paratiltings have also been assumed to be equal owing to cubic symmetry, as $J^x = J^y = J^z$. Let us introduce the notation:

$$T_0 \equiv \frac{|V|}{k} (\Delta^x)^2 = \frac{|V|}{k} (\Delta^y)^2 = \frac{|V|}{k} (\Delta^z)^2. \quad (20)$$

Then for $V > 0$, *i.e.* for the *tilting* case, expression (18) may be rewritten in the form:

$$L_t^x(T) = \frac{1 - \tanh^2 (T_0/T)}{1 - 2 \tanh (T_0/T) \cos \kappa^x a + \tanh^2 (T_0/T)}, \quad (21)$$

whereas for $V < 0$, *i.e.* for the *antitilting* case:

$$L_{at}^x(T) = \frac{1 - \tanh^2 (T_0/T)}{1 + 2 \tanh (T_0/T) \cos \kappa^x a + \tanh^2 (T_0/T)} \quad (22)$$

The dependence of (21) upon κ^x at various temperatures is shown in Fig. 3. The dependence of (22) is depicted by the same curve, displaced, however, by π/a along the κ^x axis (see also Fig. 3 in part I).

Thus Fig. 3 clearly shows the temperature behaviour of the diffuse relrods. At infinitely high temperature the relrods are uniform. As temperature

decreases a gradual pumping over of intensity from relrods into separate relpoints takes place so that when the temperature approaches zero the intensity in these relpoints becomes δ -function-shaped.

In other words, as temperature decreases the diffuse peaks which appear gradually transform into well-shaped superstructure reflections.

Using the usual notations one can say that at high temperatures there exist diffuse relrods of three families:

$$\begin{aligned} h + \frac{1}{2}, \quad k + \frac{1}{2}, \quad L \quad h \neq k \\ h + \frac{1}{2}, \quad K, \quad l + \frac{1}{2} \quad h \neq l \\ H, \quad k + \frac{1}{2}, \quad l + \frac{1}{2}, \quad k \neq l \end{aligned} \quad (23)$$

where h, k, l are the cubic indices while H, K, L are arbitrary numbers. As temperature decreases the diffuse relrods concentrate into superstructure reflections:

(a) tilting case:

$$\begin{aligned} h + \frac{1}{2}, \quad h + \frac{1}{2}, \quad l \quad h \neq k \\ h + \frac{1}{2}, \quad k, \quad l + \frac{1}{2} \quad h \neq l \\ h, \quad k + \frac{1}{2}, \quad l + \frac{1}{2} \quad k \neq l \end{aligned} \quad (24)$$

(b) antitilting case:

$$h + \frac{1}{2}, \quad k + \frac{1}{2}, \quad l + \frac{1}{2} \quad h \neq k, \quad k \neq l, \quad l \neq h. \quad (25)$$

The temperature redistribution of intensity along diffuse relplanes $I^{xy}(\boldsymbol{\kappa})$, $I^{yz}(\boldsymbol{\kappa})$ and $I^{zx}(\boldsymbol{\kappa})$ can be similarly examined since it is directed by the same factors (19).

To interpret the results obtained in terms of the phase transition theory let us introduce the following concept: *order parameters* (their physical meaning will be discussed below).

$$\eta_x = \tanh |J^x|, \quad \eta_y = \tanh |J^y|, \quad \eta_z = \tanh |J^z|. \quad (26)$$

(Fig. 4 shows the temperature behaviour of these parameters.) Let us introduce also the concept 'spontaneous tilting' (*antitilting*):

$$\eta_x \Delta^x, \quad \eta_y \Delta^y, \quad \eta_z \Delta^z. \quad (27)$$

Then the crystal behaviour is described in the follow-

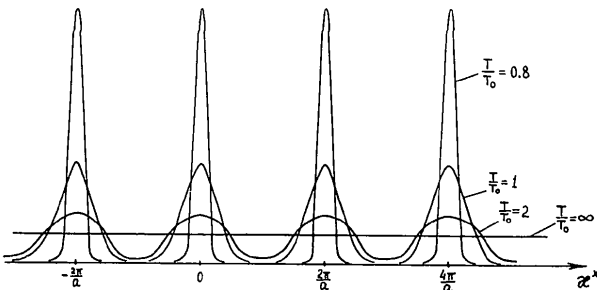


Fig. 3. The temperature redistribution of intensity along diffuse relrods and the formation of superstructure reflections.

ing way. At infinitely high temperature the X ions oscillate relative to their average equilibrium positions located precisely at the centre of a face. As temperature decreases a gradual displacement of the average position and a gradual freezing of the oscillations take place so that at zero temperature the X ions are frozen in positions displaced from a face centre by the values $\Delta^x = \Delta^y = \Delta^z$.

