

A Systematic Derivation of ${}^{\text{VI}}\text{A} \text{ } {}^{\text{VI}}\text{BX}_3$ Structures

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A systematic procedure for the derivation of crystal structures is outlined and executed for ABX_3 compounds, in which both cations A and B have an octahedral environment. The selection of the structures is based on the qualitative model of ionic bonding, including polarizability, and on the application of Pauling's second and fifth rules. The resulting structures are compared with each other and with the realized structures.

Introduction

The systematic derivation of structures for ABX_3 compounds with both A and B octahedrally coordinated is part of a broad investigation of ABX_3 structures, the purpose of which is to advance our understanding of structures and structural relations.

This investigation is accompanied by experimental efforts in order to enlarge the number of data with which the obtained structures and thus the validity of the applied selection criteria can be tested. The experimental investigation concerns ABX_3 halides, A representing an alkali and B a divalent transition or alkaline earth metal. The halides with perovskite-like structures have been derived and investigated in our laboratory by Brandwijk and Schippers (1, 2). We have chosen the smaller alkali metals lithium and sodium in the case that X represents chlorine. This experimental investigation has led to a single crystal structure determination of NaMnCl_3 (3). This compound as well as NaCdCl_3 is isostructural with FeTiO_3 (ilmenite) (4).

The structure derivation of ABX_3 compounds has been based on the qualitative model of ionic bonding, including polarizability, as outlined and used by Gorter (5) in order to explain and predict crystal structures. This paper deals with structures in

which the cations have a coordination number of six. The most isonomous six coordination, the octahedron, is to be preferred. Following Brandwijk and Schippers (1) we place the anions on a lattice that is composed of two-dimensional triangular nets (Fig. 1a). Different stacking of the triangular nets leads to different lattices. If the lattice points are occupied by contacting spheres of equal size the packing density of a lattice can be defined as the percentage occupied volume. The greatest packing density is obtained by the so-called close-packed lattices, comprising the *c* (cubic close-packed), the *h* (hexagonal

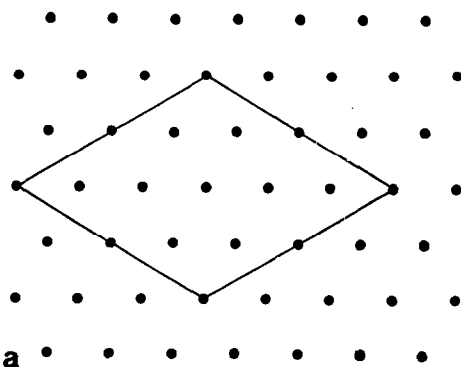


FIG. 1a. Triangular net; the first unit cell of Table 1 is drawn.

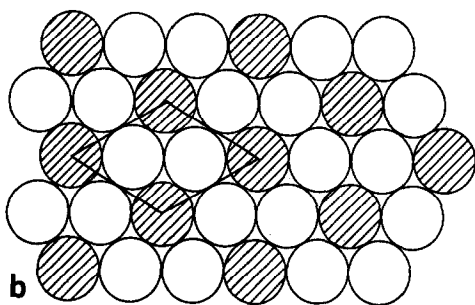


Fig. 1b. Honeycomb pattern.

close-packed), and mixed *c-h* stackings. Examples of less compact lattices are the simple hexagonal stacking and the MoSi_2 -lattice (6). It is the stacking type of the close-packed lattices that provides the lattice with octahedral interstices. The octahedral interstices between a pair of two-dimensional triangular nets constitute a triangular net themselves, their number equaling that of the lattice points in one of the sandwiching nets. If the anions are placed on one of the close-packed lattices only two octahedral interstices per three anions are to be occupied by cations to obtain the correct stoichiometry. The anions can also be placed on a lattice, in which the stacking type of the close-packed lattices is combined with a different stacking type. In the latter case one should see to it that a sufficient number of the former stacking type is present in view of the required number of octahedral interstices. The selection of structures is governed by Pauling's second and fifth rules (7). In his second rule, Pauling stated that the charge of the anions has to be compensated by the sum of the charges of the nearest cation neighbours, divided by their respective coordination numbers. Pauling has formulated his fifth rule as follows: The number of essentially different kinds of constituents in a crystal tends to be small. At the start of a structure derivation one tries to obtain the best structures according to certain selection criteria. Therefore, we have applied the fifth rule, generally known as the rule of parsimony, in a very restrictive manner: the same ions are to have the same coordination as regards number and polyhedron shape

