# The Immanent Chaotization of Crystal Structures and the Resulting Diffuse Scattering. II. Crystallochemical Conditions of Perovskite Chaotization

By F. A. Kassan-Ogly and V. E. Naish

*Institute of Metal Physics of the Ural Scientific Centre, ul. S. Kovalevskoi 18, GSP-170, Sverdlovsk, USSR*

## Abstract

In part I of this series the problem of immanent chaotization of crystal structures was described in simple models and the mathematical approach to the calculation of diffuse scattering (DS) was described. It was formulated that the loose packing of most real crystals appears to be the universal microscopical cause of DS. In the present paper the microscopical nature of chaotization is analysed and a quantitative description of the structural loose packing is given for cubic perovskites; these are particularly convenient examples because the most vivid and thorough experimental data on DS were obtained for such crystals: $KNbO_3$, $BaTiO_3$, $NaNbO_3$, $KMnF_3$.

## Introduction

The crystals with which we begin our study of this important problem belong to the class of ionic compounds and therefore it is necessary to discuss the question of *ionic radii*. We shall take the numerical values for the ionic radii for ions of different valency and their dependence upon coordination number from tables obtained by Shannon (1976), where a vast number of experimental and theoretical data have been gathered and analysed. Among numerous sources on the values of ionic radii Shannon's tables are beyond doubt the best grounded and most reliable. However, as will be seen later, even these tables would not serve as the highest authority and in some details they appear to be unsatisfactory.

We shall show that the DS obtained in a mono-Laue experiment could be a valuable and indispensable source of data for obtaining ionic radii. In all considerations concerning X-ray scattering we naturally deal with the system of so-called 'classical' ionic radii (Goldschmidt's radii) leaving aside the 'physical' radii, the whole system of which has also been given by Shannon (1976).

The crystallochemical analysis of crystals with perovskite structure has been carried out by various authors but, in our opinion, has not been completed and we pay our attention once again to this problem especially in connection with the DS description in different perovskites.

## Loose-packing types of perovskite structure

The crystal structure of perovskites $ABX_3$ is shown in Fig. 1 by two *a* and *b* choices of the unit cell. For the sake of clarity ions are not drawn to scale. In fact, they contact each other according to the very definition of ionic radii. If all ions contact each other and there are no gaps between them, such a perovskite may be called an *ideal* or close-packed perovskite. In such a crystal all atoms are mutually squeezed, have no degrees of freedom and DS is entirely absent. However there is no such perovskite since there are no ionic radii $R_A$, $R_B$ and $R_X$ with such ideal ratios. Depending on the specific values of the ionic radii in real perovskite crystals gaps between some ions always exist and hence there is some freedom for displacements and oscillations of the ions. It should be reiterated that the usual thermal vibrations owing to the small thermal gaps which persist even in close-packed structures and lead to Debye–Waller factors for Bragg reflections and to diffuse background is not taken into account here. According to the different values of $R_A$, $R_B$ and $R_X$ various types of gaps between ions may occur or, in other words, there are different types of loose packing of the perovskite structure. Let us consider all these types in turn.

Let the lattice parameter *a* or the size of the perovskite cubic unit cell be formed by the contacting of ions *A* and *X*, then some possibilities for motion of ions *B* and *X* are left. In the other real perovskite with other values of the ionic radii the lattice parameter may be formed by the contacting of *B* and *X* ions with possibilities for the motion of ions *A* and *X*, *etc.*
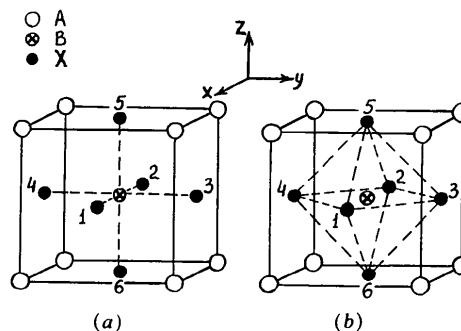


Fig. 1. Unit cell of cubic perovskite.

