

Derivation and Discussion of Crystal Structures of Compounds ABX_3 and A_2BX_6

Part I. Derivation of the Structures

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In this series of papers the crystal structures of compounds with composition ABX_3 and A_2BX_6 are derived from a basic lattice, mainly using qualitative ionic bonding rules (Part I) (A represents a large cation that can replace an anion, B is a small interstitial cation, X is halogen ion). In Part II a method will be outlined for selecting the appropriate structure for a particular compound. This method is tested on the experimental structure data of the ABX_3 halides in Part II, and applied to compounds A_2BX_6 , $A_2BK_{6-p}Y_p$ and $A_2BX_{6-p-p'}Y_pZ_{p'}$ in Parts III, IV and V, respectively (X = halogen; Y, Z = halogen, O, OH, H_2O , N or an anion vacancy).

In the present paper (Part I), we start with the derivation of the ideal structures (i.e., for A and X ions of equal diameter), for hypothetical compounds AX_3 . It is shown that, if A - A contacts are not allowed in a stacking of triangular nets (viz., in "close-packed" layers), each layer must have the composition AX_3 and the same type of order. This order can be one of two simple types (" T " and " R ") or any combination of these. From these AX_3 structures the ABX_3 and A_2BX_6 structures are derived. On the basis of mainly simple electrostatic considerations, structures with anion surroundings that are most unlikely are excluded. Use is made of the representation of anion surroundings by space-filling polyhedra (SFP). Finally, the deviations from the ideal ABX_3 and A_2BX_6 structures, resulting from variations in size of the A , B and X ions, are considered.

I.1. Introduction

In our laboratory a broad investigation is in progress into the possibility of predicting or deriving—fairly roughly—a crystal structure for any given compound $^aA_m^bB_n^xX_p$, where a , b and x represent the coordinations of the cations A and B and anions X , respectively. Having designed a structure, a compound (or compounds) must be selected that may show this crystal structure. When attempts to prepare these compounds succeed, the structure may prove to be different from the predicted one. This may mean that either we have chosen the wrong substance or that the compound may assume the predicted structure at a different temperature and/or applied pressure or that our model is wrong. Alternately, for all likely compounds another structure may be more stable, even if slightly so. The calculation of small differences in stability will remain difficult for some time to come, in

spite of the recent improvement of calculating facilities. If preparation of the selected compound fails, this may be due to the wrong choice of method, i.e., to our lack of industry, preparative skill or technical possibilities, or to the formation of other stable compounds, which together have the same overall composition.

It is, therefore, difficult to know whether a certain structure will exist or not, and equally difficult to decide when to stop our attempts at preparing a particular compound. For these reasons it would be desirable to make the prediction of structures in a systematic way. This would also be of great help in indexing an X-ray powder diagram, since a rough structure prediction usually yields the correct space group and the rough cell dimensions and atomic parameters. As an example of such an approach we selected a class of compounds of composition A_2BX_6 , on which little structural research has been done

and which have structures closely related to a class of compounds of composition ABX_3 , which have been the subject of extensive research.

In the present paper certain assumptions will be used, a/o the concept of a "basic lattice," some of Pauling's rules, and one of those used by Gorter (1). The greater part of these rules are derived from a simple ionic model, which has been shown to explain a great many structures of compounds $A_mB_nX_p$ (1, 2). Other conditions will be imposed only in order to delimit the field of investigation.

The AX_3 structures formed by the positions of A and X ions in compounds ABX_3 and A_2BX_6 are derived first. These AX_3 structures need not (and do not) exist for ionic compounds, but they do exist in certain alloys. The method by which they are derived resembles that used for Beck for the derivation of structures for alloys AB_3 (3). Next, it has to be examined which of the interstices can be completely or partly filled by B ions. Finally, the deviations from these "ideal" structures that result from a variation of the radii of A , B and X are derived.

The structures derived in the present paper will be compared with the structures of the ABX_3 halides in Part II. In the second paper (Part II), also semiempirical rules will be derived for making the selection of a structure for a particular compound possible. These rules will be checked against the vast number of experimental structural data on ABX_3 halides. In the third, fourth and fifth papers of this series, the method developed in Part I and tested in Part II will be applied to compounds A_2BX_6 , $A_2BX_{6-p'}Y_{p'}$ and $A_2BX_{6-p'-p''}Y_{p'}Z_{p''}$, respectively ($X = \text{halogen}$; $Y, Z = \text{halogen, O, OH, H}_2\text{O, N, anion vacancy}$). Reviews concerning the properties of halides and their preparation (4-7) which were published recently, have been of great use to this investigation.

1.2. Derivation of Ideal Structures

It is our contention that most structures of inorganic compounds that may be described as ionic can be derived by placing that ion type (cations or anions) of which a larger proportion is present on a "basic" lattice. Except in the so-called antistructures these ions are the anions. The ions of opposite charge are then inserted on part of the interstitial positions of this basic lattice. These ions will also form a basic lattice, as far as is possible for the given stoichiometry.

We shall arbitrarily define the basic lattice as follows: Basic lattices are composed of triangular nets and would have a "packing density" of $> 50\%$, if the lattice points were occupied by spheres of equal size that are in contact with each other. Basic lattices are: face-centred cubic (fcc), hexagonal "close-packed" (hcp)¹, "MoSi₂"², body-centred cubic (bcc), simple cubic (sc), simple hexagonal (sh), etc. The arguments for choosing this definition can be related to the problem of finding the most likely distributions of charges in space that possess translation symmetry. Since the ions have a more or less variable size, the potential energy will reach a minimum at a certain distance between cations and anions.

If the ions do not fit exactly into the interstices of a certain basic lattice a structure with lower potential energy may be attained by deforming the structure either with or without complete preservation of the symmetry, or by choosing a different basic lattice. For an example of such a derivation, see Section I.3.

In addition to the above condition that charges of the same sign have to form a basic lattice, each charge has to be surrounded by equally spaced-out charges of opposite sign, i.e., isonomously. Requirements of isonomy as well as stoichiometry may cause the basic lattices to be only partly filled.

The above working rules have to be supplemented as follows: (a) Polarization may cause the surrounding of large and polarizable ions to be less isonomous (1) and may cause a too low "packing density" of the basic lattice of the interstitial ions. (b) Large cations may replace part of the anions in a basic lattice in an ordered manner, if their size makes them fit there.

When experimentally determined structures do not obey the rules discussed above, this must be traceable to other effects like cation-cation or anion-anion bonding, lone electron pairs, etc. These effects must be treated starting from another more refined model. In the present paper we have refrained from placing our ideas against the background of the work of other investigators. An historical introduction and a more

¹ Together with the c (fcc) and the h (hcp) "close-packed" lattices mixed c - h stackings can be mentioned: these are considered separately (Section I.3).

² By "MoSi₂" those lattices are meant in which each point has the same coordination such as the lattices formed by metal and silicon ions together in MoSi₂, CrSi₂ and TiSi₂(8).

extensive discussion of the rules will be given elsewhere (9).

