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Classification, Representation and Prediction of Crystal Structures of Ionic Compounds

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The aim of this paper is to show that with the aid of a qualitative model of ionic bonding, including polarizability, many crystal structures, mainly of halides and chalcogenides, can be explained or even predicted.

Polarization of O^{2-} and F^- ions may be neglected unless these ions have very small, or small and highly charged cation neighbours. The polarizability of a few large cations is assumed also to play a rôle.

The cation polyhedron may have a shape different from that expected for the ionic model as a result of nonionic bonding types; the theoretical shapes can be used empirically in the structure prediction.

Section I deals with the background of this ionic picture. Section II deals with the sharing of corners and/or edges and/or faces of cation polyhedra. Pictures of various types of sharing polyhedra are given, with octahedra as an example. An explanation is offered for Wadsley's rule of maximal edge-sharing in his shear-structures, which seemed to violate Pauling's third rule.

In Section III a classification of crystal structures is given in plots of cation coordination versus stoichiometry, expressed as the ratio nr. anions/nr. cations, for simple compounds and complex anions. The average cation coordination is plotted against stoichiometry if one is interested in the changes of structure under high pressure.

Section IV deals with the description of crystal structures by space-filling polyhedra, which are an aid towards finding relationships between structures and towards predicting new ones.

Simple structures with close-packed anions or cations are explained by the ionic model using these SFP in Section V.

In Section VI some structure predictions (e.g., of Sc_2S_3, Li_2CuO_2, $SrCuO_2$, Sr_2CuO_3, and $SrCu_2O_2$) are discussed, and some results of recent structure determinations carried out in the author's laboratory (of the abovementioned Sr–Cu–O–compounds, β-$BaPdO_2$, $MgAl_2S_4$, $FeAl_2S_4$ and $MgGa_2S_4$) are given.

I. Introduction

It is common practice to describe and classify ionic compounds by the number of anions surrounding the different cations, which we shall call the *cation coordination number*. This is due to the fact, which has been noted long ago a.o. by Bragg (*1*), (*2*), that the cations in most crystal structures are surrounded in a more regular way by anions than the anions by cations.

A purely electrostatic picture involving only Coulomb and Born energies does not, however, explain this result.

When we consider for the present only isolated polyhedra of anions X around a cation A, or vice versa, a simple calculation of the Coulomb energy for a hard-sphere model will give the following rules:

1. The cation–anion distance A–X tends to be constant as much as possible and to be equal to the sum of cation and anion radius.
2. The shortest anion–anion distances (X–X), or cation–cation distances (A–A), respectively, tend to be a maximum, and as equal as possible as a result of electrostatic repulsion.

These distances (X–X or A–A) are equal only for all polyhedra having equilateral triangles as faces. For those with 5, 7, 8, 9, and 10 vertices the A–X distances are very unequal; only for those with 4, 6, and 12 vertices the first and second rule are strictly obeyed. These polyhedra are called the regular tetrahedron, octahedron, and icosahedron, respectively. The other polyhedra mentioned will be deformed to obtain the best compromise between rules 1 and 2. Alternatively, other polyhedra having triangular and square faces can be formed, and similarly distorted. The polyhedra best conforming to the two above-mentioned rules we shall call isonomous.[†]

The reasons why polyhedra of anions around a cation (the cation–polyhedra) are often found to be more isonomous than the polyhedra of cations around an anion (the anion polyhedra) are discussed now.

Almost all cations are smaller than even the smallest anions (F^- and O^{2-}), so that not only the number of anions that can be placed around these cations is determined by the radius ratio r_A/r_X,[‡] but also the shape of the anion polyhedron is determined by steric factors. In a model involving Born repulsion this means that the Born repulsion between the anions is more important than the electrostatic repulsion between them.

When, on the other hand, an anion is surrounded by smaller cations, Born repulsion between the cations becomes less important with respect to the electrostatic repulsion between them. Less isonomous polyhedra, i.e., varying X–X distances, even for constant A–X distances, therefore, become, at least geometrically, possible. The Madelung constant, however, will thereby be lowered, but this effect is smaller, as the central ion is larger and as the number of surrounding ions is lower.

We shall write a binary compound as ${}^{a}A_{m}^{r+}\,{}^{x}X_{p}^{t-}$ in which a and x represent the cation and anion coordination numbers (CN), respectively.[§] Compounds that can be treated as ionic compounds have low-anion charge t (1 and 2, sometimes 3 or even 4). Since $rm = tp$, the number of compounds with $p > m$ far outweighs the number for which $p < m$. Therefore, since $am = xp$, the anion CN's are lower than the cation CN's much more often than higher. This means that in many structures the low anion CN makes the expenditure in energy smaller, so that a gain in energy for nonisonomous anion surrounding (e.g., the polarization energy) can outweigh it more easily.

When an ion is surrounded nonisonomously, in particular when, e.g., the charge of the cations on one side of an anion is much higher than of those on the other side, a gain in energy can be obtained by the polarization energy $E_{\text{pol}} = z_A z_X \alpha\, e^2/(r_A + r_X)^4$ in which z_A and z_X are the cation and anion charges, α is the polarizability of the anion and r_A and r_X the cation and anion radius. The same relation holds when the cation is polarized by the surrounding anions; α then denotes the cation polarizability. The value of α is negligible for all small cations with respect to the values for all anions and a few large cations Cs^+, Tl^+, K^+, Pb^{2+}, Ba^{2+}, etc. The values of the polarizabilities of F^- and O^{2-} are assumed to be lower than for all other anions (*3*). Less regular, i.e., more one-sided surrounding of the anion by cations (c.q. of the very large cations by F^- or O^{2-}) causes an increase in the polarization energy term, which can outweigh the opposite effect of the increased electrostatic cation–cation (c.q. anion–anion) repulsion.

In each column of the periodic table α has been found to increase with r_X, and the least isonomous coordinations are, therefore, found for the largest anions. The gain in lattice energy caused by polarization is also greater, the smaller the cations and the higher their charge, or, if more than one type of cation is present, e.g., A^{r+} and B^{s+}, the larger the difference between r and s and between r_B and r_A. A cation with very high α, e.g., Cs^+, can even be polarized by small anions, like O^{2-}, when the coordination of the cation is low. Consequently, in Rb_2O, with anti-CaF_2 structure Rb still has a regular 4-coordination, but Cs_2O has a distorted $CdCl_2$ structure with very one-sided 3-coordination of the Cs^+ ion.