It is convenient to visualize the formation process of the perovskite structure as the approaching of ions which initially are far from one another. In answering the question as to which pair of ions has to contact first, one obtains a priori five possibilities: A-X, B-X, X-X, A-A and A-B (B ions are unable to contact since they are always separated by an X ion).

Let us call these types (I)-(V). From simple geometrical considerations it is easy to write down the expression for the lattice parameter $a$ in all these types:

$$\text{(I)} \quad A\text{-}X \quad a_\mathrm{I} = a_{AX} = \sqrt{2}(R_A + R_X)$$

$$\text{(II)} \quad B\text{-}X \quad a_\mathrm{II} = a_{BX} = 2(R_B + R_X)$$

$$\text{(III)} \quad X\text{-}X \quad a_\mathrm{III} = a_{XX} = 2\sqrt{2}R_X \qquad (1)$$

$$\text{(IV)} \quad A\text{-}A \quad a_\mathrm{IV} = a_{AA} = 2R_A$$

$$\text{(V)} \quad A\text{-}B \quad a_\mathrm{V} = a_{AB} = \frac{2}{\sqrt{3}}(R_A + R_B).$$

For the realization of type (I) $a_\mathrm{I}$ has to be the greatest among the rest, $a_i$. One obtains a system of four inequalities:

$$\sqrt{2}(R_A + R_X) > 2(R_B + R_X),$$

$$\sqrt{2}(R_A + R_X) > 2R_A,$$

$$\sqrt{2}(R_A + R_X) > 2\sqrt{2}R_X, \qquad (2)$$

$$\sqrt{2}(R_A + R_X) > \frac{2}{\sqrt{3}}(R_A + R_B).$$

Similar systems yield the realization of all the remaining types. It is convenient henceforth to divide all the inequalities by $R_X$ and to use only the relative radii $r_A$ and $r_B$. Then instead of (2) one obtains:

$$1 < r_A < \sqrt{2} + 1 = 1$$

$$r_A > \sqrt{2}r_B + (\sqrt{2} - 1) \qquad (3)$$

$$r_A > (\sqrt{6} + 2)r_B - (\sqrt{6} + 3)$$

and similar systems of inequalities for the remaining types (II)-(V). Each inequality in (3) generates some straight line in two-dimensional space $(r_A, r_B)$ determining some boundary between the neighbouring types (I)-(V).

Fig. 2 shows the diagram of perovskite types in two-dimensional space of relative radii $r_A$ and $r_B$. It shows the five regions of all five contact types (1). The boundaries in Fig. 2 are determined by the relations:

$$(a) \quad r_B = \sqrt{2} - 1 \qquad\qquad (b) \quad r_A = 1$$

$$(c) \quad r_A = \sqrt{2}r_B + (\sqrt{2} - 1) \qquad (d) \quad r_A = \sqrt{2} + 1$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (4)$$

$$(e) \quad r_A = r_B + 1 \qquad\qquad (f) \quad r_A = \frac{\sqrt{3} + 1}{2}r_B$$

$$(g) \quad r_A = (\sqrt{3} - 1)r_B + \sqrt{3}.$$

The points A, B and C correspond to three special ratios among $R_A$, $R_B$ and $R_X$ at which the simultaneous contacting of all nearest ions takes place, the gaps and degrees of freedom being completely absent. These are the close-packed perovskites.

In the derivation of loose-packing types in Fig. 2 only the geometry of the perovskite structure has been used and the relations of $R_A$, $R_B$ and $R_X$ have been assumed to be arbitrary (each had to be positive and non-zero). If we now take the actual crystals $ABX_3$ with perovskite structure, take $R_A$, $R_B$ and $R_X$ values for each from Shannon's tables (of course, the valency and coordination numbers $^{XII}A$, $^{VI}B$, $^{VI}X$ are also taken into account), calculate $r_A$ and $r_B$ for each crystal, and place the point obtained onto the diagram in Fig. 2, we obtain the curious picture shown in Fig. 2, comprising a system of points crowded around the point A.