In other words, the concept paratilting is valid only at infinitely high temperature. At any finite temperature there always exist the non-zero values of the spontaneous tiltings (or antitiltings). Strictly speaking in such a crystal any phase transition is absent and any such concept as order parameter in the traditional sense is also absent, *i.e.* the magnitude which is equal to zero above the transition point and is not equal to zero below it. However, at the same time it is known that in real crystals from the tilting region phase transitions with well defined transition points occur. These are KMnF_3 , SrTiO_3 , NaNbO_3 , CsPbCl_3 and many others. This inconsistency arises because we have not yet taken into account the real lattice distortions accompanying the appearance of spontaneous tilting (or antitilting).

The coupling of spontaneous tilting and structural distortions

Up to now we have tacitly assumed that temperature is involved only in the 'exchange' interaction parameters J^x , J^y and J^z which are equal in value. The real situation is quite different and real displacements of *all* ions in a crystal, not only those participating in tilting, are the main reason for this.

Let us return to Fig. 2 and remind ourselves that the unit-cell sizes are determined by the contacts of the B ion at the centre of a cell with the X ions 1, 1', 2, 2', 3, 3'. Let us assume that at a certain temperature there exists spontaneous z tilting, *i.e.* 1, 1', 2, 2' ions are displaced in the xy plane of their own faces by the value $\eta_z \Delta^z$ on the average. Then gaps between the B ion and the 1, 1', 2, 2' ions should appear and hence the unit cell as a whole should contract in the xy plane since A and X ions do not contact each other. It is obvious that the z size of a cell does not change so that

$$a_x = a_y = a(1 - t' \eta_z) \quad (28)$$

$$a_z = a, \quad (29)$$

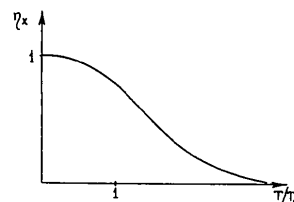


Fig. 4. The temperature behaviour of the order parameter.

where t' is a small positive magnitude ($l' = 0$, unlike the shifting case). Because of all these distortions of a lattice (every face of a lattice is contracted) all gaps between ions also vary and consequently the ion oscillation amplitudes vary as well:

$$\Delta^x = \Delta^y = \Delta(1 - t\eta_z) \quad (30)$$

$$\Delta^z = \Delta(1 - l\eta_z), \quad (31)$$

where t and l are some positive magnitudes, Δ is the oscillation amplitude of the X ions at $T = \infty$ (in a cubic phase). From cubic symmetry it is clear that quite similar considerations are valid for the x and y tiltings (antitiltings) so that:

$$\begin{aligned} a_x &= a(1 - t'\eta_x)(1 - t'\eta_z) \\ a_y &= a(1 - t'\eta_x)(1 - t'\eta_z) \end{aligned} \quad (32)$$

$$a_z = a(1 - t'\eta_x)(1 - t'\eta_y)$$

$$\begin{aligned} \Delta^x &= \Delta(1 - l\eta_x)(1 - t\eta_y)(1 - t\eta_z) \\ \Delta^y &= \Delta(1 - t\eta_x)(1 - l\eta_y)(1 - t\eta_z) \end{aligned} \quad (33)$$

$$\Delta^z = \Delta(1 - t\eta_x)(1 - t\eta_y)(1 - l\eta_z).$$

As a result the equations for the order parameters vary as well:

$$\begin{aligned} \eta_x &= \tanh \left[\frac{T_0}{T} (1 - l\eta_x)^2 (1 - t\eta_y)^2 (1 - t\eta_z)^2 \right] \\ \eta_y &= \tanh \left[\frac{T_0}{T} (1 - t\eta_x)^2 (1 - l\eta_y)^2 (1 - t\eta_z)^2 \right] \\ \eta_z &= \tanh \left[\frac{T_0}{T} (1 - t\eta_x)^2 (1 - t\eta_y)^2 (1 - l\eta_z)^2 \right], \end{aligned} \quad (34)$$