For the derivation of the ideal structures for compositions ABX_3 and A_2BX_6 , the following conditions are imposed only in order to delimit the subject:

(a) The limitation of the stoichiometry $A_mB_nX_p$ to ABX_3 and A_2BX_6 we made already at the outset.

(b) The large cations (A) together with the anions (X) form a three-dimensional lattice with overall composition AX_3 . These lattices consist of triangular nets, stacked in such a way that each lattice point has twelve nearest neighbors at equal distances: these are the well-known "close-packed" lattices.³ The choice of the close-packed lattices is also influenced by the fact that in most other lattices mentioned above no interstices with a regular surrounding of lattice points are available for the B ions.

(c) The A ions, i.e., the large ions present in smaller number, shall not be adjacent to each other. This condition results from any difference in electronegativity between A and X and is also valid for certain classes of alloys.

I.2.1. Derivation of AX_3 Structures

The close-packed lattices are composed of triangular nets lying at a certain fixed distance from each other. For deriving structures of composition AX_3 we start by examining which of the ordered arrangements of A and X ions in a triangular net (Fig. I.1) of composition AX_3 , satisfy the above condition (c). With these layers, structures of composition AX_3 can be built, if restriction (c) is taken into account.

A systematic way to find all types of order of A and X ions in a triangular net is to determine all two-dimensional unit cells that may occur in such a net. Restrictions have to be imposed in order to prevent the number of unit cells from becoming infinite. The conventions concerning lattice description impose a restriction relating to the shape of the two-dimensional unit cell. The angle between the two translation vectors has to satisfy the condition $90^\circ \leq \beta \leq 120^\circ$ (11). A unit cell that would not fulfil this condition can be transformed into a cell with the same area, the angle of which does satisfy this condition. Now a unit cell may

³ We prefer to avoid the term "close-packing," since it is often interpreted too literally. The large ions that constitute a close-packed lattice need not be in contact with each other (9, 10). That is why we prefer the term "triangular net" to "close-packed layer."

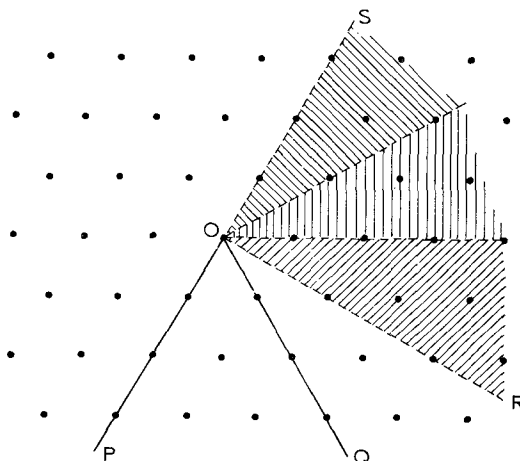


FIG. I.1. Triangular net. The positions of the lattice points in a triangular net can be described by a hexagonal coordinate system. A translation vector is represented by the coordinates of the lattice point at the end of the vector. At the determination of all two-dimensional cells (Fig. I.2), the first translation vector lies between OP and OQ. The second vector must make an angle $90^\circ \leq \beta \leq 120^\circ$ with the first, and must, therefore, lie between OR and OS.

still contain an infinite number of lattice points. Therefore, we confine our attention to two-dimensional unit cells that do not contain more than 20 lattice points. This number is, of course, arbitrary, but even so rather large three-dimensional unit cells may occur.⁴ In order to derive structures of alloys essentially the same approach was suggested by Beck (3).⁵ Because our approach deviates slightly from the procedure followed by Beck, we briefly summarize our calculation by means of a flow chart (Fig. I.2). For a more detailed description the reader is referred to Beck's paper (3).

In order to obtain layers of composition AX_3 one quarter of the lattice points have to be occupied by A ions and the remaining ones by X ions. In other words, only those two-dimensional unit cells can be selected that contain four lattice points or a multiple of four. The most simple patterns, three in all, are derived from unit cells that contain only four lattice points. Of these, two remain when condition (c) is obeyed, viz., the well-known triangular (T) (Fig. I.3(a)) and rectangular (R) (Fig. I.3(b)) types of order.

⁴ The volume of the unit cell, if the smallest anions (F^-) are used, would be about 800 \AA^3 (cubic stacking of layers).

⁵ Unfortunately, his paper came to our attention only after we had finished the calculation of the two-dimensional unit cells.