This means that most of the diagram in Fig. 2 possesses only geometric, but not physical, sense since such ionic radii do not exist in nature. Therefore, henceforth one has to keep only the actual region of the diagram limited approximately by $r_B = 1$ and $r_A = 1\cdot 5$. As a consequence only one variant of a close-packed perovskite structure corresponding to point A ($r_A = 1$, $r_B = \sqrt{2} - 1$) and only three types of loose packing remain (the rest will not be regarded owing to their absence).

### Perovskite chaotization types

The types (I)-(III) are distinguished by different abilities of the ions to move and by different abilities to break spontaneously the ideal perovskite structure, i.e. its chaotization. Thus we have come to the main theme of the paper: the loose packing of a crystal structure (three types of loose packing in real perovskites), i.e. the existence of gaps between ions appears to be the cause of immanent chaotization which is the
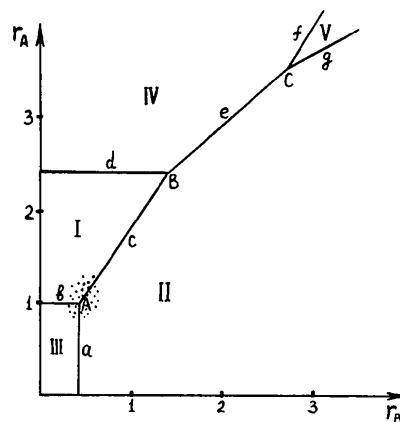


Fig. 2. Diagram of five types of perovskite loose packing, obtained in a geometrical analysis of the perovskite structure. The actual part of the diagram is shown by dots.

*cause of the instability of the ion positions, their oscillations at high temperatures and their static displacements at low temperatures.* Later on we shall see that there exist one or several critical temperatures at which oscillations begin to freeze and transform into static displacements. In other words, the perovskite undergoes one or several *structural phase transitions* from the cubic structure to the structures with lower symmetry.

Fig. 3 shows the real ionic radii and gaps between them for three types of loose packing, (I), (II) and (III). For comparison the ideal close-packed perovskite (type $O$) corresponding to point $A$ is also shown in Fig. 3. The left side of Fig. 3 depicts a face of a perovskite cube, while the right side depicts the middle section of the cube, parallel to its face.

Let us consider in detail type (I) where ions $A$ and $X$ contact each other. One can see in Fig. 3 that ion $A$ is tightly squeezed by $X$ ions in every plane ($x$, $y$ and $z$); it possesses no degrees of freedom. Ion $X$ has only one degree of freedom able to move normally to the face in which it is placed. Ion $B$ has all three degrees of freedom. Let ion $X$ with number 1 being in the $xy$ plane slightly shift upwards along the $z$ axis (see Fig. 4). Its movements are directed towards the nearest cation $B$ with number 2. Because of the Coulomb interaction energy minimum of the nearest cations and anions this $B$ ion has to shift towards the initially shifted $X$ ion. For the same reason cation 3 has to shift upwards, cation 4 downwards and so on. The most possible shifts are limited by the value of the initial gap between these ions. If the perovskite structure is still stable (temperature $T$ above the structural phase transition $T_c$) then the ion movements are just of the oscillation type owing to the restoring force with the same Coulomb nature. These are the optical

oscillations corresponding to a particular $z$ mode. When the temperature decreases below $T_c$ the $z$ mode freezes and the crystal naturally loses the cubic structure. It should be noted that in Fig. 4 the ion chain as a whole has not displaced in any direction, while the subchain of $X$ ions and the subchain of $B$ ions have displaced upwards and downwards accordingly. The displacements of subchains are inversely proportional to the ionic masses and the centre of mass of the whole chain has not shifted.