where

$$T_0 = \frac{|V|}{k} \Delta^2. \quad (35)$$

Temperature behaviour of a crystal with structural distortions

Now the problem of the crystal temperature behaviour becomes more complicated but at the same time it becomes far more realistic. Briefly, the further programme involves the following. Firstly, for any crystal taken from the tilting region (*i.e.* for concrete values of the ionic radii) one should calculate the values of the l , t and t' parameters (the A -problem - see part III). Secondly, at these values of l and t one should discover all possible solutions of the system (34) and substitute all the found values of η_x , η_y and η_z into equations (33). Thirdly, for all temperature values one should choose solutions lowest in energy:

$$E = -[\eta_x(\Delta^x)^2 + \eta_y(\Delta^y)^2 + \eta_z(\Delta^z)^2]. \quad (36)$$

Substituting one for each temperature set of η_x , η_y ,

η_z , Δ^x , Δ^y , Δ^z values found in such a way into the intensity expression for diffuse relrods (18) and diffuse relplanes (16) one will find the temperature behaviour of diffuse scattering. If necessary one can also find the temperature dependence of the Bragg reflections by substituting Δ^x , Δ^y and Δ^z into (13). The temperature behaviour of the lattice parameters can be found by η_x , η_y and η_z substitution into (32).

The first part of the programme (the A -problem) appears to be a rather complicated independent problem. In the present paper we shall not go into details of this problem, which in many aspects is analogous to the A -problem in the shifting case in part III. We shall merely give without calculations the results necessary for further analysis.

Depending upon the ionic radii the oscillations of the X ions may occur in several regimes. The two following regimes are actually found here.

First regime: at high temperatures X ions oscillate so that they meet A ions from their own cell and as temperature decreases they continue to meet A ions freezing in such positions. This regime corresponds to $t = 1$ and to l and t' values in the interval from 0 to $1 - \sqrt{2}/2 \approx 0.293$. The amplitude of the X -ion oscillations, l and t' values are given by formulas ($l' = 0$):

$$\begin{aligned} \frac{\Delta}{a} &= \frac{1 - \sqrt{2\tau^2 - 1}}{2}; & l &= 1 - \frac{\sqrt{3 - 2\tau^2} - \sqrt{2\tau^2 - 1}}{2(1 - \sqrt{2\tau^2 - 1})}, \\ t' &= 1 - \frac{\sqrt{3 - 2\tau^2} + \sqrt{2\tau^2 - 1}}{2}, \end{aligned} \quad (37)$$

where τ is the tolerance factor varying in the tilting region from 1 to $\sqrt{2}/2 \approx 0.707$ (see part II), $\tau = (r_A + 1)/[\sqrt{2}(r_B + 1)]$.

Second regime: at high temperatures X ions oscillate so that they meet X ions from neighbouring cells, as temperature decreases they continue to meet X ions from neighbouring cells participating in one of the tiltings (antitiltings) but the same X ions meet A ions from their own cells participating in the other tiltings (antitiltings). This regime corresponds to t values from 1 to 0.116, l values from 0.116 to 0.293, t' values from 0.034 to 0.293 according to the formulas:

$$\begin{aligned} \frac{\Delta}{a} &= \frac{r_B}{2(r_B + 1)}; & t' &= 1 - \frac{1 + \sqrt{2(r_B + 1)^2 - 1}}{2(r_B + 1)}, \\ l &= 1 - \frac{\sqrt{2(r_B + 1)^2 - 1}}{2r_B}; \\ t &= 1 - \frac{r_B + 1 - \sqrt{2\tau^2(r_B + 1)^2 - 1}}{r_B}. \end{aligned} \quad (38)$$

The solid curve in Fig. 5 yields the equation:

$$(r_A + 1)^2 = (r_B + 1)^2 + 1, \quad (39)$$

and serves as the boundary between these two regimes.