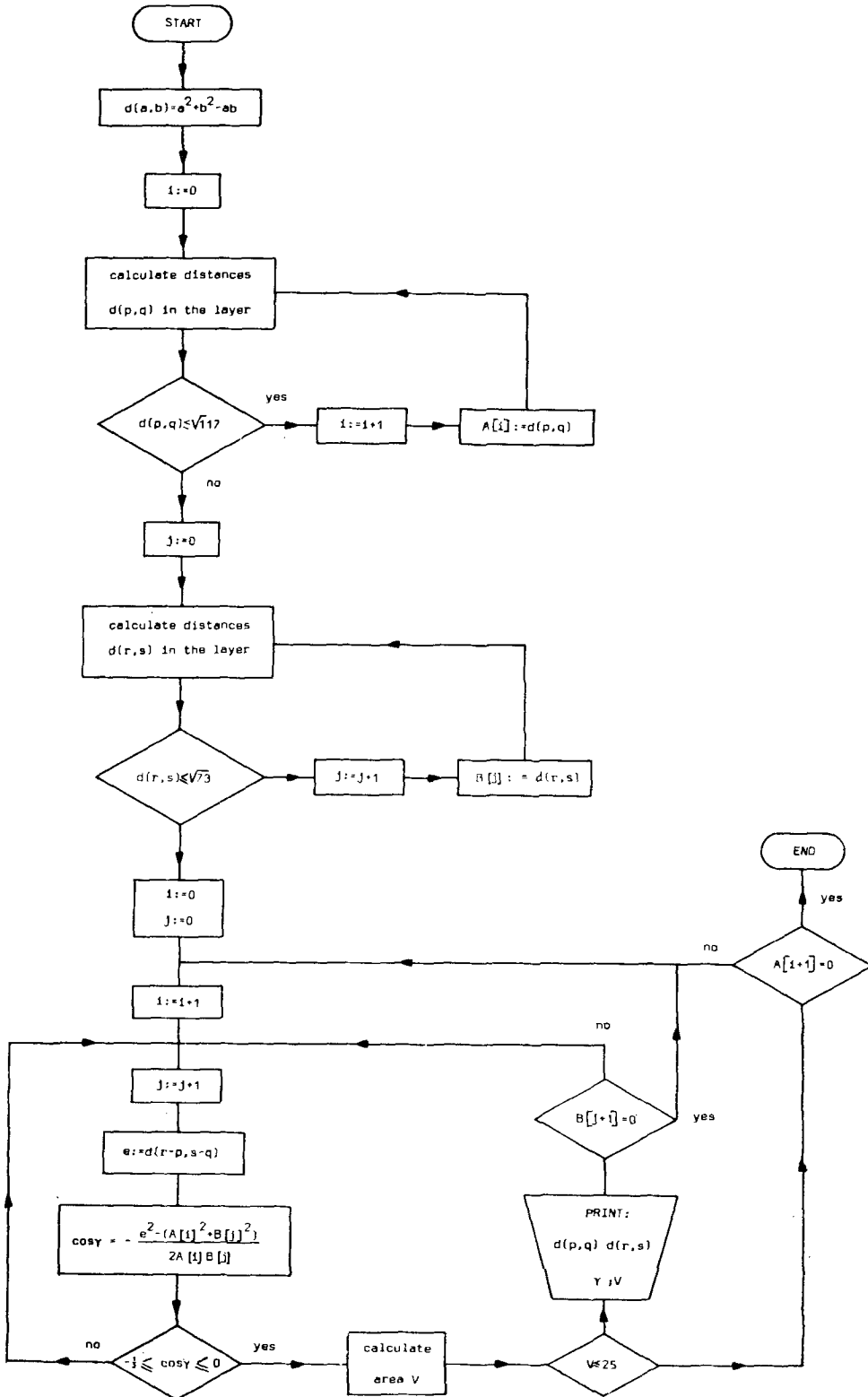


FIG. 1.2. Flow-chart for the calculation of two-dimensional unit cells. The coordinates and the length of the first translation vector are stored in the matrix $A[i]$; those of the second translation vector in the matrix $B[j]$ (Fig. I.1). An upper limit is set to the maximal length of these vectors. In the course of the calculation a number of cells occur more than once, but the redundant cells can be removed afterwards.

Within certain delimitations on the size of the three-dimensional unit cell,⁶ we have found that only AX_3 structures of which the patterns in the layer are composed of T and/or R motifs are in agreement with restriction (c). We should have liked to give a rigorous proof, also for all larger cells, but we have not been able to do so. Instead we shall give a simple reasoning that makes this seem plausible.

The ordered patterns that are not exclusively composed of T and/or R motifs can be derived from the larger two-dimensional unit cells and can be described in terms of parts (or motifs) of more simple⁷ patterns [see, e.g., Fig. I.3(d)]. In

⁶ Only those three-dimensional structures were considered that do not contain more than six different layers and of which the two-dimensional unit cell does not contain more than 20 lattice points.

⁷ Simple means that the smallest unit cell by means of which the AX_n pattern can be described does not contain more than $n + 1$ lattice points.

order to obtain the composition AX_3 , motifs of composition $AX_{3+\delta}$ have to be combined with motifs of composition $AX_{3-\epsilon}$ in the correct proportion. However, restriction (c) sets a lower limit to the anion-cation ratio in a layer and this determines the composition of the smallest motif. The limiting composition of an AX_n layer satisfying restriction (c) is AX_2 . This composition can be realized in only one way, viz., the honeycomb pattern [Fig. I.3(c)]. Such an AX_2 layer can only be stacked with an X_3 layer [restriction (c)], so that the X/A ratio is at least five. Locally the same holds for the motif of composition AX_2 . Thus, all complex patterns of composition AX_3 that contain a motif of composition AX_2 cannot be stacked in a close-packing to form an AX_3 structure without allowing $A-A$ neighbors. It remains to be examined, therefore, whether patterns of composition AX_3 that are composed of motifs of composition AX_3 only, can be stacked with each other without violating

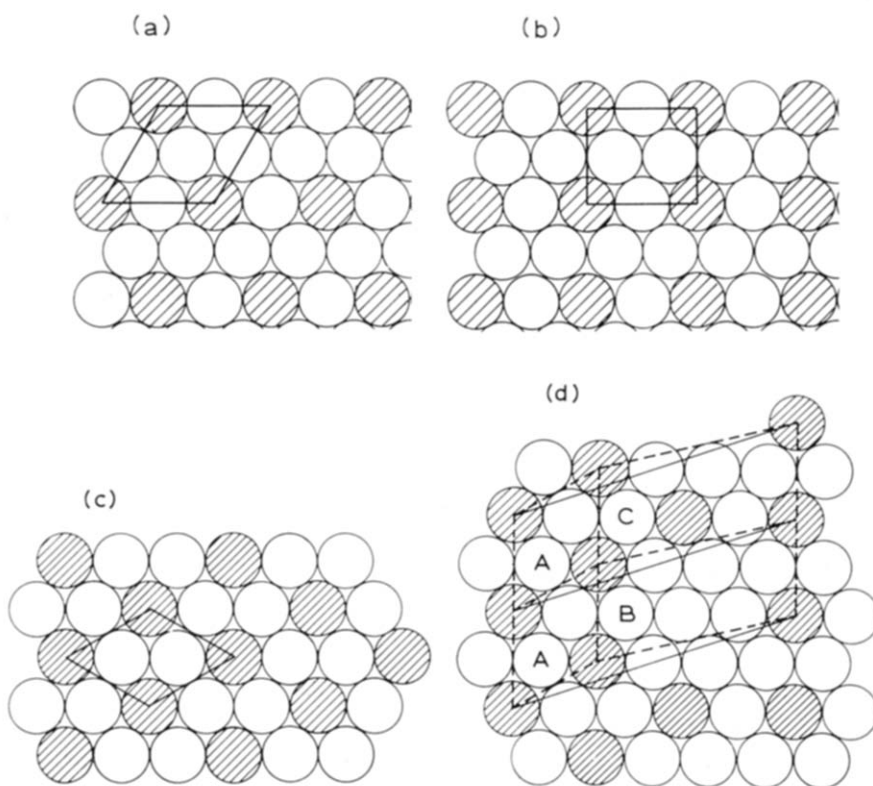


FIG. I.3. Various types of order of A and X ions in a layer. The A ions are hatched. (a) AX_3 layer with triangular type of order: T pattern; (b) AX_3 layer with rectangular type of order: R pattern; (c) AX_2 -layer, the honeycomb pattern; (d) example of AX_3 layer formed by a combination of motifs AX_n , viz., AX_2 (denoted by A), AX_6 (denoted by B) and a combination of AX_3 (R pattern) and AX_2 (denoted by C).

restriction (c). An AX_3 layer with a pattern composed of T and/or R motifs can be stacked only if the pattern in the adjoining layers is identical. Thus, structures of composition AX_3 , composed of layers with composition AX_3 meet our requirements only if the pattern in the layer is of the type T_mR_n ($m, n = 0, 1, 2, \dots$) and the patterns of adjoining layers are identical.