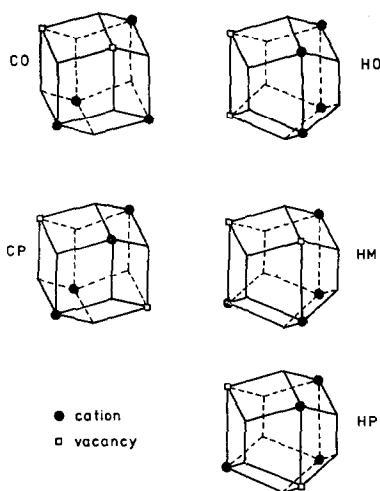
if this can be achieved for the given stoichiometry. The fulfillment of this condition entails that the second rule, commonly named the rule of charge compensation, is fulfilled. Let us consider for example an $\text{A}^{2+}\text{B}^{4+}\text{X}_3$ compound: a structure consisting of anions surrounded by three B-ions, and anions surrounded by $1\text{B} + 4\text{A}$ ions, is allowed as regards the rule of charge compensation, but our application of the rule of parsimony prohibits such a structure. So each anion has to be surrounded by four cations. Consequently, the anions can only be placed on a close-packed lattice. An alternative lattice, viz a combination of the stacking type of close-packed lattices with a different stacking type, always involves three-coordinated anions (or even less).

Since only two of three octahedral interstices in a close-packed anion lattice are to be occupied by cations for reasons of stoichiometry this investigation is subdivided in two parts. In the first part the distribution of cations and vacancies over the octahedral interstices is studied, while in the second the types of order of A and B ions over the occupied sites are considered.

Derivation of $^{\text{VI}}\text{M}_2\text{X}_3$ Structures

The main problem is how the derivation can be done systematically and thus as complete as possible. The anion lattices under consideration have in common that the octahedral interstices constitute triangular nets. Therefore, we decided to introduce systematics by the application of two-dimensional unit cells in the triangular nets. In order to delimit the field of investigation the volume of the two-dimensional unit cells is not allowed to exceed an arbitrarily chosen limit of eighteen lattice points.

In close-packed lattices only two space-filling polyhedra (SFP) (5) can occur. The surrounding of the anion by cations can be visualized in these SFP's by occupying four octahedral sites with cations (Fig. 2). Two types of order are possible for the SFP of a cubic close-packed lattice and three for the SFP of a hexagonal close-packed lattice. In Fig. 2 a nomenclature for the anion polyhedra is introduced. Since the anion poly-

FIG. 2. Space-filling polyhedra for $V^1M_2X_3$.

hedra will be referred to throughout, a small explanation of the code words is given. The first symbol is *C* or *H* to indicate whether the anion polyhedron is derived from the SFP of a *ccp* or a *hcp* lattice. The second symbol specifies on which sites the vacancies are created: *O* (ortho), *P* (para), and *M* (meta) stand for sites with the shortest, the largest and the intermediate distance, respectively. In our ionic model the anion polyhedra *CP* and *HO* are excluded on the grounds of simple electrostatic considerations. Directing the attention to an anion layer, sandwiched by two triangular nets of octahedral interstices, one can see that each octahedral site belongs to three anions of this layer. Each anion requires four cation neighbours, together counting for $\frac{4}{3}$ cations. If the anion layer houses p anions the surrounding cation layers together necessarily contain $\frac{4}{3} \times p$ cations. In other words, if the composition* of a layer is $y/3$ cations + $(3 - y)/3$ vacancies ($1 \leq y \leq 3$) the composition of the adjacent cation layers has to be $(4 - y)/3$ cations + $(y - 1)/3$ vacancies and so on. Since the number of cations in two adjacent cation layers ($\frac{4}{3} \times p$) has to be an integer the value of p is restricted to

* The composition of a layer is defined as the respective numbers of cations and vacancies in the cation layer divided by the number of anions in the anion layer.

TABLE I
TWO-DIMENSIONAL UNIT CELLS

Translation periods (a_0)		Angle (deg.)	No. of lattice points
2V3	2V3	120	12
4	V7	100.90	12
2	2V7	100.90	12
6	V3	90	12
3	V13	106.10	12
2	3V3	90	12
3	2V3	90	12
1	6V3	90	12
1	13	92.20	15
3	V19	96.58	15
3	V21	109.10	15
5	V7	100.90	15
V13	V13	93.58	15
1	9V3	90	18
2	V61	93.67	18
3	3V3	90	18
3	2V7	100.90	18
6	V7	100.90	18
V13	V19	97.32	18
9	V3	90	18
2V3	V21	100.90	18

multiples of three. Summarizing, the two-dimensional unit cells have to contain a multiple of three lattice points; the composition of a cation layer has a lower limit of $\frac{1}{3}$ cation + $\frac{2}{3}$ vacancy and an upper limit of $\frac{2}{3}$ cation + $\frac{1}{3}$ vacancy; the choice of the composition of one cation layer determines the composition of all other cation layers. The results of a study in two-dimensional unit cells with a content of 12, 15, and 18 sites comprise the results from the smaller unit cells, so we are merely concerned with these larger unit cells. The appropriate unit cells are gathered in Table I. Care has been taken that no unit cells were included that could be derived from another tabulated unit cell by means of linear combinations of its translation vectors.