Solution of system (34)

In the general case system (34) has four types of solutions:

- | | |
|---|---------------------------|
| (1) $\eta_1 \eta_1 \eta_1$ | symmetrical |
| (2) $\eta'_2 \eta'_2 \eta_2 (\eta_2 > \eta'_2)$ | pseudotetragonal |
| (3) $\eta_3 \eta_3 \eta'_3 (\eta_3 > \eta'_3)$ | pseudoorthorhombic |
| (4) $\eta_4 \eta'_4 \eta''_4$ | general (low-symmetrical) |

The second and the third solutions would be called merely tetragonal and orthorhombic if η'_2 and η'_3 were equal to zero. However, the very structure of equation (34) does not allow zero values for the η parameters (contrary to the shifting case - see part III). As will be seen later on the names 'pseudotetragonal' and 'pseudoorthorhombic' possess profound physical meaning. For the same reason the first solutions (symmetrical) should be called pseudocubic at high temperatures and pseudorhombohedral at low temperatures. Forestalling the calculations one can say that the fourth solution (general) never becomes minimal in energy (36) and thus we shall not regard it henceforth.

For the first solution the system is reduced to one equation:

$$\eta_1 = \tanh \left[\frac{T_0}{T} (1 - l\eta_1)^2 (1 - t\eta_1)^4 \right]. \quad (40)$$

The energy of the first solution is:

$$E_1 = -3(1 - l\eta_1)^2 (1 - t\eta_1)^4 \eta_1 \quad (41)$$

(hereafter the irrelevant constant Δ^2 is omitted).

For the pseudotetragonal solution the system (34) is reduced to two equations:

$$\eta'_2 = \tanh \left[\frac{T_0}{T} (1 - l\eta'_2)^2 (1 - t\eta'_2)^2 (1 - t\eta_2)^2 \right] \quad (42)$$

$$\eta_2 = \tanh \left[\frac{T_0}{T} (1 - l\eta_2)^2 (1 - t\eta'_2)^4 \right].$$

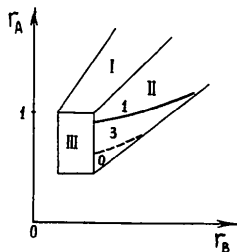


Fig. 5. A schematic division of the tilting region II: (1) perovskites with one transition; (3) perovskites with three transitions; (0) perovskites without transitions.

The energy of the pseudotetragonal solution is:

$$E_2 = -(1 - l\eta_2)^2 (1 - t\eta'_2)^4 \eta_2 - 2(1 - l\eta'_2)^2 (1 - t\eta'_2)^2 (1 - t\eta_2)^2 \eta'_2. \quad (43)$$

For the pseudoorthorhombic solution the system (34) is reduced to two equations:

$$\eta_3 = \tanh \left[\frac{T_0}{T} (1 - l\eta_3)^2 (1 - t\eta_3)^2 (1 - t\eta'_3)^2 \right] \quad (44)$$

$$\eta'_3 = \tanh \left[\frac{T_0}{T} (1 - l\eta'_3)^2 (1 - t\eta_3)^4 \right].$$

The energy of the pseudoorthorhombic solution is:

$$E_3 = -2(1 - l\eta_3)^2 (1 - t\eta_3)^2 (1 - t\eta'_3)^2 \eta'_3 - (1 - l\eta_3)^2 (1 - l\eta'_3)^4 \eta_3. \quad (45)$$

Numerical calculations

The analysis of the numerical calculations of equations (40), (42) and (44) at various values of the parameters l and t gives the following conclusions. The symmetric solution exists over the whole temperature region. Pseudotetragonal and pseudoorthorhombic solutions may exist in the restricted temperature intervals (T'_1, T_1) and (T_3, T'_3) , respectively, which always overlap so that $T_3 < T'_1 < T'_3 < T_1$.

The hatched area in Fig. 6 corresponds to the values of the parameters l and t at which pseudotetragonal and pseudoorthorhombic solutions may exist.

Energy-minimization analysis gives the following conclusions. First, in the existence intervals of the pseudotetragonal and pseudoorthorhombic solutions the symmetrical solution is always disadvantageous while the relative advantage of the pseudotetragonal and pseudoorthorhombic solutions is exchanged at some point T_2 between T'_1 and T'_3 . Furthermore, at $t \rightarrow 1$ the values of T_3 and T'_1 go to zero. Fig. 7 shows in outline the dependence of T_1 , T_2 and T_3 upon the

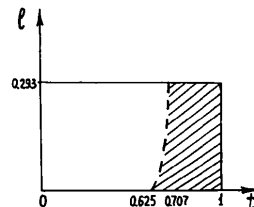


Fig. 6. The origin of the regimes with one and three transitions in (l, t) parameter space.