More structures of composition AX_3 can be derived by examining a less well-balanced distribution of the A ions over the layers. In other words, we have to determine if layers of composition $AX_{3+\delta}$, mixed with layers of composition $AX_{3-\epsilon}$ in the proper ratio, may give rise to a structure of composition AX_3 . The same arguments as given above can be used here. The limit for a layer of composition $AX_{3-\epsilon}$ is reached for $\epsilon = 1$. Such an AX_2 layer can only be stacked with a layer completely filled with anions, giving rise to a composition AX_5 . Layers with compositions intermediate between AX_3 and AX_2 must have patterns that are partly composed of the motif of the honeycomb pattern. Layers of this type cannot be stacked with layers of compositions $AX_{3+\delta}$ to form an AX_3 structure without violating restriction (c). Thus, if the composition of the layer deviates from AX_3 , no structure of composition AX_3 can be derived that meets our requirements.

I.2.2. Derivation of ABX_3 and A_2BX_6 Structures

When triangular nets occupied by large ions are stacked to form a lattice in the manner of close-packed spheres [condition (b)], interstitial positions of various types are left. The two largest of these sites⁸ are surrounded by six and four large ions: when all of these are anions, the interstitial positions, called octahedral and tetrahedral sites, respectively, may be occupied by small cations.

For structures AX_3 that are composed of identical layers with T_mR_n patterns (Section I.2.1), the number of available octahedral and tetrahedral sites is as follows: (a) Between two T motifs only one interstitial position, viz., an octahedral site, can be occupied by a small cation. (b) Between two R motifs neither octahedral nor tetrahedral sites are available for B ions.

This means that for various patterns T_mR_n the

⁸ Three-coordinated sites will not be taken into account nor will square-pyramidal 5-coordinations. Trigonal-bipyramidal holes cannot be filled since the two face-sharing tetrahedra of which they are composed cannot be occupied.

composition for complete occupation of octahedral sites by B ions is $A_{m+n}B_mX_{3(m+n)}$. Only one pattern, T , exists from which structures for the composition ABX_3 can be derived. Structures of composition A_2BX_6 can be derived by complete occupation of the octahedral sites in all AX_3 structures that are composed of TR or generally T_nR_n patterns, and by partial occupation of octahedral sites in structures composed of T , T_2R or generally T_mR_n patterns with $m > n$. Before investigating these possibilities of cation-vacancy order in the octahedral sites, we must examine whether restrictions, as mentioned in Section I.2, may also be applied to this case, in order to reduce the number of possible structures. No restrictions as a result of Coulomb repulsion between the cations will be imposed on the type of order in the layer of octahedral sites, because the smallest distances between the octahedral sites in this layer, in structures of composition ABX_3 , $A_3B_2X_9$, etc. are at least twice the smallest $X-X$ distances in the AX_3 net. Since we made the arbitrary restriction that the largest two-dimensional cell in an AX_3 layer does not contain more than twenty particles (Section I.2), we shall confine ourselves in this case to cells that do not contain more than five positions over which small cations and vacancies can be ordered. The Coulomb repulsion between two layers of octahedral sites will not be influenced very much either by the type of order of cations and vacancies in these layers. Therefore, we have maintained the arbitrary limit to the number of layers (see footnote 6): the translation period in the stacking direction does not contain more than six layers⁹ with a different type of order of cations and vacancies.

Although the number of possible types of order in one layer is small, a large number of structures arises in three dimensions because the stacking order of the layers of octahedral sites is arbitrary. The number of possible A_2BX_6 structures derived from structures of composition ABX_3 , $A_3B_2X_9$, etc., irrespective of the stacking sequence of the AX_3 layers, has been calculated. Within the geometrical delimitations we made, 147 structures are obtained by leaving half of the octahedral sites empty in an ABX_3 structure, and distributing the B ions equally over all layers. If a less well-balanced distribution of the B ions is considered, another 70,000 structures are added

⁹ That is, irrespective of the stacking of the AX_3 layers that can be hexagonal (h), cubic (c) or mixed hexagonal-cubic (hhc , hc , $hhcc$, hcc , etc.).

to this number. By leaving some of the octahedral sites vacant in structures of compositions $A_3B_2X_9$, $A_4B_3X_{12}$, etc., about 7000 structures for the composition A_2BX_6 can be found.¹⁰

A small part of this large number of A_2BX_6 structures remains if only those structures are permitted in which the cation arrangement around all anions is isonomous. Of these structures only those are allowed in which most and preferably all anions have the same coordination [Pauling's rule of parsimony (12)]. The anion coordination will be investigated in Section I.2.3 with the aid of the space-filling polyhedra (SFPs) of the anions.

I.2.3. Selection of A_2BX_6 Structures by means of Space-Filling Polyhedra of the Anions

The SFPs of the anions are the smallest polyhedra formed by constructing midway

¹⁰ More detailed information is available on request.

planes between an anion and all anions surrounding it (I). The cations can generally be found on the corners, edges and faces of these polyhedra, or even inside them. Although the term SFP, according to the name, suggests that all SFPs in the whole structure are of the same type, this need not be the case. If the anions are spread over more than one crystallographic position, there is one different SFP for each crystallographic position.¹¹ The SFPs of the anions, constructed as mentioned above, for the c and h stackings of AX_3 layers with T and R patterns are drawn in Fig. I.4. Not more than these four different space-filling polyhedra (SFP)

¹¹ The concept SFP is used in a more general sense than Niggli's "Wirkungsbereich." The latter is constructed in the same way as a SFP, but the midway planes are between one point of a crystallographic position and its neighboring points. For a more extensive discussion see Ref. (9).