If the number of cations surrounding an anion is large, electrostatic repulsion between the cations can more effectively prevent the polarization energy from causing irregular surrounding of the anion. This occurs if in a compound A_mX_p p/m is not much different from unity and if the cation coordination is not low (since $rm = tp$).[†]

Thus, the polarizability of the anions is the second reason for the greater isonomy of the cation polyhedra, as often found, and the above-mentioned steric of the Born repulsion between the anions of the cation polyhedron the third. When, however, the anion polarizability is not large, as in F^- and O^{2-}, and the cations are neither very small (as H^+), nor small and highly charged, (as Si^{4+} and W^{6+}), we should expect isonomous surrounding of the anions also, as is found almost without exception.

If a crystal structure is not known the requirements given above in many cases lead to a correct prediction of the crystal structure type, starting from assumed cation coordinations. These are derived from the radius ratio rule, which must not be applied in

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[†] From νεμεσϑαι, medium form of νεμειν, to be spaced out.

[‡] This is Pauling's first rule, which says that the ratio of cation to anion radius determines the cation coordination number.

[§] In the following, these CN's will be indicated by a Roman superscript to the *left* of the symbol of the element.

[†] It may be noted that often when $p < m$, the anion coordination is found to be even more regular than the cation coordination. Such compounds A_mX_p often have antistructures of known A_pX_m compounds.

too rigorous a manner (see covalent bonding in this section).

We now wish to say a few words about the bonding and interaction types so far not mentioned.

We shall not discuss structures containing permanent dipoles (OH^-, H_2O, etc.) in this paper, so that their interactions with ions, with each other and with induced dipoles are not discussed here (*4*). Only the London–van der Waals interaction remains to be discussed. For a pair of ions (1 and 2) this can be taken to be $[(3/2)I_1 I_2/(I_1 + I_2)]\cdot\alpha_1\alpha_2(r_1 + r_2)^{-6}$, where I_1 and I_2 are the ionization energies of ions 1 and 2, respectively (*5*). Since the decline with distance is very rapid, all except nearest-neighbour interactions, i.e., in ionic compounds between A^{r+} and X^{t-}, are usually neglected. The London-van der Waals interaction is thought to be the cause of the increased coordination of the largest metal ions (with high α) in the chlorides with respect to the fluorides, contrary to what is expected from the radius ratio rule. If we compare the structure of $^{\mathrm{VI}}CsF$, with that of $^{\mathrm{VIII}}CsCl$, that of $^{\mathrm{VIII}}BaF_2$, $^{\mathrm{VIII}}PbF_2$, $^{\mathrm{VIII}}CaF_2$ and $^{\mathrm{VIII}}CdF_2$ with the same structure with those of $^{\mathrm{IX}}BaCl_2$, $^{\mathrm{IX}}PbCl_2$, $^{\mathrm{VI}}CaCl_2$ and $^{\mathrm{VI}}CdCl_2$, we see that the large ions Cs^+, Ba^{2+}, Pb^{2+} in the chlorides have higher CN, Cd^{2+} and Ca^{2+}, however, a lower CN.

It seems at present difficult to say whether the London-van der Waals interaction due to anion-anion contacts plays a rôle in determining these structures, and structures with polarizable anions in general. This is often assumed in the layer and chain structures like $^{\mathrm{VI}}CdCl_2$, $^{\mathrm{VI}}CrCl_3$, $^{\mathrm{VI}}TiI_3$, $^{\mathrm{IV}}HgI_2$, $^{\mathrm{IX}}PbFCl$ etc. It may be noted that in CaF_2 and CdF_2 F^- has six F^- neighbours but that both in $CaCl_2$ and in $CdCl_2$ the Cl^- ions have twelve Cl^- neighbours.

When metallic conductivity is present in compounds A_mX_p, the structure may still be that predicted by the ionic model, provided there is a great difference in electronegativity between A and X. It is found that often the anion coordination is then more isonomous, probably because polarization cannot occur as a result of a shielding effect of the conduction electrons.

Covalent bonding plays an important rôle in many compounds that we shall treat as ionic. Since ab initio calculations of bonding energies are very complicated the ionic model has its merits for calculating lattice energies, but this model should not be modified for covalency, because its success is due only to the fact that the covalent part of the bonding energy is replaced by electrostatic energy. Ionic models in which use is made of locally diminished charges because of local covalent bonding should be avoided.

The shape of the cation polyhedra may be influenced by all bonding effects of a nonionic nature. These may be covalent bonding, ligand-field effects for transition ions, or the presence of electron lone pairs, such as occur in ions with a $s^2p^6d^{10}s^2$ outer electron configuration. The shape of the coordination polyhedron may be the same as would result from ionic bonding, or different. In the former case, the coordination number may either be the same as would result from the radius ratio rule, as e.g., in $^{\mathrm{IV}}BeO$, or not, as in the isostructural $^{\mathrm{IV}}ZnO$. Similarly, the linear $F^{\mathrm{II}}HF^-$ ion in e.g., $NaHF_2$ can be understood with the ionic model, assuming the radius ratio r_{H+}/r_{F-} to be practically zero. The linear group O^{2-}–$^{\mathrm{II}}Cu^+ - O^{2-}$ occurs a.o. in $AlCuO_2$, isostructural with $NaHF_2$. It cannot be explained with the ionic model, since the radius ratio rule would require a 6-coordination for Cu^+. The linear coordination of Cu^+ in Cu_2O has been described as being due to *d–s* hybridization (*6*), but another explanation of the structure, based on a Cu–Cu interaction, has been put forward (*7–9*).

If the shape of the coordination polyhedron is different from that expected for the ionic model as, e.g., for the square coordination of Cu^{2+}, Pd^{2+} etc., we do not know the stabilization energy which makes the structure different from that expected for ionic bonding. We can only predict structures for the extreme cases where this stabilization is either dominant or absent.

For ions with lone electron pairs we can leave one ligand site per lone pair empty; usually the electron pair takes up more space than the anions (*10*). The radius ratio rule seems to have some validity here also. The knowledge of the structure a compound would have if the structure were ionic is useful.