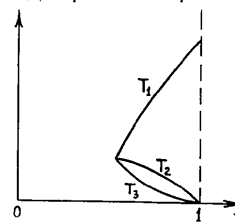


Fig. 7. The dependence of the phase-transition temperatures upon the t parameter.

value of the t parameter at any taken value of l from the hatched area in Fig. 6.

Let us return once again to Fig. 5, the dotted curve in which exactly corresponds to the dotted curve in Fig. 6. Now the meaning of this curve in Fig. 5 becomes clear. It is the boundary above which in the region of the second regime the crystals undergo three phase transitions whereas below this boundary the crystals no longer undergo any transitions. It is also clear now that the crystals with one transition correspond to the first regime.

Let us consider in detail two typical cases - one from the region with one transition and the other from the region with three transitions in Fig. 5. It is quite sufficient to take, for example, $\tau = 0.95$ for the first case and $r_B = 0.8$ and $r_A = 0.85$ for the second. The results of the numerical calculations for these cases are shown in Fig. 8: for a crystal with one transition - on the left; for a crystal with three transitions - on the right. Fig. 8(a) shows the temperature

behaviour of the order parameters, Fig. 8(b) the energies, and Fig. 8(c) the lattice parameters.

For the sake of comparison with experiment let us also calculate the temperature behaviour of the *superstructure reflections* determined in the main by a factor of the type (18). Without loss of generality let us confine ourselves to the tilting case, *i.e.* let us take $V > 0$ in (5). Then the superstructure reflections are described by expression (23) so that one should substitute the calculated values of η_x , η_y and η_z into the expressions of type (18) and also put $\cos \kappa^x a = \cos \kappa^y a = \cos \kappa^z a = 1$. The results of the calculation are shown in Fig. 8(d). The behaviour of the superstructure reflections in a crystal with antitilting is just the same but the positions of the reflections are determined by expression (24).

It is convenient to calculate the temperature behaviour of the *octahedra rotation angles* often discussed in experimental papers [see, for example, Glazer & Megaw (1972), Clarke (1977), and Ahtee, Glazer & Megaw (1972)]. The notations ψ for tilting and φ for antitilting angles are often used (see, for example, Alexandrov *et al.*, 1981). Then in our designations one obtains:

$$\begin{aligned} \psi_x &= \tan^{-1} \left(\frac{2\eta_x \Delta^x}{a_y} \right), & \psi_y &= \tan^{-1} \left(\frac{2\eta_y \Delta^y}{a_z} \right), \\ \psi_z &= \tan^{-1} \left(\frac{2\eta_z \Delta^z}{a_x} \right) \end{aligned} \quad (46)$$

(similarly for φ). Fig. 8(e) shows the results of the calculations.

Comparison with experiment and discussion

Let us now depict as a whole the phenomenon occurring in a crystal with tilting ($V > 0$) or antitilting ($V < 0$).

At high temperatures the crystal is in a pseudocubic state with small (but not zero) equal values of all three spontaneous tiltings and with large amplitudes of X-ion oscillations. If the crystal corresponds to the first regime ($t = 1$) according to the values of the ionic radii so, as temperature decreases, it undergoes only one phase transition of second order at T_1 into a tetragonal phase. Just below T_1 one of the spontaneous tiltings increases sharply while the other two sharply decrease (Fig. 8a). With further temperature decrease one of the spontaneous tiltings smoothly increases to a finite value at $T = 0$ while the other two go to zero at $T = 0$. The behaviour of the octahedra rotation angles is quite similar (Fig. 8e). At $T = 0$ the phase becomes genuinely tetragonal. The diffuse scattering undergoes the following evolution. At high temperatures there exist three families of diffuse relrods and three families of diffuse replanes with weakly pronounced peaks in the relpoints of the future superstructure reflections. As temperature