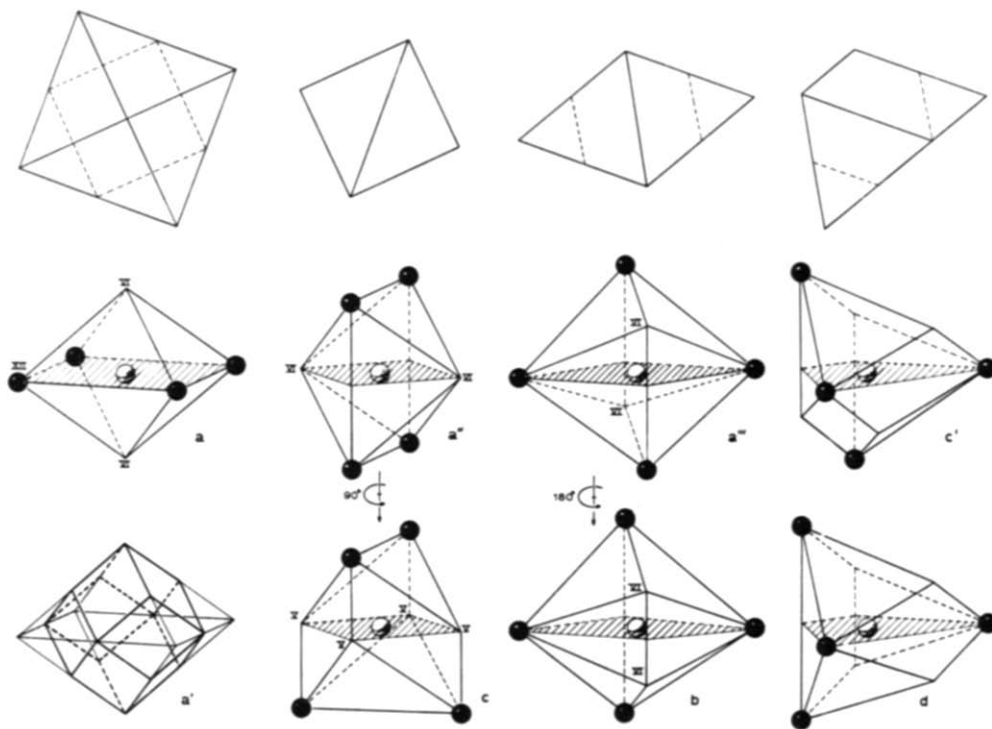


FIG. I.4. The anion coordination in "close-packed" structures composed of AX_3 layers with T_mR_n pattern, indicated by means of their space-filling polyhedra (SFP). Black spheres are A ions, white spheres X ions. In the first column the relation between the anion coordination in a fcc anion lattice (denoted by a') and that in a fcc AX_3 structure (denoted by a). The remaining primes denote different orientations of the polyhedra. In a c -stacked T motif only the anion polyhedron (denoted by a) occurs and in a h -stacked T motif only the SFP (denoted by b). The anion coordinations in both the h - and c -stacked R motif are of two different kinds: c -stacking: $1 \times (a)$ and $2 \times (c)$ and h -stacking: $1 \times (b)$ and $2 \times (d)$. The number of anions by which the corners of the SFPs are coordinated are indicated by a Roman figure (in the text by a Roman superscript to the left of the symbol of the ion). The equatorial plane in each SFP is hatched. The SFP (denoted by d), can be derived from the SFP (denoted by c') by replacing the bottom half by its mirror image.

occur for the anion when the occupation of interstitial positions available for smaller cations is not taken into account. "Close-packed" structures with other types of order in the AX_3 layers and/or mixed cubic-hexagonal stackings do not give rise to new types of SFPs, but consist of a mixture of these four SFPs.

I.2.3.1. A_2BX_6 Structures Based on AX_3 Layers with T Pattern

In the structures that result when the stacking sequence of AX_3 layers with T pattern is cubic, hexagonal or mixed cubic-hexagonal, only two different anion coordinations occur, when a possible occupation of the octahedral sites by the smaller cations is not taken into account [Figs. I.4(a) and (b)]. The smaller cations in the $X^{VI}A^{VI}B^{VI}X_3$ structures are located on the 6-coordinated positions, indicated as VI in the figures. In order to derive structures of composition A_2BX_6 from the ABX_3 structures, half of these smaller cations have to be removed. Only six different SFPs result in this way: one with two cations, one with one cation, and one with no cation in the octahedral positions, both in the c (Fig. I.1.4(a)) and in the h (Fig. I.1.4(b)) stacking. The anion coordination as shown by the SFP for the c stacking with vacant octahedral sites will not occur in A_2BX_6 compounds, since the coordination of the anion by a square of A ions is very unfavorable even when the polarizability of the anion is large.¹² This SFP can only be expected if the anion in the center is replaced by a water molecule or also perhaps by an hydroxyl ion, because the H^+ ion(s) then complete the anion coordination in such a way that the coordination becomes more isonomous. This is also valid for the anion coordination shown by the SFP of the h stacking with vacant octahedral sites. If the SFPs without B ions are not allowed, the SFPs with two octahedral sites occupied can not occur either in A_2BX_6 structures, so that only the two SFPs with one octahedral site occupied are left. Stacking of the SFPs with one octahedral site occupied leads to a number of A_2BX_6 structures, in which the AX_3 layers can form a cubic, a hexagonal and any mixed cubic-hexagonal stacking.

C Stacking. The SFP of Fig. I.4(a) with one

¹² In the structures of alloys of composition AB_3 the coordination of the B atom by a square of A atoms can occur, because the electrons are not localized like, e.g., in the structure of Cu_3Au .

octahedral site filled can be stacked in only one way as will be obvious from the following reasoning. If one octahedral position is chosen to contain a B ion, the choice for six other octahedral positions is fixed. Three out of these are situated in the layer with octahedral positions immediately above the first one and the remaining three are situated in the layer below. Each of these six positions in turn fixes the choice for the octahedral sites immediately surrounding it. The structure that results will have B ion layers alternately filled and empty. This is the structure of K_2PtCl_6 (13).

H Stacking. The SFP of Fig. I.4(b) with one octahedral site occupied can be stacked in several ways. The only restriction is that, if one octahedral position is chosen to contain a B ion, the choice for all octahedral positions on one row parallel to the c axis is fixed. The octahedral sites on this row will be alternately filled and empty. In other words: the pattern in one layer is repeated in the next layer, but now the positions of B ions and vacancies are interchanged. Thus, only the type of order in one layer can be varied independently. The number of structures that can thus be derived is 15.

The space groups and the cell dimensions of these structures are given in Table I.1. Only one of these 15 structures has each kind of ion in only one crystallographic position, viz., the structure in which the layers with octahedral sites are alternately vacant and occupied by B ions. This structure is adopted by K_2GeF_6 (14). The remaining 14 structures have been excluded, since they do not follow so well the rule of parsimony.

Mixed Cubic-Hexagonal Stackings. It is clear that for each of the mixed cubic-hexagonal stackings only one structure will be found, because one c -stacked AX_3 layer determines the type of order in the two surrounding layers of octahedral sites: one layer is filled with B ions and the other is empty. All these structures with mixed stackings, therefore, have layers of octahedral sites that are alternately occupied and empty.

I.2.3.2. A_2BX_6 Structures Based on AX_3 Layers with T_mR_n Patterns

A disadvantage of the structures containing the SFPs of Figs. I.4(a) and (b) with only one octahedral site occupied may be that the surrounding of the anion is rather irregular. This is true to a greater extent for the anion coordination