In the movements considered above only $X$ ions from $xy$ faces were shifted and only $z$ movements of $B$ ions were taken into account. It is clear that similar chains could also be formed in the $x$ and $y$ directions. In paper III it will be strictly proved that the coincidence of the structural phase transition temperatures $T_c^x$, $T_c^y$ and $T_c^z$ is energetically disadvantageous so that the freezing of three families of chains will take place one by one. Above all three critical temperatures there exist optical oscillations along all three directions.

As far as the form of movement peculiar to the loose-packing type I involves anion shifts along the chain directions we shall call this process *shifting*. Fig. 4 shows the oscillation (or displacement) mode with $k = 0$, *i.e.* with conservation of the cell. A similar process with $k \neq 0$, *i.e.* with doubling of the translational period in the plane perpendicular to the chain direction, is also possible; we shall call this *antishifting*. At $T > T_c^i$ we shall call the corresponding process *parashifting*. It is essential that extended one-dimensional objects appear in the consideration and hence the problem has been reduced to a two-dimensional Ising problem [see Kassan-Ogly & Naish (1986)].

Let us also consider in detail type (II) where $B$ and $X$ ions contact each other. One can see in Fig. 3 that ion $B$ is tightly squeezed by $X$ ions in all directions and does not possess any degree of freedom. The $X$ ion located in the $xy$ face cannot move along the $z$ axis but possesses two degrees of freedom in the $x$ and $y$ directions. An ion has three degrees of freedom. Let the $X$ ion with number 1 (see Fig. 5a) slightly shift in the $+x$ direction. Again from
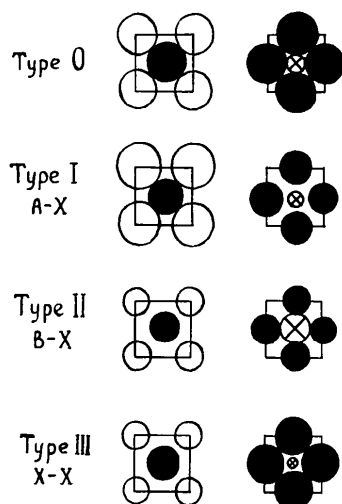


Fig. 3. Three actual types of perovskite loose packing. The contacts of ions and gaps between them are shown. Left column: the faces of the perovskite unit cell. Right column: the middle section of the unit cell.
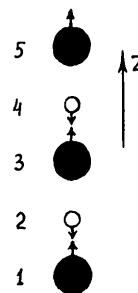


Fig. 4. Electrostatic mechanisms of spontaneous chaotization in perovskites of type (I). The origin of shifting.

Coulomb energy considerations it is clear that ion $X$ with number 2 has to move in the $+y$ direction (Fig. 5$b$). For the same reason ion $X$ with number 3 has to shift in the $-x$ direction and so on. As a result one obtains a completely determined system of $X$-ion shifts in the $xy$ plane (Fig. 5$c$). (If one takes into consideration $A$-ion motion one obtains the system of atomic shifts over the whole crystal, but such movements are energetically much more disadvantageous.) Hence we shall not take the movements of $A$ ions into consideration at all. If the initial $X$ ion shifts in the $+y$ direction so one will obtain the system of shifts identical to Fig. 5($c$), but with another crystallographically equivalent orientation. It is also seen that in each perovskite cell 'circular' motion of $X$ ions 1, 2, 3 and 4 in the $xy$ plane takes place (Fig. 1$b$) while atoms 5 and 6 remain motionless. As a result the concerted 'rotation' of all octahedra in the $xy$ plane occurs (with engagement as between gears). It should be noted that such motion is not a strict rotation of octahedra since they change their shape in the $xy$ plane. Such motion appears to be a certain vibrational mode of the perovskite lattice described in the literature and called tilting [see, for example, Alexandrov, Anistratov, Besnosikov & Fedoseeva (1981) or Megaw (1973)]. It is clear that besides the $z$ tilting mentioned above $x$ and $y$ tilting may take place as well. In $z$ tilting the correlation between the rotations of octahedra from neighbouring layers is absent at first sight. If the interaction between layers were taken into account so the same (tilting) or opposite (antitilting) rotation would be profitable. At high temperatures simultaneous but independent rotation in neighbouring layers takes place which will be called henceforth paratilting. After cooling below $T_c^1$ one of the tiltings (or antitiltings) freezes and one obtains the first structural phase transition. Later on it will be shown that temperatures $T_c^x$, $T_c^y$, $T_c^z$ are different; their coincidence is energetically disadvantageous. Thus type (II) is characterized by the existence of two-dimensional extended objects including only $X$ ions and therefore the problem is reduced to a one-dimensional Ising problem [see Kassan-Ogly & Naish (1986)].