The translation periods of a unit cell are expressed in a_0 (i.e., the shortest anion-anion distance); the angle enclosed by the translation periods is given in degrees and the volume of the

unit cell in the number of lattice points it contains. The first unit cell, drawn in Fig. 1a serves as an example.

Since the two cation layers that enclose an anion layer can have several compositions the following subdivision is made (\square and M indicating a vacancy and a cation, respectively):

- A. all cation layers have the same composition: $\frac{2}{3}M + \frac{1}{3}\square$
- B. cations layers with composition $(2+p)/3M + (1-p)/3\square$ and $(2-p)/3M + (1+p)/3\square$ alternate ($0 < p < 1$).
- C. cation layers with composition M and $\frac{1}{3}M + \frac{2}{3}\square$ alternate.

c-Stacking

All possible cation-vacancy types of order in a triangular net that belong to group A and B can be derived in a straightforward way for each two-dimensional unit cell. The superposition of a second cation layer has to meet the requirement that all anions between the two cation layers have the same polyhedron, viz., the *CO* polyhedron. Eight of the eleven resulting structures are not triclinic and listed in Tables IIA and IIB. Among them structure No. 3 has been realized in Sc_2S_3 (8). The high temperature modification of CrCl_3 (9) corresponds to structure No. 2, provided cations and vacancies are interchanged. The cations occupy the $4g$ position ($0^{1/3}0$).

TABLE IIA

 ${}^{\text{VI}}\text{M}_2\text{X}_3$ -STRUCTURES WITH A C-ANION LATTICE

No.	Space-group	Z	a	b	c	α	β	γ
1	C 2/c	8	V3	3	V11	90	100.02	90
2	C 2/m	4	V3	3	V3	90	109.47	90
3	F ddd	16	2V2	2	6	90	90	90
4	C ccm	16	2V2	2	6	90	90	90
5	P 2/c	12	V3	9	V3	90	109.47	90
6	P 2/m	12	V3	9	V3	90	109.47	90
7	P 2/m	12	V3	9	V3	90	109.47	90
8	C 2/m	12	V3	9	V3	90	109.47	90

In group C one pattern is allowed in the cation layer with composition $\frac{1}{3}M + \frac{2}{3}\square$, viz., the honeycomb pattern (Fig. 1b). The number of the resulting structures, however, is not limited since the layers can be stacked together in more than one way without violating