TABLE I
STRUCTURES OF COMPOSITION A_2BX_6 DERIVED BY REMOVING HALF OF THE B IONS FROM THE h -STACKED ABX_3 STRUCTURE^a

Two-dimensional unit cell ^b				Occupation of octahedral sites in the			Space group	Cell parameters, expressed in the shortest $X-X$ distance			Number of units A_2BX_6 in the cell
Area	A	B	γ	1st layer	2nd layer						
—	—	—	120°	1	0	$P\bar{3}m1$; D_{3d}^3	$a = 2$		$c = 2/3\sqrt{6}$	$Z = 1$	
2	1	2	120°	1/2	1/2	$Pn\bar{m}$; D_{2h}^{12}	$a = 2\sqrt{3}$	$b = 2/3\sqrt{6}$	$c = 2$	$Z = 2$	
4	2	$\sqrt{3}$	90°	1/2	1/2	$Pbcn$; D_{2h}^{14}	$a = 2/3\sqrt{6}$	$b = 4$	$c = 2\sqrt{3}$	$Z = 4$	
4	4	1	120°	1/2	1/2	$Pnma$; D_{2h}^{16}	$a = 4\sqrt{3}$	$b = 2$	$c = 2/3\sqrt{6}$	$Z = 4$	
3	3	1	120°	1/3	2/3	$C2/m$; C_{2h}^3	$a = 6\sqrt{3}$	$b = 2$	$c = 2/3\sqrt{6}$	$\beta = 90^\circ$ $Z = 6$	
3	$\sqrt{3}$	$\sqrt{3}$	120°	1/3	2/3	$P\bar{3}1m$; D_{3d}^3	$a = 2\sqrt{3}$		$c = 2/3\sqrt{6}$	$Z = 3$	
4	2	2	120°	1/4	3/4	$P\bar{3}m1$; D_{3d}^3	$a = 4$		$c = 2/3\sqrt{6}$	$Z = 4$	
4	2	$\sqrt{3}$	90°	1/4	3/4	$P2/m$; C_{2h}^1	$a = 2\sqrt{3}$	$b = 4$	$c = 2/3\sqrt{6}$	$\beta = 90^\circ$ $Z = 4$	
4	4	1	120°	1/4	3/4	$P2/m$; C_{2h}^1	$a = 4\sqrt{3}$	$b = 2$	$c = 2/3\sqrt{6}$	$\beta = 90^\circ$ $Z = 4$	
5	$\sqrt{3}$	$\sqrt{7}$	109°6'	1/5	4/5	$C2/m$; C_{2h}^3	$a = 2$	$b = 10\sqrt{3}$	$c = 2/3\sqrt{6}$	$\beta = 90^\circ$ $Z = 10$	
5	1	5	120°	1/5	4/5	$C2/m$; C_{2h}^3	$a = 2\sqrt{3}$	$b = 10$	$c = 2/3\sqrt{6}$	$\beta = 90^\circ$ $Z = 10$	
5	$\sqrt{3}$	$\sqrt{7}$	109°6'	2/5	3/5	$C2/m$; C_{2h}^3	$a = 2\sqrt{3}$	$b = 10$	$c = 2/3\sqrt{6}$	$\beta = 90^\circ$ $Z = 10$	
5	$\sqrt{3}$	$\sqrt{7}$	109°6'	2/5	3/5	$C2/m$; C_{2h}^3	$a = 2\sqrt{3}$	$b = 10$	$c = 2/3\sqrt{6}$	$\beta = 90^\circ$ $Z = 10$	
5	1	5	120°	2/5	3/5	$C2/m$; C_{2h}^3	$a = 10\sqrt{3}$	$b = 2$	$c = 2/3\sqrt{6}$	$\beta = 90^\circ$ $Z = 10$	
5	1	5	120°	2/5	3/5	$C2/m$; C_{2h}^3	$a = 10\sqrt{3}$	$b = 2$	$c = 2/3\sqrt{6}$	$\beta = 90^\circ$ $Z = 10$	

^a In all structures only one anion coordination occurs: viz., the SFP of Fig. I.4(b) with one octahedral site occupied.

^b The area is expressed in the number of B ions in the two-dimensional unit cell, the axes A and B are expressed in the shortest $B-B$ distance (= two times the shortest $X-X$ distance).

in the c than for that in the h stacking. Choosing AX_3 layers with TR pattern this irregular anion coordination can be partly avoided.

In a structure derived by stacking AX_3 layers with TR pattern, various types of anion coordination occur. In the c -stacking, the SFP of Fig. I.4(a) with two B ions, that with one B ion, and the SFP of Fig. I.4(c) occur in the proportion 1:1:1. In the h stacking, the SFP of Fig. I.4(b) with two B ions, that without B ions, and the SFP of Fig. I.4(d) occur in the proportion 3:1:2. The SFP of Fig. I.4(b) without B ions will most probably not occur for ionic compounds because of its nonisonomous anion coordination. Therefore, the hexagonal stacking and thus the mixed hexagonal-cubic stackings of the AX_3 layers with TR pattern and with more complicated T_mR_n patterns are not expected for A_2BX_6 compounds. A_2BX_6 structures based on the c stacking of AX_3 layers with T_2R_2 pattern are not expected either, since they contain a nonisonomous anion coordination, viz., the SFP of Fig. I.4(a) without B

ions. The same argument is used to exclude A_2BX_6 structures derived from all other T_mR_n patterns in which at least two successive R motifs occur.

In structures composed of AX_3 layers with T_nR patterns, $(n-1)/2$ octahedral positions must remain empty to attain the composition A_2BX_6 . The anion coordination of Fig. I.4(a) without B ions can be avoided only, however, if not more than $(n-2)/2$ octahedral positions remain empty. Therefore, these A_2BX_6 structures can also be excluded. For the same reason A_2BX_6 structures derived from a c stacking of more complex patterns like T_2RTR can be excluded.

Therefore, A_2BX_6 structures can be built only from AX_3 layers with T pattern and c -stacked AX_3 layers with TR pattern. The conditions which determine whether a particular compound A_2BX_6 will have a structure based on the TR pattern or one of the structures based on the T pattern, will be discussed in greater detail in Part III of this series of papers.

I.2.4. Removal or Substitution of Anions in the Ideal Structures

By removing some anions from structures of compositions A_2BX_6 , $A_3B_2X_9$, etc., new structures arise with compositions $A_2BX_5\Diamond$, $A_2BX_4\Diamond_2$, $A_3B_2X_7\Diamond_2$, etc.¹³ From the SFPs of the anions (Fig. I.4), it is evident where the anion vacancies in these structures might occur. In the structures derived in this paper anions may be removed most easily from those positions that are surrounded by cations with a low charge and/or by a small number of cations.¹⁴ This condition is fulfilled for the anions of the SFPs of the *R* pattern (Figs. I.4(c) and (d)) and for the anions of the SFPs of the *T* pattern if the two octahedral sites were vacant (Figs. I.4(a) and (b)). A more extensive discussion of A_2BX_6 structures in which the *X* ions are partly removed will be given in Parts IV and V of this series of papers.

In the foregoing, structures have been derived for compounds of composition ABX_3 and A_2BX_6 . It would be a logical extension to examine how the anions would arrange themselves in these structures if they were of a different kind, in other words, to derive structures of compositions ABX_{3-p} , Y_p , and A_2BX_{6-p} , Y_p , in which *X* may differ from *Y* both in size and charge. These types of order of *X* and *Y* can be determined in at least two ways: (1) For each type of anion the most suitable SFP may be selected and these SFPs can be stacked in such a way that the desired composition is obtained. (2) Instead of starting from the SFP of the anion it is possible to determine the ways in which the various types of BX_{6-p} , Y_p , octahedra can be joined. This has been investigated by Smirnova (15) for a more general class of compounds.