Finally let us consider type (III) where $X$ ions contact each other. One can see in Fig. 3 that $X$ ions are squeezed completely and $A$ and $B$ ions have three degrees of freedom. There is no such simple mechan-
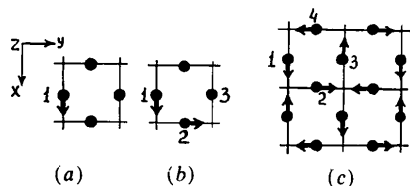
ism for the formation of extended objects and vibrations of $A$ and $B$ ions are not concerted. As was shown in paper I such a case is not interesting since it leads only to the diffuse background while the existence of chains in type (I) and planes in type (II) leads to shining relplanes and relrods. However, even in type (III) the extended objects are also possible but the mechanism of their formation is far more complicated. This question will be considered elsewhere.

## Stability of the perovskite structure

Let us return to type (I). Ion $B$ is free to move within its octahedron interstice and the value of its amplitude is determined by the size of the interstice and its radius $R_B$. If $R_B$ is very small ion $B$ can pass through three $X$ ions in the [111] direction and leave the octahedron interstice. This is the first possibility to be realized with decreasing $R_B$. One can see from Fig. 6($a$) and ($b$) that it can occur at $(R_B + R_X) < a/\sqrt{6}$. The inverse inequality determines the boundary condition of stability of the perovskite structure in type (I). Making use of the relation $a = \sqrt{2}(R_A + R_X)$ for type I [see (1)] one can obtain the stability condition of type (I) in the form:

$$\text{type (I):} \quad r_A < \sqrt{3}r_B + (\sqrt{3} - 1). \qquad (5)$$

Let us similarly consider type (II). The instability of ion $X$ in paratilting occurs when the $X$ ion begins to move freely between $A$ ions (see Fig. 6$c$). This occurs when $2(R_A + R_X) < a$. Using the relation (1) $a = 2(R_B + R_X)$ for type (II) one obtains the stability condition for type (II):

$$\text{type (II):} \quad r_A > r_B. \qquad (6)$$

Quite similarly one can obtain the stability condition for the motion of $A$ and $B$ ions in type (III):

$$\text{type (III):} \quad r_A > \sqrt{2} - 1 \quad \text{and} \quad r_B > \frac{2}{\sqrt{3}} - 1. \qquad (7)$$

The diagram of the perovskite loose-packing types in Fig. 2($a$) should be depicted in a new way: (1) it is sufficient to regard only the actual part of the diagram with $r_A \lesssim 1.5$ and $r_B \lesssim 1$; (2) let us restrict



(a)        (b)        (c)

Fig. 5. Electrostatic mechanism of spontaneous chaotization in perovskites of type (II). The origin of tilting.
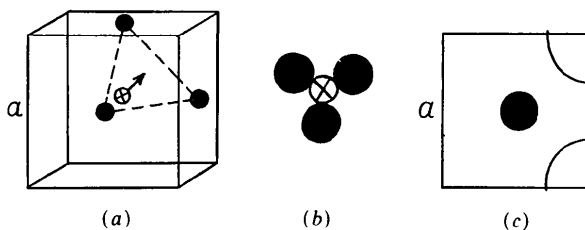


(a)        (b)        (c)

Fig. 6. Appearance of instability in the cubic perovskite structure. ($a$) and ($b$) for perovskites of type (I). ($c$) for perovskites of type (II).

the regions of types (I), (II) and (III) by the stability boundaries (5–7); the resulting diagram is shown in Fig. 7(a), which also shows the types of motion inherent in each region.