TABLE IIB

POSITIONAL PARAMETERS OF THE ${}^{\text{VI}}\text{M}_2\text{X}_3$ -STRUCTURES WITH A C-ANION LATTICE

No.	M	x	y	z	X	x	y	z
1	4c	$\frac{1}{4}$	$\frac{1}{4}$	0	8f	$\frac{1}{8}$	$\frac{1}{12}$	$\frac{1}{8}$
	4e	0	$\frac{1}{12}$	$\frac{1}{4}$	8f	$\frac{1}{8}$	$\frac{5}{12}$	$\frac{1}{8}$
	8f	$\frac{1}{4}$	$\frac{1}{12}$	$\frac{1}{4}$	8f	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{8}$
2	2a	0	0	0	4i	$\frac{1}{4}$	0	$\frac{1}{4}$
	2d	0	$\frac{1}{2}$	$\frac{1}{2}$	8j	$\frac{1}{4}$	$\frac{1}{6}$	$\frac{1}{4}$
	4h	0	$\frac{1}{6}$	$\frac{1}{2}$				
3	16g	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{24}$	16f	$\frac{1}{8}$	$\frac{3}{8}$	$\frac{1}{8}$
	16g	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{5}{8}$	32h	$\frac{1}{8}$	$\frac{3}{8}$	$\frac{1}{24}$
4	4c	0	0	0	8h	0	$\frac{1}{4}$	$\frac{1}{4}$
	4d	0	$\frac{1}{2}$	0	8l	$\frac{1}{4}$	$\frac{1}{2}$	0
	8j	0	$\frac{1}{2}$	$\frac{1}{6}$	16m	0	$\frac{1}{4}$	$\frac{1}{12}$
	8k	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	16m	$\frac{1}{4}$	0	$\frac{1}{8}$
5	8k	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{5}{12}$				
	2e	0	$\frac{1}{4}$	$\frac{1}{4}$	4g	$\frac{1}{4}$	$\frac{1}{36}$	0
	2e	0	$\frac{13}{36}$	$\frac{1}{4}$	4g	$\frac{1}{4}$	$\frac{5}{36}$	0
	2e	0	$\frac{7}{36}$	$\frac{1}{4}$	4g	$\frac{1}{4}$	$\frac{1}{4}$	0
	2e	0	$\frac{7}{12}$	$\frac{1}{4}$	4g	$\frac{1}{4}$	$\frac{5}{36}$	0
	2e	0	$\frac{25}{36}$	$\frac{1}{4}$	4g	$\frac{1}{4}$	$\frac{17}{36}$	0
	2e	0	$\frac{29}{36}$	$\frac{1}{4}$	4g	$\frac{1}{4}$	$\frac{7}{12}$	0
	2e	0	$\frac{11}{12}$	$\frac{1}{4}$	4g	$\frac{1}{4}$	$\frac{25}{36}$	0
	2f	$\frac{1}{2}$	$\frac{1}{12}$	$\frac{1}{4}$	4g	$\frac{1}{4}$	$\frac{25}{36}$	0
	2f	$\frac{1}{2}$	$\frac{5}{12}$	$\frac{1}{4}$	4g	$\frac{1}{4}$	$\frac{11}{12}$	0
	2f	$\frac{1}{2}$	$\frac{9}{12}$	$\frac{1}{4}$				
2f	$\frac{1}{2}$	$\frac{31}{36}$	$\frac{1}{4}$					
2f	$\frac{1}{2}$	$\frac{35}{36}$	$\frac{1}{4}$					
6	1b	0	$\frac{1}{2}$	0	2m	$\frac{1}{4}$	0	$\frac{1}{4}$
	1c	0	0	$\frac{1}{2}$	2n	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$
	1d	$\frac{1}{2}$	0	0	4o	$\frac{1}{4}$	$\frac{1}{6}$	$\frac{1}{4}$
	1h	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	4o	$\frac{1}{4}$	$\frac{2}{9}$	$\frac{1}{4}$
	2i	0	$\frac{1}{6}$	0	4o	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{4}$
	2i	0	$\frac{5}{18}$	0	4o	$\frac{1}{4}$	$\frac{4}{9}$	$\frac{1}{4}$
	2i	0	$\frac{7}{18}$	0	4o	$\frac{1}{4}$	$\frac{1}{18}$	$\frac{1}{4}$
	2j	$\frac{1}{2}$	$\frac{1}{3}$	0	4o	$\frac{1}{4}$	$\frac{1}{6}$	$\frac{1}{4}$
	2k	0	$\frac{1}{9}$	$\frac{1}{2}$	4o	$\frac{1}{4}$	$\frac{5}{18}$	$\frac{1}{4}$
	2k	0	$\frac{2}{9}$	$\frac{1}{2}$	4o	$\frac{1}{4}$	$\frac{7}{18}$	$\frac{1}{4}$
2k	0	$\frac{4}{9}$	$\frac{1}{2}$					
2l	$\frac{1}{2}$	$\frac{1}{18}$	$\frac{1}{2}$					
2l	$\frac{1}{2}$	$\frac{1}{6}$	$\frac{1}{2}$					

TABLE IIB—continued

No.	M	x	y	z	X	x	y	z	
7	1b	0	$\frac{1}{2}$	0	X Identical to No. 6 M	x	y	z	
	1c	0	0	$\frac{1}{2}$		x	y	z	
	1d	$\frac{1}{2}$	0	0		x	y	z	
	1h	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$		2i	0	$\frac{1}{6}$	0
	2i	0	$\frac{5}{18}$	0		2i	0	$\frac{7}{18}$	0
	2j	$\frac{1}{2}$	$\frac{1}{3}$	0		2j	$\frac{1}{2}$	$\frac{1}{6}$	0
	2j	$\frac{1}{2}$	$\frac{2}{9}$	0		2j	$\frac{1}{2}$	$\frac{4}{9}$	0
	2k	0	$\frac{1}{3}$	$\frac{1}{2}$		2l	$\frac{1}{2}$	$\frac{1}{18}$	$\frac{1}{2}$
	2l	$\frac{1}{2}$	$\frac{1}{6}$	$\frac{1}{2}$					
	8	2b	0	$\frac{1}{2}$		0	4i	$\frac{1}{4}$	0
2c		0	0	$\frac{1}{2}$	8j	$\frac{1}{4}$	$\frac{1}{6}$	$\frac{1}{4}$	
4g		0	$\frac{1}{6}$	0	8j	$\frac{1}{4}$	$\frac{2}{9}$	$\frac{1}{4}$	
4g		0	$\frac{5}{18}$	0	8j	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{4}$	
4g		0	$\frac{7}{18}$	0	8j	$\frac{1}{4}$	$\frac{4}{9}$	$\frac{1}{4}$	
4h		0	$\frac{1}{3}$	$\frac{1}{2}$					
4h		0	$\frac{4}{9}$	$\frac{1}{2}$					

the restrictions. In a cubic close-packed lattice the location of the triangular nets is not uniquely defined; perpendicular to each body-diagonal of a face-centered cube a series of triangular nets can be found. If one of these series of cation layers belongs to group C, having a honeycomb pattern in the layers of composition $\frac{1}{3}M + \frac{2}{3}\square$, the other series of cation layers can belong to group A or group B, but never to group C. The proof is very simple: a second series of cation layers intersects the first series; the layers of composition M and $\frac{1}{3}M + \frac{2}{3}\square$ contribute equally to each cation layer in the second series; therefore, each new cation layer is at least for one half-filled with cations. Thus a study of group C is superfluous: its structures are either derived in groups A and B or discarded when they overstep the volume limit.

h-Stacking

In group C only the honeycomb pattern is allowed in the cation layer with composition $\frac{1}{3}M + \frac{2}{3}\square$. The number of resulting structures, however, is not limited. Being interested in ABX_3 compounds we did not set bounds to the number of possibilities at this stage.