Utilizing structures with ordered arrangements of *X* and *Y*, the ABX_3 and A_2BX_6 structures derived above may be used to set limits to the number of possible structures. In order to select from the derived structures those that are the most suitable for a certain compound, rules have to be constructed. A more extensive discussion of structures of A_2BX_6 compounds with different types of anions will be given in Parts IV and V of this series of papers.

¹³ \Diamond Denotes an anion vacancy.

¹⁴ The coordination of the cations must also be taken into account, especially when their charge is high and/or their coordination is low (the inverse application of Pauling's second rule). The above-mentioned structures are in accordance with this condition.

I.3. Deviations from the Ideal Structures¹⁵

Starting from a basic lattice we derived structures with compositions ABX_3 and A_2BX_6 . Among these, those structures are "favorable" that meet the following requirements as far as possible:

(a) The surrounding of each of the anions, as well as of the cations, by ions of opposite sign, has to be as isonomous as possible, when its polarizability is low or, if not, also when the coordination of the ion is high (1).

(b) The charge of each of the anions has to be compensated by the sum of the charges of the cations immediately surrounding it, divided by their respective coordination numbers. It is preferable to correct these coordination numbers for variations in the cation-anion distances [See, e.g., Baur's paper (16) on Pauling's second rule, also for references].

(c) Pauling's first rule (12): "A coordinated polyhedron of anions is formed about each cation, the cation-anion distance being determined by the radius sum and the coordination number of the cation by the radius ratio." For the ABX_3 and A_2BX_6 structures that are derived here, the fact that the starting point was the basic lattice limits the number of different cation coordination polyhedra. The radius ratio rule may be used as a first approximation to find out whether the interstices in the basic lattice are too large or too small. When this is the case, such deformation will take place that yields a gain in potential energy so large than any possible loss in isonomy is outweighed.

(d) Pauling's fifth rule (12): "The number of essentially different kinds of constituents in a crystal tends to be small." We prefer a more restrictive formulation (9): The same ions will prefer to have the same coordination, as regard number and polyhedron shape, of oppositely charged ions, if this can be achieved for the given stoichiometry and if the structure meets the requirements a-c. This may mean that chemically identical ions prefer to occupy an identical crystallographic position,¹⁶ with the above restrictions. Neither for Pauling's fifth rule nor for either of the other formulations, have we

¹⁵ In this section deformations of the ideal ABX_3 and A_2BX_6 structures as a result of the electronic structure of the *B* ions, e.g., Cu^{2+} , Sn^{2+} , will be left out of consideration.

¹⁶ That is, the same crystallographic position with only one value for each of the parameters.

found a justification from electrostatic theory so far.

The ABX_3 structure with c -stacked AX_3 layers is completely in accordance with the above requirements. In the ABX_3 structure with h -stacked AX_3 layers the surrounding of the anion is less isonomous than in the case of the c stacking, but this disadvantage can be overcome by the polarization energy. For the composition A_2BX_6 the structure derived from the h stacking of the T pattern has a more isonomous anion coordination than the structure with the c stacking of these AX_3 layers. This anion coordination of the c stacking (Fig. I.4(a)) becomes more regular when the anion is moved from the center of the SFP towards the octahedral position occupied by the B ion. ABX_3 and A_2BX_6 structures derived from mixtures of the h and c stackings do not conform to requirement (d) but a gradual change of radius ratios of the ions and the anion polarization stabilizes these structures. In the c -stacked A_2BX_6 structure derived from the TR pattern, the anions do not meet the requirements (b) and (d), but the coordinations of two thirds of the anions are more isonomous than in the c -stacked A_2BX_6 structure derived from the T pattern.

So far the third of the above requirements was irrelevant to the derivation of the structures, because our restriction to the close-packed lattices means that the A ion is 12-coordinated, and in the course of the derivation it appeared that the only interstitial position that can be occupied by a small cation is a position surrounded by an octahedron of anions. When we wish to select compounds that may have one of these structures, requirement (c) has to be taken into account. For, if a choice is made for the ions A , B and X , the A ions will generally not be of the same size as the X ions and the B ions will not fit exactly into the octahedral holes. Since the structures derived above are very favorable, they will have a fair tolerance for deviations from the ideal size ratios. How large this tolerance exactly is, will depend on the difference in energy between the ideal structure and a deformed structure with a lower potential energy. When the mutual size ratios of the A , B and X ions deviate too strongly from the ideal values, the structures will adjust themselves, i.e., they deform to make the cations fit into the interstices. These deformations are discussed by introducing a difference in size between A and X ions (Section I.3.1) or by varying the r_B/r_X ratio (Section I.3.2), both between certain limits.

I.3.1. Deformations of the Ideal Structures Due to a Difference in Size Between A and X Ions

We have started by assuming that the A and X ions together constitute a basic lattice and limited ourselves to "close-packed" lattices. When the difference in size between A and X ions becomes so large that the ideal structures have to deform, those deformations are most likely in which the A ions fit best. The stability of various deformations applied to make the A ions fit may be roughly compared by calculating the space filling, i.e., the percentage of space filled by hard spheres. A similar approach is usual for deriving structures of alloys [See, e.g., Ref. (17)] and was used by van Vucht (18) for structures of alloys AB_3 .¹⁷ It is, however, a rather difficult problem to find that deformation of the three-dimensional AX_3 structure that possesses the best space-filling. We ought to consider, however, that the ideal structures were very favorable and the "advantages" of these ideal structures (i.e., in how far they meet the requirements a–d enumerated above) have to be preserved as much as possible. Consequently, in designing deformed structures we must maintain the symmetry of the ideal structures, i.e., preserve the three-fold and/or four-fold axes, as long as possible.

ABX_3 Structures. First those deformations will be derived in which the *three-fold* axis is maintained.

A necessary condition for a three-dimensional structure to possess trigonal symmetry is that the layers possess trigonal symmetry. In order to maintain the trigonal symmetry in the AX_3 layer, when the A ion is *larger* than the X ion, the layer has to deform as given in Fig. I.5(a) [$T(1)$ layer]. When this layer is stacked hexagonally, the densest packing is obtained when the large ion of the adjoining layer fits in the large X_3 triangle. Besides, this structure conforms equally well to the requirements a–d as the ideal structure. The cubic stacking of these $T(1)$ layers gives rise to two different structures: a structure with two different types of octahedral holes and a structure with equal but much deformed octahedral holes. In both structures the advantages of the ideal structure as regards requirements a, c and d, are lost for the greater part. Therefore, we consider

¹⁷ His assertion that the space filling for the h stacking of deformed AX_3 layers with R pattern is better than that for the h stacking of the deformed AX_3 layers with T pattern (Fig. I.5(a)) appeared to be in error, as he communicated to us.