We wish to quote van Arkel (*11*):

> "When we assume that the metal compounds are ionic compounds, it must be possible to predict their crystal structures. The differences (between the predicted structures and those found) that we encounter in some cases, teach us something about the influence of types of bonding other than purely ionic. . . ."

Authors sometimes express surprise at finding structures that can be derived with the ionic model in a simple way, whereas those that can "teach us something about the influence of types of bonding other than purely ionic" are accepted as normal.

The principles outlined above are mainly due to van Arkel (7), who contributed greatly to the understanding of the properties and structures of inorganic compounds. It is our intention to show that this very simplified picture of ionic bonding leads to a surprising number of correct structures. For close-packed and other simple anion lattices the number of likely structures is limited and can even be constructed in a systematic way.

The predictions of new structures along these lines include structures having cations in, e.g., 7- and 5-coordinations, which coordinations have originally been regarded as typical for nonionic bonding.

We shall pay some attention to the possibilities of sharing corners, edges and faces in Section II. In our opinion, descriptions given before (*12*), (*13*) are ambiguous, and the only good classification of the various possibilities of sharing is by drawing the polyhedra, indicating the elements shared.

In Section III an example is given of a classification of inorganic compounds (not containing organic ligands) according to stoichiometry and cation coordination(s).

The need was felt for a method of drawing small parts of the lattice, showing at least one central cation and the surrounding anions (and vice versa), which nevertheless contains all information on the complete structure. This method is described in Section IV, and use is made of it in Section V, which is devoted to discussion of known structures of simple compounds. In Section VI some structures predicted by us are described.

II. Corner-, Edge- and Face-Sharing of Polyhedra

When in an ionic compound AX_p the cation coordination is equal to p, we shall call this a molecular compound or ortho-compound. Similarly, if in a compound $A_mB_nX_p$ the coordination of B is equal to p/n we call the compound an ortho-compound, according to van Arkel's definition (*14*), and the ion $BX_{p/n}$ an ortho-ion.

Usually this name is only used if the charge of B is higher than that of A, or when its radius is smaller. According to these two restrictions, however, the spinel $^{VI}Ni_2{}^{IV}GeO_4$ would contain the complex ion GeO_4^{4-}, but the spinel $^{VI}Al_2{}^{IV}ZnO_4$ would not contain the complex ion ZnO_4^{6-}. $^{VIII}Ca_3{}^{VI}Al_2{}^{IV}Si_3O_{12}$, with garnet structure, contains ortho-ions $^{VI}AlO_6$ as well as $^{IV}SiO_4$.

When in a compound AX_p the cation coordination is larger than p, sharing of corners and/or edges and/or faces of the cation coordination polyhedron must occur. This may result in structures containing finite polymeric molecules, or in A–X networks which are extended in one, two or three dimensions. The latter three types of structures are called chain, layer and framework (*15*) structures, respectively. In the vapour, these networks must break up to give finite molecules with necessarily lower metal coordination, or the compounds will decompose.

Similarly in a compound $A_mB_nX_p$, if the coordination of B is larger than p/n the polyhedra around B have to share corners and/or edges and/or faces. We will call the group B_nX_p a complex ion, irrespective whether it is an ortho-ion or forms finite polymeric ions or one-, two-, or three-dimensional networks. It has been proved useful, a.o. for comparison with simple binary compounds, to have a look at complex ions B_nX_p even if B is larger, or has lower valency, than A.

Sometimes, X ions are present that have no B neighbours. In that case the formula is written $(AX_x)BX_{p-x}$;† BX_{p-x} is then the complex ion. An example of this situation is the compound $(TiO)^{2+}$ SO_4^{2-}, which of course does not contain SO_5^{4-} ions, but contains one O^{2-} ion not coordinated to the S^{6+} ion. The compound $^{VII}La_2{}^{V}TiO_5$ does not, as might have been thought, contain an ortho-ion $^{V}TiO_5^{6-}$, but chains $^{V}TiO_4^{4-}$ (*16*); the formula is thus written $(^{VII}La_2O)^{V}TiO_4$. Especially in chain and layer compounds large deviations from Pauling's second rule occur; this rule says that the charge of the anion equals the sum of the bond strengths of the anion to its nearest neighbours. (Bond strength = charge cation/its coordination number). This is, however, the only rule we have, short of calculating the Madelung constant, for deciding which combination of valencies will be most stable in a certain structure.

Pauling's third rule says that in a truly ionic model corner sharing gives a more stable structure than edge sharing, and this a more stable structure than face sharing, all for the same stoichiometry. This is corroborated by experiment as long as polarization effects can be neglected.

The Figs. 1–3 together show, for regular octahedral coordination as an example,‡ some possibilities for the sharing of corners and/or edges and/or faces of a cation polyhedron. We shall call such figures "sharing polyhedra." We have restricted ourselves to some simple stoichiometries M_2X_p where p is a whole number and down to $p = 4$ as a minimum. Even for such simple stoichiometries two or more sharing polyhedra (here octahedra) can occur in one structure, e.g., in the "hexagonal $BaTiO_3$" or $RbNiF_3$ structure (Fig. 3). For more

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† The parentheses indicate that only the BX_{p-x} part of the formula belongs to the complex ion.

‡ Similar figures can be given for all other coordination polyhedra. These will be published elsewhere by the author.