In group A the only possible pattern is the honeycomb pattern of $\frac{2}{3}M + \frac{1}{3}\square$. As to the

number of resulting structures the same arguments count as for group C. The anion polyhedra in groups A and C are *HP* and *HM*, respectively. The structure of Al_2O_3 , Cr_2O_3 , etc. (10), belongs to group A, whereas both Cr_2S_3 (11) structures belong to group C. The low temperature modification of $CrCl_3$ (9) is obtained when cations and vacancies in the six-layer structure of Cr_2S_3 are interchanged.

In group B the anion polyhedra *HP* and *HM* occur simultaneously. On the grounds of our restrictive application of the rule of parsimony this group has to be excluded.

As regards the *c-h* stackings of anion layers no structures exist fulfilling the condition that all anions are to have the same polyhedron shape.

Derivation of ${}^VI A {}^VI B X_3$ Structures

In the case that A and B are cations with a different charge, anion surroundings like $3A + B$ violate both Pauling's second and fifth rules. If A and B have an identical charge only the rule of parsimony (or better our restrictive application of this rule) opposes

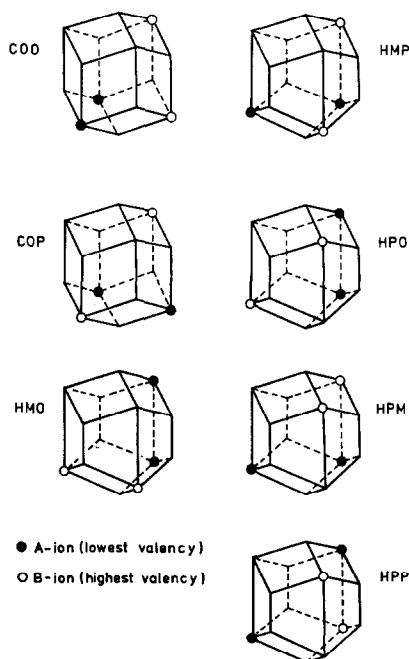


FIG. 3. Space-filling polyhedra for ${}^VI A {}^VI B X_3$.

TABLE IIIA

^{VI}A^{VI}BX₃-STRUCTURES

No.	Anion polyhedron	Space-group	Z	a	b	c
1	COO	F dd2	16	2V2	2	6
2	HMO	P $\bar{3}$ 1m	2	V3	V3	$\frac{2}{3}$ V6
3	HPO	P6 ₃ 22	2	V3	V3	$\frac{2}{3}$ V6
4	HMP	P 312	2	V3	V3	$\frac{2}{3}$ V6
5	HMP	P $\bar{3}$ 1c	4	V3	V3	$\frac{4}{3}$ V6
6	HMP	P $\bar{3}$ 1c	4	V3	V3	$\frac{4}{3}$ V6
7	HMP	R $\bar{3}$	6	V3	V3	2V6
8	HPM	P 312	2	V3	V3	$\frac{2}{3}$ V6
9	HPM	P $\bar{3}$ 1c	4	V3	V3	$\frac{4}{3}$ V6
10	HPM	R $\bar{3}$	6	V3	V3	2V6
11	HPP	P 312	2	V3	V3	$\frac{2}{3}$ V6
12	HPP	R 3c	6	V3	V3	2V6