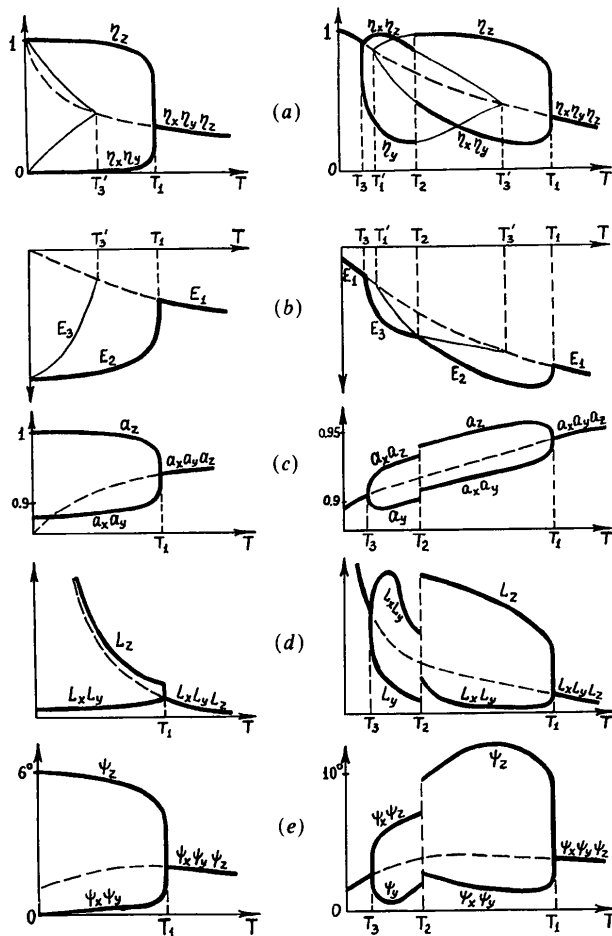


Fig. 8. The temperature dependence of various physical characteristics of perovskites from the tilting region: (a) components of the order parameter; (b) energies of solutions; (c) lattice parameters; (d) superstructure reflection intensities; (e) tilting (antitilting) angles; left - crystal with one transition; right - crystal with three transitions.

decreases the gradual redistribution of intensity along diffuse relrods and relplanes takes place. The weak peaks gradually grow while the 'in-between' intensity gradually decreases. At the transition temperature the peaks of one of the families sharply increase while the other two sharply decrease so that the non-uniformity of one family is sharpened while the uniformity of the others is partially restored. With further temperature decrease the non-uniformity of the intensity gradually increases and at $T=0$ only well pronounced superstructure reflections are left for diffuse relrods. This behaviour is illustrated by the left-hand side of Fig. 8(d). A similar evolution takes place for relplanes.

If according to the ionic radii the crystal corresponds to the region with three phase transitions ($t \neq 1$), so, qualitatively, a similar but more complicated phenomenon occurs in it (see the right-hand side of Fig. 8d). As temperature decreases at T_1 the phase transition of second order from pseudocubic into pseudotetragonal first takes place, then at T_2 the crystal undergoes the phase transition of first order to the pseudoorthorhombic phase and finally at T_3 it undergoes the phase transition of second order to the pseudorhombohedral phase. The behaviour of the order parameters, lattice constants, angles of octahedra rotations and superstructure reflections may be traced in Fig. 8(a)-(e) (right-hand side).

Strictly speaking all our considerations are applicable only to crystals in which either tilting or antitilting takes place. Apparently RbMnCl_3 , TiMnCl_3 and SrTiO_3 belong to such a kind and also Na_xWO_3 , the only crystal with three tilting transitions already observed (see, for example, Clarke, 1977). However, in a great number of crystals investigated, including KMnF_3 and NaNbO_3 , the phenomena caused both by tilting and antitilting are simultaneously present. For a description of such crystals the theory should be developed in a rather simple way, namely, instead of one parameter of 'exchange' interaction V in (5) taken in the approximation of the nearest planes one should introduce at least one more interaction parameter for the next-nearest-planes interaction, for example, so that these two parameters could compete with each other ($V_1 > 0$; $V_2 < 0$ or $V_1 < 0$; $V_2 < 0$). The difficulties of comparison with experiment arises because diffuse-scattering data are only available for such crystals. For example, the fragmentary temperature evolution of diffuse scattering has only been traced in NaNbO_3 by Denoyer *et al.* (1971) and only one more picture of diffuse scattering at only one temperature has been obtained for KMnF_3 by Comes *et al.* (1971).

Nevertheless, the majority of the characteristic features of crystal behaviour obtained in our theory are corroborated by the results of experiments carried out just on these crystals. The temperature behaviour of the tilting and antitilting superstructure reflections

in NaNbO_3 shown in Fig. 1(b) and Fig. 6 of Comes *et al.* (1971) and by Hidaka, Ohama, Okazaki, Sakashita & Yamakawa (1975) for KMnF_3 are the most vivid examples of this kind.