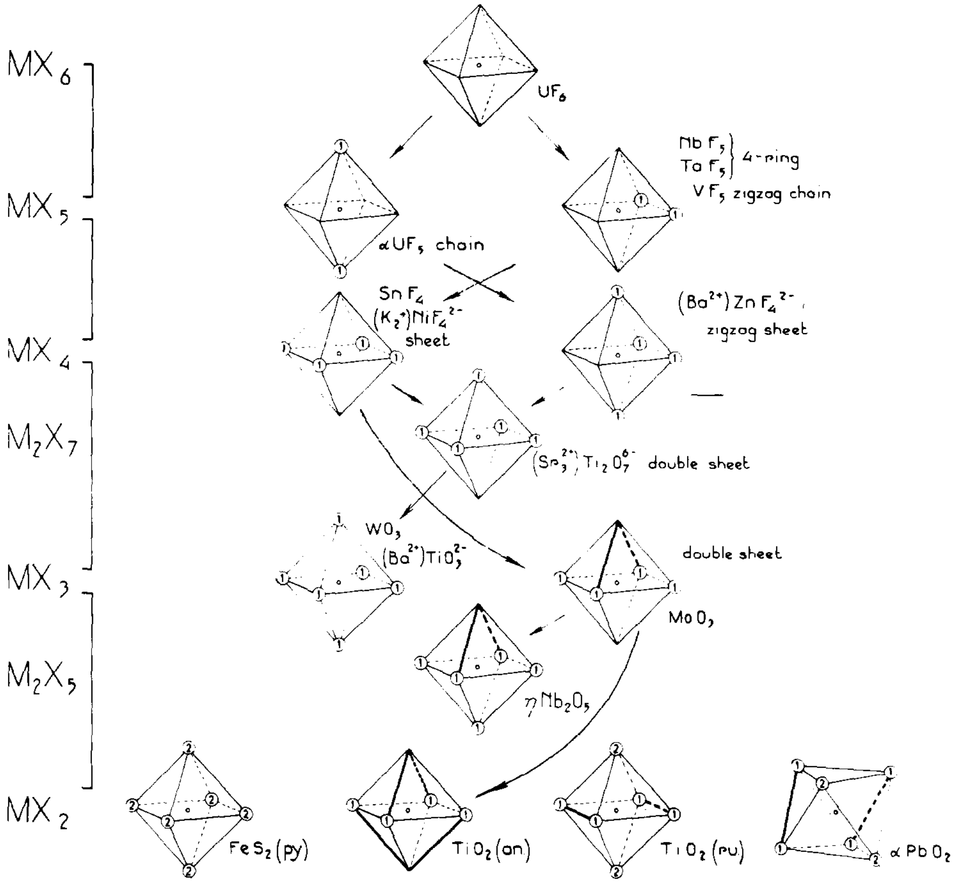

FIG. 1. Some sharing octahedra for ionic compounds from MX_6 to MX_2. Mainly corner sharing. (① corner once shared; ② corner twice shared; / edge once shared.)

complicated stoichiometries the occurrence of different sharing polyhedra (octahedra) is the rule rather than the exception, as e.g., in the shear structures found by Wadsley et al. (*17*) and (*18*). The stoichiometry for the different sharing polyhedra† in one structure is very often different, even in the titanium bronzes, $(Na_x)TiO_2$, in which the over-all stoichiometry of the complex ion (TiO_2) is simple.

It is possible to make the "family tree" of sharing polyhedra complete, with three "parents," with one corner, one edge and one face, respectively, and to extend it to more "generations," for regular octahedra down to the stoichiometry ^{VI}MX. This does not seem useful, however, for finding possible crystal structures, because it seems difficult to see whether a certain sharing polyhedron (octahedron) can occur alone, or if not, with which other(s) it should be combined to give a possible structure.

We shall now discuss Figs. 1–3. Starting from molecules MX_6 (Figs. 1, 2), these can occur for fluorides and chlorides. The packing of the molecules to a molecular lattice may still be accomplished in various ways, and will generally be different for fluorides and chlorides. The sharing of one corner leads to a stoichiometry $MX_{5+1/2} = M_2X_{11}$, which occurs in the ion $M_2OCl_{10}^{4-}$ in the compounds $K_4(M_2OCl_{10})$, where M = Ru^{4+}, Os^{4+}, Re^{4+} or W^{4+}. In this ion O^{2-} occupies the bridging position, which is in agreement with what would be expected for the ionic model.

The stoichiometry $MX_{4+2/2} = MX_5$ is obtained by sharing two corners or one edge. An electrostatic model leads to the linear chain of α-UF_5 and of $WOCl_4$ (Fig. 1) only, since the sharing of two adjacent corners (Fig. 1) leads to a lower Madelung constant. The occurrence of the octahedron sharing two adjacent corners in the zig-zag chains of VF_5, etc., and in the square tetrameric ring of NbF_5 and TaF_5 cannot be explained with the ionic model,

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† The stoichiometry of a sharing polyhedron is read off from the picture by counting each vertex for $1/(v + 1)$ part if the number of sharing elements at that vertex = v.