TABLE IIIB

POSITIONAL PARAMETERS OF THE ^{VI}A^{VI}BX₃-STRUCTURES

No.	A	x	y	z	B	x	y	z	X	x	y	z
1	8a	0	0	$\frac{1}{2}$	8a	0	0	$\frac{1}{12}$	16b	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{12}$
	8a	0	0	$\frac{7}{12}$	8a	0	0	$\frac{11}{12}$	16b	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{5}{12}$
2	1a	0	0	0	2d	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	6k	$\frac{1}{3}$	0	$\frac{1}{3}$
	1b	0	0	$\frac{1}{2}$								
3	2b	0	0	$\frac{1}{4}$	2c	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	6g	$\frac{2}{3}$	0	0
4	1b	0	0	$\frac{1}{2}$	1a	0	0	0	6l	$\frac{1}{3}$	0	$\frac{1}{4}$
	1f	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{2}$	1d	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$				
5	2a	0	0	$\frac{1}{4}$	2b	0	0	0	12i	$\frac{1}{3}$	0	$\frac{1}{8}$
	2d	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	2c	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$				
6	4f	$\frac{1}{3}$	$\frac{2}{3}$	0	2b	0	0	0	12i	$\frac{1}{3}$	0	$\frac{1}{8}$
					2c	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$				
7	6c	0	0	$\frac{1}{8}$	3a	0	0	0	18f	$\frac{1}{3}$	0	$\frac{1}{12}$
					3b	0	0	$\frac{1}{2}$				
8	1a	0	0	0	1b	0	0	$\frac{1}{2}$	6l	$\frac{1}{3}$	0	$\frac{1}{4}$
	1c	$\frac{1}{3}$	$\frac{2}{3}$	0	1f	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{2}$				
9	2a	0	0	$\frac{1}{4}$	4f	$\frac{1}{3}$	$\frac{2}{3}$	0	12i	$\frac{1}{3}$	0	$\frac{1}{8}$
	2d	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$								
10	6c	0	0	$\frac{1}{8}$	6c	$\frac{2}{3}$	$\frac{1}{3}$	0	18f	$\frac{1}{3}$	0	$\frac{1}{12}$
11	1a	0	0	0	1c	$\frac{1}{3}$	$\frac{2}{3}$	0	6l	$\frac{1}{3}$	0	$\frac{1}{4}$
	1d	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$	1f	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{2}$				
12	6a	0	0	0	6a	0	0	$\frac{1}{3}$	18b	$\frac{1}{3}$	0	$\frac{1}{12}$

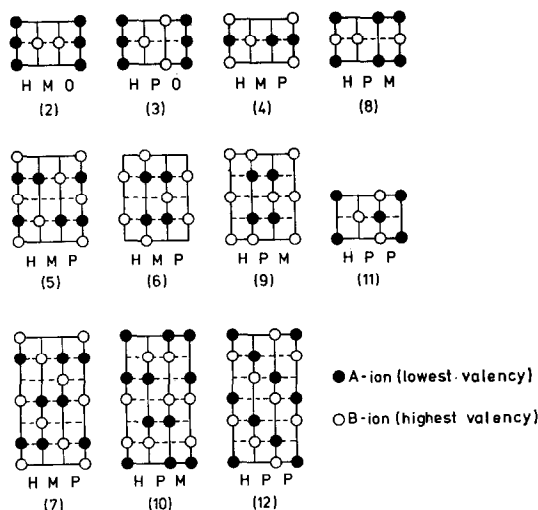


FIG. 4. [110] sections of structures 2-12.

such A-B arrangements. The different anion polyhedra, originated by the ordering of $2A + 2B$ ions over the occupied octahedral sites are shown in Fig. 3. The meaning of the third symbol in the code words can be understood from the discussion about Fig. 2. It is noteworthy that A and B merely represent different cations without further specification. If A and B represent cations with a different valency, the interchange of A and B will cause a change in the contribution of some of the anion polyhedra to the electrostatic energy. In behalf of this situation we have drawn in Fig. 3 the electrostatically more favourable alternative with A representing the cation with the lower valency.

c-Stacking

Just one structure fulfils the condition that all anions are to have an identical polyhedron. This structure can be obtained from M_2X_3 structure No. 3 and described in the "zellengleiche" subgroup F dd2 (Table III, No. 1). All anions have the *COO* polyhedron. We did not find structures in which all anions have a *COP* polyhedron; it can even be demonstrated that such a structure is impossible. This fact also explains the existence of the ReO_3 structure.

h-Stacking

The anion polyhedra *HMO* and *HMP* can occur in group C while *HPM*, *HPO*, and *HPP* belong to group A. Both *HMO* and *HPO* can be realized in only one structure (Table III, Nos. 2 and 3). The remaining anion polyhedra can be realized in more than one structure. By taking into account the most obvious structures another nine structures are obtained (Table III, Nos. 4-12). The [110] sections of structures Nos. 2-12 are shown in Fig. 4.

Discussion of the Results

The restrictive treatment of Pauling's fifth rule encounters a difficulty in the case of the *COP* polyhedron. We have seen that no structure can be devised in which all anions have a *COP* polyhedron. Electrostatically the *COP* polyhedron becomes different from and more valuable than the *COO* polyhedron if A and B have different valencies. The greater the valency difference, the more favourable the *COP* polyhedron is. Since the *HPO*, *HPP*, and *HMP* polyhedra offer reasonable alternatives in the case of a great valency difference, we do not expect the *COP* and the *COO* polyhedron to be realized together. If we try to realize the *COP* polyhedron

together with one of the hexagonal polyhedra in a mixed c - h lattice, we observe that the presence of a *COP* polyhedron always invokes the presence of *COO* polyhedra. These considerations made us omit the diverging derivation of structures with more than one anion surrounding.

Several effects influence the realization of a certain structure: in addition to the Madelung energy and the Born repulsion also the polarization energy can be very important. Other effects may be the presence of free-electron pairs and covalency effects. The magnitudes of such effects are strictly related to the compound under consideration and very difficult to compute, so we will confine ourselves to some qualitative remarks. The Madelung energy of the idealized structures decreases for:

$A^{3+}B^{3+}X_3$ in the series *HPO* (*HPM*, *HPP*);
COO; *HMO* (*HMP*).