It should be noted that similar considerations for the remaining types (IV) and (V) give additional boundaries so that the stability diagram of cubic perovskite has the shape of an enclosed polygon (Fig. 7b). Some considerations concerning the influence of the ionic-radii values on phase transitions in perovskites are given by Rousseau, Gesland, Julliard, Nouet, Zarembowitch & Zarembowitch (1975) and by Boyer & Hardy (1981).

## Other structural types of $ABX_3$ compounds

Beyond the boundaries (and even within, in part) of stability of cubic perovskite the other $ABX_3$ structural types may be placed on the plane $(r_A, r_B)$. The systematic study of all $ABX_3$ types is rather a complicated independent problem and it is beyond the scope of the present paper. However, it should be noted that other $ABX_3$ structural types differ from the cubic one by the set of distortions which are not small in general. Among these types one should consider, of course, calcite, aragonite, ilmenite, the $LiNbO_3$ structure, the $CsNiCl_3$ structure, etc. Moreover, the coordinate axes correspond to $r_A = 0$ or $r_B = 0$, i.e. to the structural types of binary compounds the $Cu_3Au$ structure or the $ReO_3$ structure, for example. For each type of structure a similar geometric analysis could be carried out and the types of loose packing, the regions of stability and the corresponding motions could be found. In one of the following papers we shall consider such questions in some binary compounds.

## Realization of perovskite types and diffuse scattering

Fig. 8 shows the actual part of the whole diagram of cubic perovskite and various experimentally studied

crystals are denoted as points. It can be seen that real perovskites are of all three types.

It is natural to expect that for all perovskites of region (I) (shifting) in the mono-Laue experiment the specific families of streaks would be observed on the X-ray pattern that corresponds to the *shining planes* in relspace. The origin of these relplanes is connected with type (I) loose packing, *i.e.* with the existence of one-dimensional rigid movable objects (chains) as had been shown in paper I. As for the perovskites of region (II) (tilting) specific families of spots (diffuse but not the Bragg ones) corresponding to *shining relrods* are expected to be present on the X-ray pattern in the mono-Laue method. The origin of these relrods is connected with the existence of loose packing of type (II), *i.e.* with the existence of two-dimensional movable rigid objects.

At present the experimental data on diffuse scattering in the mono-Laue method are available for $KNbO_3$ (Comes, Lambert & Guinier, 1970), for $BaTiO_3$ (Harada & Honjo, 1967), for $KMnF_3$ (Comes, Denoyer, Deschamps & Lambert, 1971), and for $NaNbO_3$ [Denoyer, Comes & Lambert (1970, 1971), and also Ishida & Honjo (1973)]. The X-ray patterns for the first three crystals convincingly correspond to their positions on the perovskite diagram and to the



Fig. 7. Diagram of perovskite types and stability boundaries. (a) Actual part of diagram. (b) Complete diagram, obtained in geometrical analysis.



Fig. 8. Distribution of real cubic perovskites over the diagram of loose-packing types, based on Shannon's values of ionic radii (Å).

theoretical predictions mentioned above. NaNbO$_3$ is the sole and unique example in which tilting, anti-tilting and perhaps shifting simultaneously coexist. This special case of coexistence will be considered elsewhere.

The detailed quantitative description of diffuse scattering in various perovskite types, the temperature evolution of DS, and the spontaneous structural phase transitions in such crystals will be given in papers III and IV for the most typical examples (KNbO$_3$ shifting; KMnF$_3$ tilting), while only the classification of the possible types and the geometrical analysis of their loose packing is the main goal of the present paper.