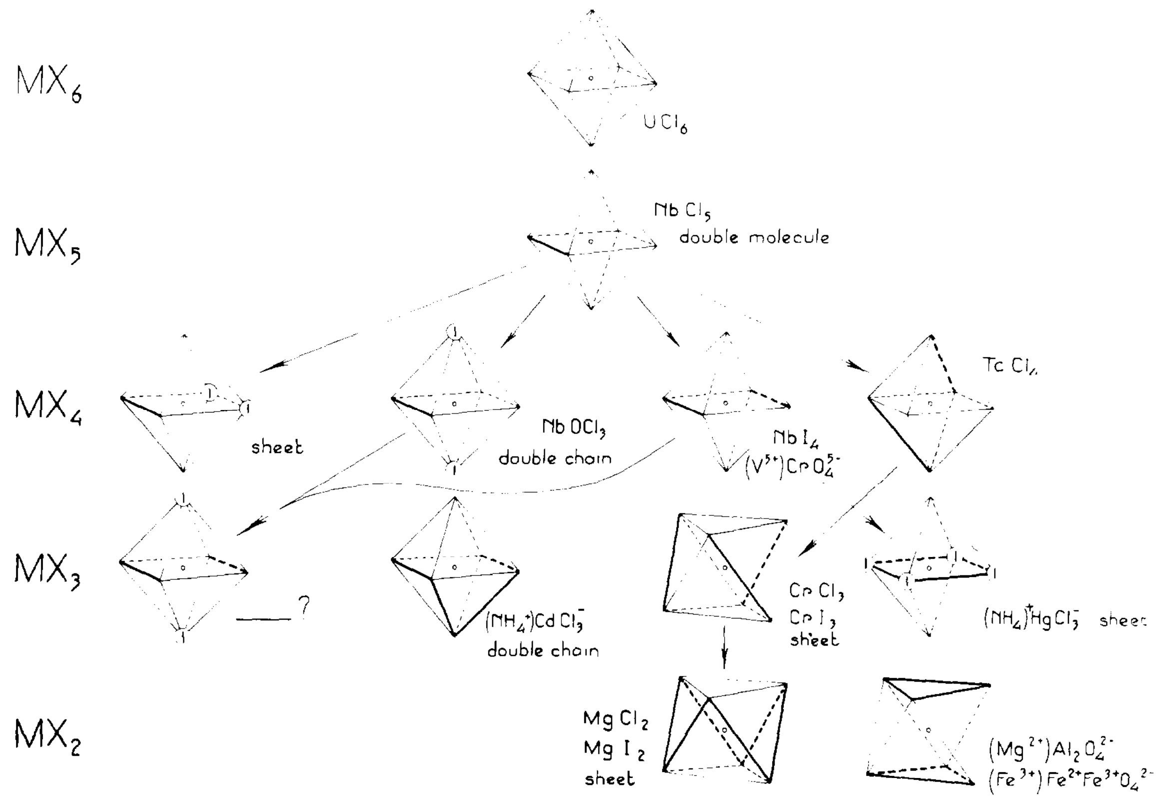

FIG. 2. Some sharing octahedra for compounds with polarizable anions and also for oxidic complex ions. Mainly edge-sharing.

unless the slight distortions from the ideal model considered here would cause a sufficient gain in polarization energy.

The sharing of one edge (Fig. 2) leads to the double molecule of $NbCl_5$ (Nb_2Cl_{10}) which leads to an even lower Madelung constant, but here the two bridging Cl^- ions can be strongly polarized by the two Nb^{5+} ions, which gain in energy can compensate for the higher electrostatic energy with respect to the MF_5 fluoride structures.

When we further compare Figs. 1, 2, and 3, we see that also for stoichiometry $MX_4 = MX_{2+4/2}$

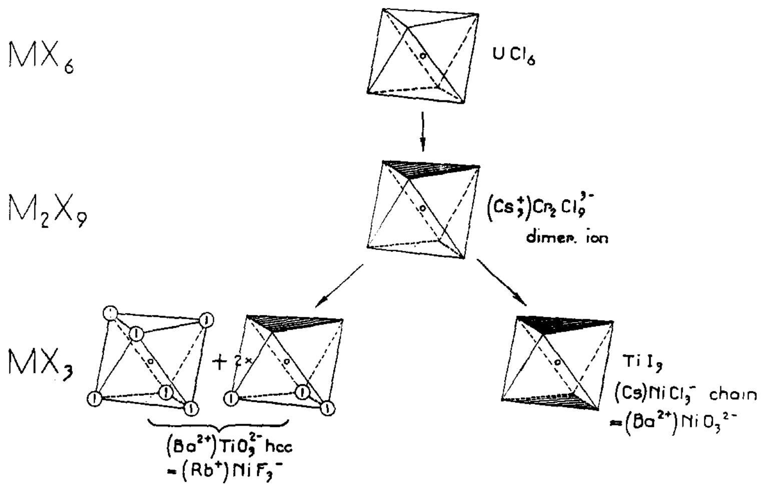

FIG. 3. As Fig. 2, face sharing first.

fluorides like SnF_4 have four corners shared, whereas the few other structures of the tetrahalides which are known, NbI_4 and $TcCl_4$, have two edges shared.

Similarly ReO_3, ScF_3, WO_3 and all trifluorides have six shared corners (Fig. 1). In most of these structures the angle M–X–M is <180°, because the high charge ratio causes the polarization of O^{2-} and F^- to be noticeable.† On the other hand, in the structures of the trichlorides like $CrCl_3$ and the tri-iodides like CrI_3, the octahedra share three unconnected edges (Fig. 2), in the structure of β-$TiCl_3$ and TiI_3 two unconnected faces (Fig. 3). A notable exception is the structure of MoO_3 (Fig. 1), where edge-sharing occurs, giving a double layer structure, where it might have had the WO_3 structure. It is in such cases that one should look for nonionic bonding effects.

In Fig. 2, where more edge sharing occurs, no simple oxide compounds are found, but we have given some examples of oxidic complex ions, that do occur with more edge-sharing than is necessary. This is easily understood, since the cations outside the complex ion considered do contribute to the charge distribution, even if they are larger and/or have lower charge. In a complex ion containing O^{2-} or F^- ions most often more edges and/or faces are shared than in the corresponding simple oxide, in order to make room for the other cation(s).‡

When the anion/cation ratio is reduced to $2\frac{1}{2}$, some vertices must be shared by more than two octahedra, e.g., giving a formula $MX_{3/3+3/2}$. The sharing of a vertex by three octahedra can be achieved by sharing with two octahedra by corners (double corner sharing, indicated by ② in the figures) or by one corner and one edge, by one corner and one face, by two joined edges, by one edge and one face, or by two faces, joined at the vertex. Double corner sharing leads to octahedra in different orientations, and there is not a large number of geometrical possibilities for doing this.§

Therefore, in oxides and fluorides for stoichiometries MX_p with $p < 3$ we should expect vertices to be shared by corner- and edge-sharing more often than by double corner sharing. For MX_p with $p < 2$, increased sharing is achieved by edge-sharing only, because triple corner sharing to join four octahedra seems to be impossible.

Not many structures of oxides or fluorides M_2X_5 with octahedral cation coordination are known. The sharing polyhedron of Fig. 1 occurs alone in three different structures: in V_2O_5, if idealized to give V^{5+} an octahedral coordination (*22*), in one of the forms (η) of Nb_2O_5 (*23*) and in the structure proposed for one form (α) of Ta_2O_5 (*24*). A structure with three singly shared and three doubly shared corners is not known.

For MX_2 stoichiometry, six corners doubly shared are present in the pyrites and marcasite structures of e.g., FeS_2, but these structures cannot be those of a compound $M^{4+}X_2^{2-}$ because of the small S–S separation in the ion $(S_2)^{2-}$. The known oxides and fluorides $M^{VI}X_2$, therefore, have edge-sharing (Fig. 1) but not maximal edge-sharing, as in $MgCl_2 = CdCl_2$, MgI_2, etc. (Fig. 2). The fact that double corner sharing must given octahedra in different orientations is the basis of the principle of maximal edge-sharing formulated by Wadsley for the numerous compounds in the systems WO_3–Nb_2O_5 and TiO_2–Nb_2O_5. In these series the stoichiometry, i.e., the anion–cation ratio, varies by as little as 0.1% from one compound to another. By extremely careful X-ray work (*25*)–(*33*), later supplemented by an elegant electron microscopy technique combined with electron diffraction (*34*)–(*37*), several structures could be solved in his laboratory.