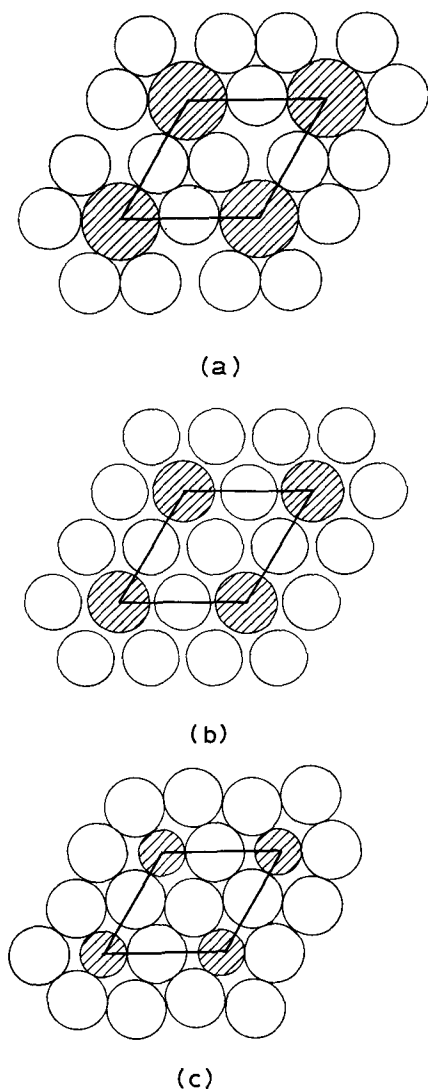


FIG. 1.5. Deformations of AX_3 layers with T pattern, due to a too large A ion [$T(1)$ layer, Fig. 1.5(a)] or a too small A ion [$T(3)$ layer, Fig. 1.5(c)]. A $T(2)$ layer is equally expanded in all directions, so that the full cubic symmetry is preserved (Fig. 1.5(b)).

it unlikely that one of these deformations will be realized, and the ideal structure has to expand equally in all directions with preservation of the symmetry. The AX_3 layers forming this structure are shown in Fig. 1.5(b) [$T(2)$ layer]. This subject is discussed more extensively in Part II of this series of papers.

When the A ion is *smaller* than the X ion, the three-fold axis will be maintained when the AX_3 layer is deformed as shown in Fig. 1.5(c) [$T(3)$

layer].¹⁸ Only the c stacking of these layers is expected, for in the h stacking the anion coordination is nonisonomous.

The *four-fold* axis is present only in the structure with c -stacked AX_3 layers. When the A ion is *larger* than the X ion, no irregular deformation in which the four-fold axis is maintained is probable, for in the structure the BX_6 octahedra are joined by all corners and those can only expand in all directions to make room for the large A ion. When the A ion is *smaller* than the X ion, an irregular deformation of the BX_6 octahedra cannot occur either, because requirement (b) is then violated. The potential energy can only be decreased by turning the octahedra around the four-fold axis. When the rotation around this axis is so large that the A ions have to shift from their original positions, their coordination number is lowered from 12 to 8 and the symmetry of the structures may be lowered. The A ions can be displaced in more than one way, of which the most simple case is realized in the $GdFeO_3$ structure (20). More details are given in Part II.

A_2BX_6 Structures. In the A_2BX_6 structures derived from the T pattern the most likely deformations can be determined easily with the aid of the deformations derived for the ABX_3 structures. When the A ion is larger than the X ion, the c stacking of $T(1)$ layers (Fig. 1.5(a)) is also allowed, since only one half of the octahedral positions are occupied. So the full symmetry of the ideal structure is preserved. When the A ion is smaller than the X ion $T(3)$ layers (Fig. 1.5(c)) will be formed. However, for these A_2BX_6 structures not the h stacking, but the c stacking of these layers is unfavorable, due again to a nonisonomous anion coordination. Rotation around the four-fold axis results in the same framework of twisted octahedra as for the ABX_3 structures. This time the deformation is not carried forward by corner sharing of the octahedra, but by anion-anion repulsion. Here again the A ions can be displaced in various ways.

The c -stacked A_2BX_6 structure derived from the TR pattern has tetragonal symmetry. It has to be deformed first in order to be able to compete with the other ideal A_2BX_6 structures and afterwards deformations due to the differences in size of A and X ions have to be considered. The value of the parameters of the A and X ions for which this structure is more favorable have

¹⁸ This deformation can also be described by a rotation of the AX_3 triangles around the three-fold axes, as has been done by H. D. Megaw (19).

not been calculated as far as we know.¹⁹ No conclusions can yet be made, therefore, as to whether the parameters of a particular compound may be influenced by a difference in size between A and X ions or not. A more extensive discussion of these deformations is given in Part III.

I.3.2. Deformations of the Ideal Structures Due to Deformed BX_6 Octahedra

Most of these deformations are the same as when the A and X ions differ in size. An increase in size of the BX_6 octahedron has the same effect as a decreasing r_A/r_X ratio, and vice versa.

When the B ion is too large for the octahedral position, an expansion of the BX_6 octahedra can occur either equally along all $B-X$ directions or by preserving only the three-fold axis. When the BX_6 octahedra are expanded by preserving only the three-fold axis, the deformation of the AX_3 layers may be similar to $T(1)$ layers or $T(3)$ layers. For ABX_3 compounds only the h stacking of $T(1)$ layers is allowed (Section I.3.1) and in this stacking the B ions are now situated above the large X_3 triangles. Such a structure is not very probable, because the X ion moves in the direction of the A ions (Fig. I.4(b)). For A_2BX_6 compounds, both the c and the h stackings of $T(1)$ layers are allowed (Section I.3.1) and in this stacking the B ions are situated now above the large X_3 triangle. The c structure thus derived is not expected to occur, since the B ion prevents the anion coordination from adjusting itself. The h structure may occur for particular compounds, as will be discussed in Part III. Structures derived from $T(3)$ layers for ABX_3 compounds can only occur when the stacking of the layers is cubic (Section I.3.1). Structures of composition A_2BX_6 are expected only when the stacking of the $T(3)$ layers is hexagonal (Section I.3.1). Increase in size of the BX_6 octahedra with preservation of the four-fold axis gives rise to the same deformations of ABX_3 and A_2BX_6 structures as in the case of a decreasing r_A/r_X ratio.

When the B ion is too small for the octahedral hole, a contraction of the BX_6 octahedra occurs. When this contraction is equal in all directions, the effect resembles the effect of an increasing r_A/r_X ratio. The same is true for a contraction of the BX_6 octahedra in which only the three-fold axis is maintained for h -stacked AX_3 layers.

¹⁹ H. G. von Schnering pointed out (21) that the value of the parameters must be adjusted in order to make the structure more favorable.

In order to extend our understanding of structures ABX_3 and A_2BX_6 in which the radii of A and B gradually approach each other, we must probably start from other basic lattices. Examples of such types are LuMnO_3 (22), Y_2O_3 (23) and $\beta\text{-Rh}_2\text{O}_3$ (24). An experimental and theoretical investigation on ABX_3 halides of this type has been started in our laboratory, but the results are not yet available. Nevertheless, using the above reasoning the structures of a vast number of compounds reported in the literature can be classified and the structures of new compounds can be predicted, as will be shown in the following parts.

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