$A^{2+}B^{4+}X_3$ in the series *HPO*; *HPP*; *HPM*
(*HMP*); *HMO*; *COO*.

$A^{1+}B^{5+}X_3$ in the series *HPO*; *HPP*; *HMP*;
HPM; *HMO*; *COO*.

In structures Nos. 10 and 12 a further improvement is achieved by deformations that yield a better cation distribution. The cations even approach a body centered cubic (*bcc*) lattice. The A-B type of order in the *HPM* structure (No. 10) corresponds with the NaI (12) type of order whereas *HPP* structure No. 12 is of the CsCl type. These structures can also be deduced by starting with a *bcc* lattice of cations and placing the anions in the tetrahedral interstices. The 24 tetrahedral sites on the SFP of a *bcc* lattice are distributed as six clusters of four sites. In order to avoid short anion-anion distances the four closest neighbours of an occupied site are not allowed to be occupied too. Of the 35 different anion arrangements, providing each cation with six anion neighbours, the one that corresponds with structures 10 and 12 is shown in Fig. 5. In the case of $A^{3+}B^{3+}X_3$ compounds, the Madelung energy favours the distorted structures 10 and 12 over *HPO* structure No. 3. In the case of $A^{2+}B^{4+}X_3$ and $A^{1+}B^{5+}X_3$ compounds, the Madelung energy favours the

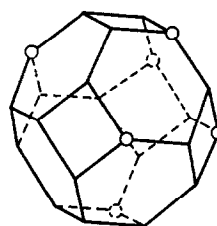


FIG. 5. Space-filling polyhedron of a *bcc* lattice of cations with the anion arrangement, that corresponds to structures 10 and 12.

HPP structure No. 12 increasingly over the *HPM* structure No. 10 but the position of the *HPP* structure with respect to the *HPO* structure No. 3 depends on the extent of the deformations.

Even in the case of oxides and fluorides a considerable contribution from the polarization energy has to be expected for compounds that have cations with different valencies. Polarization energy stabilizes for $A^{2+}B^{4+}X_3$ and $A^{1+}B^{5+}X_3$ compounds the *COO* and *HMO* polyhedra, followed by the *HPM* and *HMP* polyhedra at the cost of the *HPP* and *HPO* polyhedra.

The influence of the Born repulsion can be visualized by considering the ions as hard spheres. In order to reach a minimum of potential energy further distortions have to take account of differences in size between the A and B ions in their relation to one another and to the anions. The *HPM* structure (No. 10) can manage such problems simply by changing the distances between the anion layers.

Our conclusions regarding oxides and fluorides that are devoid of non-ionic effects are: the ilmenite structure No. 10 is to be expected for $A^{3+}B^{3+}X_3$ and $A^{2+}B^{4+}X_3$ compounds; in the case of $A^{1+}B^{5+}X_3$ compounds the *HPP* structure No. 12 is the best provided the polarization energy is not dominating and the radii of the cations are not too different. If the cations have significant different radii the *HPM* structure No. 10 will probably be stabilized. A substantial contribution from the polarization energy might cause the realization of the *HMO* structure No. 2 or the *COO* structure No. 1. Especially in the case of large and/or highly charged anions one should take

account of a considerable contribution from the polarization energy.

Up to now the *HPM* structure No. 10 has been realized in ilmenite, in many other oxides (13) and in $NaMnCl_3$ and $NaCdCl_3$ (3). The *HPP* structure No. 12 has been found in $LiNbO_3$ and $LiTaO_3$ (14). Structure No. 3 (*HPO*) has been reported to be the crystal structure of $LiIO_3$ (15, 16). In this compound the iodine ion has a free electron pair, which accounts for the difference in structure between $LiNbO_3$ and $LiIO_3$. Free electron pairs often cause a deformed six-coordination with three anions at a smaller and three at a larger distance. The resulting coordination can be described as a tetrahedron, constituted by three anions and the electron pair. An example is $CsSnCl_3$ (17) in which compound Sn^{2+} has three nearest anion neighbours. The desired deformations can easily be achieved in the *HPO* structure, in the *HPP* structure however they unavoidably invoke a bad lithium surrounding.

$LiSbO_3$ (18) is reported to adopt a crystal structure in which one anion has a *HPO* polyhedron and two have *HMO* polyhedra. The bad screening of the filled d^{10} core in Sb^{5+} results in a higher effective nuclear charge than Nb^{5+} and Ta^{5+} have. Therefore, the influence of the polarization energy is more important in $LiSbO_3$ than in $LiNbO_3$ or $LiTaO_3$. Recently Goodenough and Kafalas (19) have discussed the observed structure of $LiSbO_3$ in comparison with the *HPP* structure and ascribed it to the covalent contribution to the $Sb-O$ bonds. However, the occurrence of the observed structure is unexpected according to Pauling's fifth rule inasmuch as a structure with all anions in a *HMO* polyhedron is available. $NaSbO_3$ (20) is reported to adopt the ilmenite structure which can be expected on the grounds of the polarization energy and the large radius difference between the sodium and antimony ions. The realization of the ilmenite structure instead of a perovskite-like structure is caused by the contribution of the polarization energy (19). According to Brandwijk and Schippers (2) no favourable structure can be derived from any stacking of AX_3 layers when the contribution of the polarization energy is important and the A ion is

smaller than the X ion. The same arguments hold for $NaBiO_3$ (21).