Let us consider briefly the concepts 'tilting' and 'antitilting angles'. From the analysis of geometrical distortions of the lattice at tilting carried out in detail one can see that the octahedra rotations in the elementary z tilting inevitably involve deformation of the octahedra in the xy plane so that this is no longer pure rotation although one can keep such characteristics as the tilting angle ψ_z . Depicting two neighbouring octahedra being turned by ψ_z in different directions one can see the disorientation of the octahedra axes and simply because of this visual fact the notion 'tilting' appeared. As we have seen above all our considerations do not need such an approach nor do they need the very concept 'tilting', but we use such a concept if only because it is deep-rooted in the literature. The language of tilting and antitilting angles is quite admissible for a crystal with three tiltings (antitiltings) of different orientations and even for a crystal with tiltings and antitiltings occurring simultaneously.

Remarks on order parameter

It is very likely that the main difficulty for the comparison with experiment is connected with the fact that in the description of tilting crystals many authors urgently strive to use the traditional concept of order parameter usually understood as the magnitude which is equal to zero on one side of the phase transition and is non-zero on the other. As we have already seen the magnitudes η_α determined by equations (34) and playing the role of order parameters never equal zero even above the highest transition temperature. That is why we have called the highest phase the *pseudocubic*, but not merely cubic. The same conclusion was drawn previously by Rousseau (1979), Bulou, Nouet *et al.* (1980) and Bulou, Ridou *et al.* (1980). The widely held belief that the order parameter should necessarily grow as temperature decreases is also inapplicable to the magnitudes η_x , η_y and η_z . If one adheres to these traditional concepts it is difficult to give a consistent description of the phenomena occurring in a perovskite from the tilting region and consequently to interpret the experimental data. Such difficulties are clearly seen in many papers by various authors. The temperature dependence of tilting angle, presented by Clarke (1977), may serve as an example. In reality ψ values differ from zero even above the highest transition temperature (one has to carry out thorough measurements of ψ above that temperature) whereas as temperature decreases below the interval presented by Clarke the tilting angle tends to decrease (one has to carry out these measurements as well and not

confine oneself to the restricted temperature interval). Ahtee, Glazer & Megaw (1972) had come to the same conclusion regarding the insufficiency of the traditional concept of order parameter in a description of tilting crystals (their magnitude $\bar{\Delta}$ is analogous to our spontaneous tilting $\eta\Delta$) and who said directly that "the name 'order parameter' is unfortunate when applied to displacive transitions such as those studied here We prefer to call them 'displacive parameters'."

It should be reiterated (as in part III) that although the whole phenomenon occurring in tilting perovskites is usually described by the set of displacements of all atoms nevertheless it is quite sufficient for a complete description to know *only three magnitudes* η_α determined by equations (34), which is an indubitable merit of our theory. The name 'order parameter' may be kept for η_α remarking, however, that it differs from the traditional understanding of order parameter as 'zero-non-zero' magnitude. There are no principle obstacles for the description of the whole phenomenon occurring in crystals from the tilting region in these terms since all the experimentally measurable quantities could be calculated through η_α as is shown in Fig. 8.

Although there have been extensive investigations of numerous 'tilting' perovskites [see, for example: Hidaka & Ono (1977) for NaNiF_3 ; Ahtee, Ahtee, Glazer & Hewat (1976) and Ahtee, Glazer & Hewat (1978) for SrZrO_3 ; Ahtee, Kurki-Suonio, Vahvaselka, Hewat, Harada & Hirotsu (1980) for CsPbCl_3 ; Rousseau (1979), Bulou, Novet *et al.* (1980), and Ridou *et al.* (1981) for RbCaF_3 ; Bulou, Ridou *et al.* (1980) for KCaF_3 ; Hirotsu, Harada, Iizumi & Gesi (1974) for CsPbBr_3 ; Plesko, Kind & Roos (1978) for CsPbCl_3 and RbCdCl_3 ; and others], nevertheless for a successful development of the theory and for a clarification of our representations on the mechanism of immanent chaotization far wider and more thorough measurements of the main characteristics of perovskites over a wide temperature interval (the precise measurements of lattice parameters and the temperature dependence of the superstructure reflections are the most important) are needed, as are studies of the temperature evolution of diffuse scattering in the mono-Laue method.

We hope that the proposed theory will help the experimental investigations to be carried out more purposefully than before. At present there are very few experimental data on diffuse scattering, while the whole phenomenon deserves far more attention in many classes of crystal structures.