From the structural principles found, Wadsley could predict many new compositions which were afterwards found to exist, and the structures of which conformed to the predicted ones. They consist of blocks of octahedra, which have one axis vertical, joined by six corners as in ReO_3, which blocks are finite in two dimensions and infinite in the third direction, which we call the vertical direction. These blocks are joined to other blocks at their vertical sides by the sharing of nonhorizontal octahedron edges, thus placing the "other" blocks half the height of an octahedron below the first-mentioned ones. Thus, there are two sets of perpendicular "shear planes" which connect the blocks.

We saw it is the the stoichiometry that determines the amount of sharing, and since in all these† structures the octahedra have parallel orientation, and taking into account that double corner-sharing and also face-sharing† leads to nonparallel orientation, the stoichiometry determines the amount of edge-sharing. The other blocks may be either identical with the original ones, or different. In the struc-

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† Van Arkel (*19*) remarked that WO_3 has the more normal structure than ReO_3, because polarization is expected here. It now appears that ReO_3 has metallic conductivity.

‡ An exception is the structure of ReO_3, where large holes are already present to take up large ions, giving cubic perovskites like $^{XII}Sr^{VI}TiO_3$.

§ Different orientations do occur, and more easily for single corner sharing e.g., in (K)SbO_3 (*20*) and $(La_4O)(ReO_3)_6$ (*21*).

† In the mutually parallel shear planes in the structures of the compounds $Ti_2O_3 \cdot n\,TiO_2$ (*38*), face-sharing does occur.

tures with all blocks identical, which are the simplest ones, tetrahedral positions are found to be occupied where four blocks, two of each level join.

As an example of the use of sharing polyhedra, we wish to show how the other compositions and structures can be derived in a simple way, when one structure is known. For simplicity's sake we take the simplest series, with all blocks equal, as an example.

When the finite dimensions of each block are *m* and *n* octahedra (*m* and *n* vary from 5 to 3 and may be equal or unequal), then each layer one octahedron high contains (*m*-2)(*n*-2) sharing octahedra in the centre like in ReO_3 (WO_3 in Fig. 1). Further, we have $2(n\text{-}2) + 2(m\text{-}2)$ sharing octahedra like that of η-Nb_2O_5 with stoichiometry $MO_{2\frac{1}{2}}$ on the sides of the layer, and four at the corners. These four are almost the same as the ones at the sides but have one corner not shared with another octahedron, viz., one corner that is not in or opposed to the shared edges. This corner of the octahedron is joined to the filled tetrahedron. The stoichiometry of these corner-octahedra is MO_3. By multiplying the number of octahedra by their stoichiometry for each type and adding the results, we obtain the stoichiometry $M_{nm}O_{3nm-(m+n)+4}$, to which we have to add one ion to the tetrahedral position A. Thus, we obtain the stoichiometries, and taking as cations W^{6+} and Nb^{5+}, also the chemical formulae (Table I).

TABLE I

Dimensions block in ReO_3 cell edge	Stoichiometry	Chemical formula
5 × 5	$^{IV}A^{VI}M_{25}O_{69}$	$W_8Nb_{18}O_{69}$
5 × 4	$^{IV}A^{VI}M_{20}O_{55}$	$W_5Nb_{16}O_{55}$
4 × 4	$^{IV}A^{VI}M_{16}O_{44}$	$W_3Nb_{14}O_{44}$
4 × 3	$^{IV}A^{VI}M_{12}O_{33}$	$WNb_{12}O_{33}$
3 × 3	$^{IV}A^{VI}M_9O_{25}$	PNb_9O_{25} or Nb_2O_5
5 × 3	$^{IV}A^{VI}M_{15}O_{41}$	$W_2Nb_{15}O_{41}$

The first four were found in Wadsley's laboratory and in addition a combination of the 4 × 4 and 3 × 4 blocks, with formula $W_4Nb_{26}O_{77}$ (*31*), (*30*), and (*33*). The 3 × 3 blocks were found in $^{IV}PNb_9O_{25}$ (*28*). The structure of H-type Nb_2O_5(=$^{IV}Nb^{VI}Nb_{27}O_{70}$) does not belong to this series. Here the blocks of 3 × 4 are joined by the shear planes to blocks 3 × 5, mutually joined at horizontal octahedron edges near the verticle edges of the blocks (*27*). Since the series described above does not lead to a stoichiometry M_2O_p with $p < 5$, the structures of the compounds between TiO_2 and Nb_2O_5 must contain shared horizontal octahedron edges (and, as a consequence, more shared nonhorizontal ones).

III. The Classification of Crystal Structures for Simple or Complex Inorganic Compounds

Since the cations have isonomous coordination more often than the anions, it seems appropriate to classify inorganic crystal structures according to cation coordination. A classification according to stoichiometry for simple compounds is often used also for complex ions in ternary or more complex compounds. See, e.g., Wyckoff (*39*). So far we have not seen structures classified in a diagram where on one axis the stoichiometry is plotted, expressed as the ratio of the number of anions to the number of cations (the anion/cation ratio), on the other axis the cation coordination. Such diagrams are given for some simple compounds in Figs. 4 and 5.