## Tolerance factor

In the literature, in the discussion of the stability region for the perovskite structure the concept of tolerance factor is often used, first introduced by Goldschmidt (1926).

$$\tau = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)} = \frac{r_A + 1}{\sqrt{2}(r_B + 1)}. \qquad (8)$$

For the ideal perovskite structure $\tau = 1$, while the deviations from number 1 allowed by various authors do not coincide. Goldschmidt himself expressed the stability of the perovskite structure by the empirical relation $0.8 < \tau < 1$; other authors allow a small excess over unity. One can see from our relations (4) that $\tau = 1$ corresponds to the straight line $(c)$ on the diagram (Fig. 7). Away from $(c)$ the tolerance factor changes and accepts the greatest deviations from unity on the boundaries of stability in types (I) and (II). Some boundary values of the tolerance factor are shown in Figs. 7 and 8.

Thus the question of the theoretically allowed values of the tolerance factor is solved: for shifting perovskites $1 < \tau < \sqrt{3/2}$, for tilting perovskites $1/\sqrt{2} < \tau < 1$, for perovskites from region (III) $1/\sqrt{2} < \tau < \sqrt{3/2}$. The most likely interval for the tolerance factor in perovskites is $0.707 \lesssim \tau \lesssim 1.225$. According to Shannon's tables all real perovskites cover approximately the same interval of $\tau$, as shown in Fig. 8.

## Remarks on Shannon's ionic radii

The so-called 'classical' radii in Shannon's tables have been determined by X-ray experimental data on interatomic distances and on the essential assumption of nearest-ion contacts. This assumption is valid for those compounds or for those ions in a crystal where such contacts take place in reality, while we have already seen that some contacts are often absent and in such situations the ionic radii turn out to be exaggerated. This mistake appears to be the greatest for measurements of lattice parameters in a high-temperature cubic phase. As we shall see later on (in

paper III) the structural phase transitions (one or several) occurring as temperature decreases involve sequential vanishing of gaps between ions. In the lowest-temperature phase there are no gaps at all and the contacts of ions take place everywhere. Therefore, the procedure for the experimental determination of ionic radii turns out to be correct only for the lowest-temperature measurements ($T < T_c^i$). At these temperatures perovskite has no cubic structure and one should measure several lattice parameters, not a single one as in the cubic phase. Strictly speaking, *the ionic radii have to be calculated with the help of X-ray measurements in the low-temperature phase where DS vanishes completely.* In all other cases non-controlled exaggeration of ionic radii takes place.

Now the cause of the exaggeration has been revealed let us analyse some examples in which the values of the radii are markedly exaggerated. Let us consider the question of the O$^{2-}$ ionic radius with coordination number 6 (as in cubic perovskites). Shannon (1976) gives the value 1·40 Å in this case. Considering perovskites YAlO$_3$ and LaAlO$_3$ from region (III) belonging to the $X$-$X$ type one ought to use the formula $a_{III} = a_{XX} = 2\sqrt{2}R_X$ for the cubic lattice parameter $a$ which is equal to 3·96 Å. The experimental values taken from a review table by Fesenko (1972) are 3·67 Å for YAlO$_3$ and 3·78 Å for LaAlO$_3$, *i.e.* in both cases they are less than the calculated value. When the oxygen radius is equal to 1·40 Å the agreement is impossible. In these cases agreement would take place if the oxygen radius were taken to be 1·30 or 1·33 Å accordingly. Taking into account the fact that these two perovskites are the most close-packed in comparison with the remainder it can be said that these values of the oxygen radius are nearer to the real value than are those obtained from measurements on loose-packed perovskites of types (I) and (II).

Another example is BaTiO$_3$. According to Shannon's ionic radii BaTiO$_3$ belongs to the $A$-$X$ type and its lattice parameter in the cubic phase should be $a_1 = a_{AX} = \sqrt{2}(R_A + R_X) \approx 4.24$ Å. The experimental value is again far less, 3·97 Å. This means that either the $R(O^{2-})$ value or the $R(Ba^{2+})$ value, or both, were exaggerated.