References

- AHTEE, A., AHTEE, M., GLAZER, A. M. & HEWAT, A. W. (1976). *Acta Cryst.* B32, 3243-3246.
- AHTEE, M., GLAZER, A. M. & HEWAT, A. W. (1978). *Acta Cryst.* B34, 752-758.
- AHTEE, M., GLAZER, A. M. & MEGAW, H. D. (1972). *Philos. Mag.* 26, 995-1014.
- AHTEE, M., KURKI-SUONIO, K., VAHVASELKA, A., HEWAT, A. W., HARADA, J. & HIROTSU, S. (1980). *Acta Cryst.* B36, 1023-1028.
- ALEXANDROV, K. S., ANISTRATOV, A. T., BESNOSIKOV, B. V. & FEDOSEEVA, N. V. (1981). *Phase Transitions in Crystals of Haloid Compounds*. Novosibirsk (USSR): Nauka.
- BOYER, L. L. & HARDY, J. R. (1981). *Phys. Rev. B*, 24, 2577-2591.
- BULOUE, A., NOUET, J., HEWAT, A. W. & SHAFER, F. J. (1980). *Ferroelectrics*, 25, 375-378.
- BULOUE, A., RIDOU, C., ROUSSEAU, M. & NOUET, J. (1980). *J. Phys. (Paris)*, 41, 87-96.
- CLARKE, R. (1977). *Phys. Rev. Lett.* 39, 1550-1553.
- COMES, R., DENOYER, F., DESCHAMPS, L. & LAMBERT, M. (1971). *Phys. Lett. A*, 34, 65-66.
- COMES, R., LAMBERT, M. & GUINIER, A. (1970). *Acta Cryst.* A26, 244-254.
- DENOYER, F., COMES, R. & LAMBERT, M. (1971). *Acta Cryst.* A27, 414-420.
- FESENKO, E. G. (1972). *A Family of Perovskites and the Ferroelectricity*. Moscow: Atomizdat.
- FLOCKEN, J. W., GUENTHER, R. A., HARDY, J. R. & BOYER, L. L. (1985). *Phys. Rev. B*, 31, 7252-7260.
- GLAZER, A. M. & MEGAW, H. D. (1972). *Philos. Mag.* 25, 1119-1135.
- HIDAKA, M., OHAMA, N., OKAZAKI, A., SAKASHITA, H. & YAMAKAWA, S. (1975). *Solid State Commun.* 16, 1121-1124.
- HIDAKA, M. & ONO, M. (1977). *J. Phys. Soc. Jpn*, 43, 258-263.
- HIROTSU, S., HARADA, J., IIZUMI, M. & GESI, K. (1974). *J. Phys. Soc. Jpn*, 37, 1393-1398.
- ISHIDA, K. & HONJO, G. (1973). *J. Phys. Soc. Jpn*, 34, 1279-1288.
- KASSAN-OGLY, F. A. & NAISH, V. E. (1986a). *Acta Cryst.* B42, 297-306.
- KASSAN-OGLY, F. A. & NAISH, V. E. (1986b). *Acta Cryst.* B42, 307-313.
- KASSAN-OGLY, F. A. & NAISH, V. E. (1986c). *Acta Cryst.* B42, 314-325.
- LINES, M. E. & GLASS, A. M. (1977). *Principles and Application of Ferroelectrics and Related Materials*. Oxford: Clarendon Press.
- MEGAW, H. D. (1973). *Crystal Structures. A Working Approach*. Philadelphia: Saunders.
- MØLLER, C. K. (1959). *Mat. Fys. Medd. K. Dan. Vidensk. Selsk.* 32, No. 2.
- PLESKO, S., KIND, R. & ROOS, J. (1978). *J. Phys. Soc. Jpn*, 45, 553-557.
- RIDOU, C., ROUSSEAU, M. & BOUILLLOT, J. (1981). *Ferroelectrics*, 36, 463-465.
- ROUSSEAU, M. (1979). *J. Phys. (Paris) Lett.* 40, L439-L443.
- ROUSSEAU, M., GESLAND, J. Y., JUILLARD, J., NOUET, J., ZAREMBOWITZ, J. & ZAREMBOWITZ, A. (1975). *Phys. Rev. B*, 12, 1579-1590.
- STIRLING, W. G. (1972). *J. Phys. C*, 5, 2711-2730.