On each point of the diagram one or more structures can occur which have the same cation coordination and the same stoichiometry. When *n* vertices

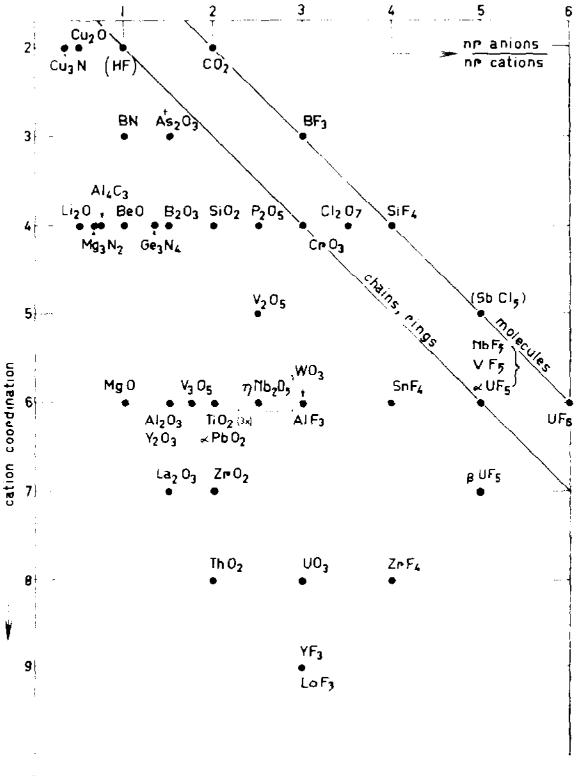

FIG. 4. Diagram showing cation coordination versus stoichiometry, (expressed as nr anions:nr cations), for the crystal structures of simple binary fluorides, oxides and nitrides.

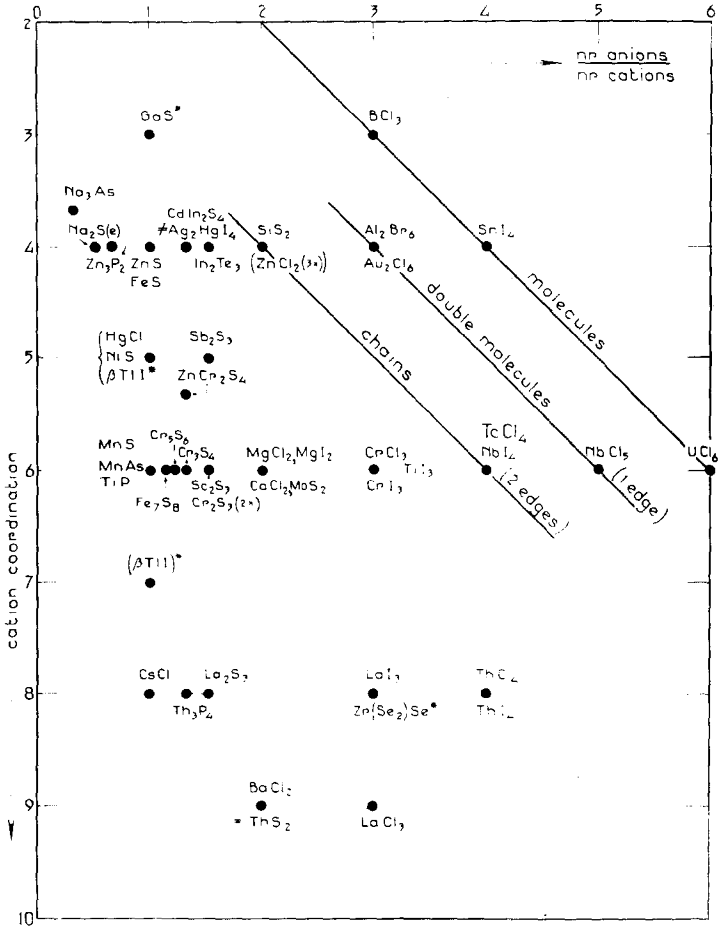

FIG. 5. Diagram of cation coordination versus stoichiometry, now for simple binary compounds containing polarizable anions.

of the cation polyhedron ^aAX_p ($p = a$) are shared only once, the anion–cation ratio becomes $p = a - n/2$, irrespective whether they are shared by n corners, by $n/2$ edges or by $n/3$ faces.

Thus, by successively sharing each vertex by a single corner we obtain the result that all double molecules lie on a straight line (Fig. 4) through all compositions $^aAX_{a-1/2}$, all single chain and ring structures on the line $^aAX_{a-1}$ and some sheet structures on the line $^aAX_{a-2}$. For only single edge sharing for each vertex, double molecules lie on the line $^aAX_{a-1}$, chain structures on $^aAX_{a-2}$. For single face sharing for each vertex, double molecules have the composition $^aAX_{a-3/2}$, chains the composition $^aAX_{a-3}$. These lines are indicated in the diagrams. We give separate figures for compounds of anions with low or with high polarizability, because often, as we saw, the latter may give less isonomous anion coordination. The difference in sharing behaviour discussed in Section II is only one of the consequences of this.

For complex ions the same type of diagram can be given. (Fig. 6.) In this case also a separation of compounds with polarizable anions from those with F^- and O^{2-} as anions is desirable, but sometimes less necessary, as we have discussed in Section II.

In compounds $^aA_m{}^xX_p$, (x = average anion CN), when a, m, and p are whole numbers, $x = am/p$ may be a whole number or a fraction. When x is a whole number, all anions may have the same anion CN, as in the structures of αAl_2O_3 and Sc_2O_3, but this need not be so, as, e.g., in Bi_2Te_3, which is $^{VI}Bi_2{}^{VI}Te^{III}Te_2$. When x is a fraction, at least two kinds of anion CN must occur. In $^{VII}La_2O_3$, the average anion CN is $4\frac{2}{3}$, which can be made up from $(1\times)6$ and $(2\times)4$, or from $(2\times)5$ and $(1\times)4$, or otherwise. In La_2O_3 the first-named combination of anion CN's occurs, i.e., it is $^{VII}La_2{}^{VI}O^{IV}O_2$. The cation and anion CN's