There is only one answer in this situation: the correct values of the static ionic radii should be determined from the low-temperature measurements or *in those phases where DS is completely absent.* Such measurements are unfortunately almost always absent in the literature, whereas the calculations based on measurements in the cubic phase possessing DS are wrong. The whole system of Shannon's radii may be revised in the way proposed.

There exists one more reason for the exaggeration of the ionic radii – the dynamic effects. The ions participating in oscillations are disposed at greater distances from one another than are motionless ions. In

this case the radii may be regarded as effective 'dynamical' radii which are greater than genuine static radii. In Bragg measurements we deal with just the dynamical radii.

The corrections of the ionic radii beyond doubt will somehow redistribute the arrangement of crystals shown in Fig. 8. Some of the crystals would transfer from one region to another and would belong to another perovskite type and one can expect another specific DS picture in them.

## Analysis of structural distortions

At present when rather few experiments on DS have been carried out in the mono-Laue method the belonging of a certain compound to one type or another could be revealed without the help of the DS picture but with the help of precise X-ray measurements of Bragg scattering and its changes at structural phase transitions. If, for example, the X-ray pattern decoding below $T_c$ shows tilted octahedra, then we are dealing with the perovskite from region (II) (tilting). In other words one can determine the 'frozen' types of movement according to the data on Bragg diffraction in low-temperature low-symmetry phases and thus classify the type of perovskite.

In the description of the loose packing of the perovskite structure and DS patterns the concept of rigid extended objects (chains or planes) plays, of course, the fundamental role. Based on results of paper I one can say that the experimental evidence for their existence is given by the DS patterns obtained in some perovskites. At the same time two possibilities may be allowed. Either these objects undergo dynamical movements or they are essentially static displacements and distributed at random over the crystal. To answer this natural question without ambiguity let us consider, for example, the highest temperature phase of $BaTiO_3$. It is cubic above $T_c$ and tetragonal below $T_c$. Independent of the direction in which the subchains of Ti and O atoms in any unit cell are shifted, downwards or upwards, a unit cell is obliged to become tetragonal at static displacements. Hence it follows that below $T_c$ static displacements of chains take place in $BaTiO_3$. From the fact that above $T_c$ the crystal is cubic it follows immediately that there are no static displacements in the cubic phase. Only the equal optical dynamic oscillations of these chains along the $x$, $y$ and $z$ directions take place – just chains not atoms since a peculiar DS pattern with shining planes in relspace is observed in the cubic phase, whereas the independent vibrations of separate atoms would give a smooth continuous background. Thus the whole picture of the phenomenon occurring in $BaTiO_3$ can be elucidated from an analysis of diffuse scattering and lattice distortions obtained from Bragg diffraction data.

The rigorous quantitative description of structural distortions in perovskites of different types at spontaneously appearing shifting or tilting appears to be the essential part of the general problem – the quantitative description of the temperature evolution of the crystal structure looseness and the corresponding phase transitions, and also the quantitative description of the temperature dependence of the diffuse scattering in such crystals over the whole temperature region. Such a quantitative theory will be set forth in papers III and IV for the examples of two main cubic perovskite types (I) and (II). It will also be shown that such a theory gives an adequate description (both qualitative and quantitative) of all the experimental data in these compounds available at present.

We must emphasize a very important conclusion. Despite the fact that the group-theoretical analysis gives many possible modes in perovskites, and certainly 'shifting' and 'tilting' ones among them, nevertheless our analysis based on the sizes of ionic radii gives that in the perovskites from the 'shifting' region the 'shifting' mode is favourable while the 'tilting' mode is 'forbidden', and vice versa for the perovskites from the 'tilting' region. This is the reason (and it is by no means accidental) why in some perovskites only the 'shifting' modes and in others only the 'tilting' modes are 'soft' ones.

We believe that the analysis of a loose packing based on the radii sizes will help investigators to predict or to find out by experiment the 'soft' modes in other types of crystals.

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