In the crystal structure of Mo_2S_3 (22) the anions are located on a close-packed lattice with *chh* stacking of the triangular nets. The occurrence of such a structure in which three kinds of anion surroundings are present, viz., three, four, and five coordinated anions, has to be ascribed to metal-metal interactions. These interactions explain the short metal-metal distances in the zigzag metal chains.

So far we have dealt with a close-packed lattice of anions and placed the cations in the octahedral interstices. Considering compounds with increasing r_M/r_X ratio the close-packed anion lattice becomes less and less close-packed. Another kind of structure might then become more favourable. Such a structure can be derived by starting the structure derivation with a close-packed lattice of cations and placing the anions in the tetrahedral interstices. Of the close-packed lattices only the *ccp* lattice is suitable since in the *hcp* and the mixed *c-h* lattices short anion-anion distances always appear. On the SFP of a *ccp* lattice six of the eight available tetrahedral sites have to be occupied by anions to provide each cation with six anion neighbours. The three possible cation surroundings are depicted in Fig. 6. The most isonomous one is 6_p , followed by the 6_m polyhedron. Only one structure exists with all cations in a 6_p polyhedron (Table IV). This structure has been ascribed to Ag_2O_3 (23), Bi_2O_3 (24), $AgSbO_3$ (25), and $PbReO_3$ (26); for the latter two compounds the structure has been derived from the pyrochlore (27) structure that in its turn can be derived from the fluorite (28) structure. The Cu_2O structure (Cu has a $2p$ coordination instead of $6p$) is obtained by interchanging anions and vacancies. The number of structures with all cations in a 6_m or a 6_o polyhedron is not limited by Pauling's rules. Examples of structures with the non-isonomous 6_m polyhedra are, as we expected, only found for anti-compounds: Zn_3P_2 (29) and α, γ $ZnCl_2$ (30, 31) (in the structures of $ZnCl_2$, 2_m instead of 6_m coordinations occur because the cations and vacancies have interchanged relative to M_3X_2). To our knowledge structures with 6_o

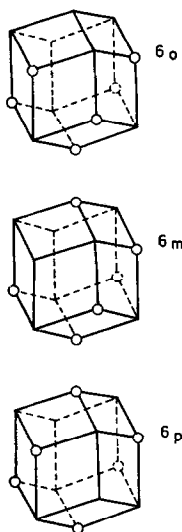


Fig. 6. Space-filling polyhedra of a *ccp* cation lattice with anion arrangements 6_o , 6_m , and 6_p .

polyhedra have not been reported as yet, but in SiSi_2 the 2_o polyhedron has been realized.

Dealing with these fluorite-derived structures we notice the appearance of a structure that combines 6_p and 6_m polyhedra in the ratio $1 \times 6_p + 3 \times 6_m$; for example in Mn_2O_3 , Y_2O_3 , etc. (32). The sole A_3BX_6 compound, reported to have this structure is Cu_3TeO_6 (33). The structure does not obey Pauling's fifth rule. Nevertheless, the realization of this structure can easily be understood: in the structure with all cations in a 6_p polyhedron the anion distribution cannot be improved by moving them towards the vacancies. Related to the anion distribution is the surrounding of the cation: 6_p is an octahedron, squashed along the threefold axis. An improvement of the anion distribution leads to a less squashed octahedron. If one tries to de-

sign a structure containing 6_p and 6_m polyhedra in which such improvements of the anion distribution are possible and the number of 6_p polyhedra with respect to the number of 6_m polyhedra is a maximum, the Mn_2O_3 structure is immediately obtained.

Evaluation

The procedure devised in order to obtain the complete set of structures that meet the imposed requirements could successfully be applied to the ordering of cations and vacancies over the octahedral interstices in close-packed lattices. The application of the rule of parsimony makes a correct structure prediction possible in the majority of the investigated cases. The Mn_2O_3 structure forms an exception but can be understood on the grounds of a better anion distribution. We are not able to explain the second exception, viz., the LiSbO_3 structure.

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TABLE IV

${}^{\text{VI}}\text{M}_2\text{X}_3$ -STRUCTURE WITH A C-CATION LATTICE

Space-group: $\text{Pn}3\text{m}$
$Z = 2$
$a = a_0\sqrt{2}$
$M: 4b\ 0\ 0\ 0$
$X: 6d\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$
Cation polyhedron: 6_p

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