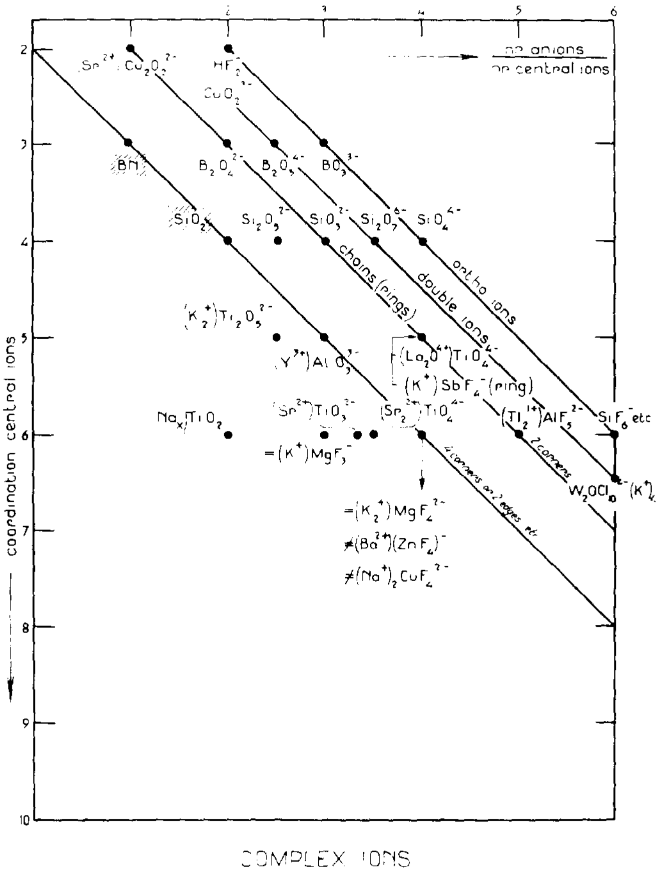

FIG. 6. Diagram showing coordination central ion versus stoichiometry for complex ions, here only complex anions.

may be both fractional as, e.g., in γFe_2O_3: ${}^{VI}Fe_5{}^{IV}Fe_3{}^{IV}O_6{}^{III}O^6$. Compounds containing ions which differ chemically, but have the same CN, can be listed together with simple compounds. We do this always for anions, and for cations when the degree of order is unknown. When these ions are cations, one ion may be chosen as the central ion of a complex ion. Thus ilmenites ${}^{VI}M{}^{VI}TiO_3$ may be listed under simple compounds as ${}^{VI}Al_2O_3$, from which it is derived by ordering, but also under complex ions as $({}^{VI}M){}^{VI}TiO_3$; the ions in the TiO_3^{2-} ion lie roughly on the same positions as in the CrI_3 structure. When in one compound two or more different cation CN's occur, they may be listed under complex ions, choosing one to be the central ion, but for some purposes it may be useful to place them in a diagram like Fig. 7, giving the average cation coordination versus anion/cation ratio. This we do, e.g., when we wish to see how a structure may change under high pressure.

In Fig. 7 we have limited ourselves mainly to structures where the cation coordinations do not differ much, i.e., by only 2 (or 3), because a gradual increase in pressure will often first give a transformation involving only a small increase in cation CN, or, when the structure is not dense, none at all. We shall refer to this diagram in Section VI.

Finally, it may be noted that in the diagrams given we have made no distinction between cation coordination polyhedra of different shape, in particular between isonomous and nonisonomous shapes, e.g., between tetrahedra and flat squares, or between regular octahedra and triangular prisms. It is, of course, desirable to do so when a more complete discussion is given.

IV. The Representation of Crystal Structures by Space-Filling Polyhedra

A study of the literature on many crystal structures of "ionic" compounds reveals that the polyhedra around many cations and around the anions with low polarizability are isonomous. This becomes less

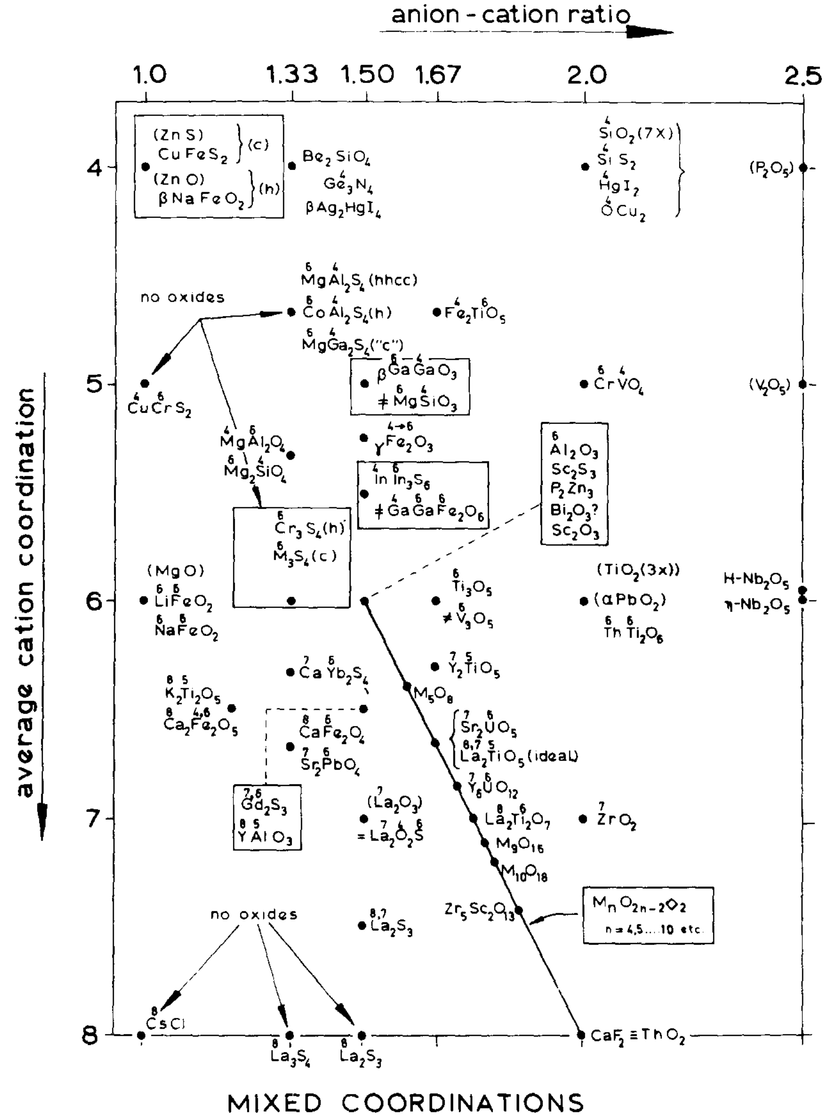

FIG. 7. Diagram showing average cation coordination versus stoichiometry for some binary and ternary compounds with mixed coordinations. For the coordinations and compositions indicated by arrows, no oxides occur. On the line drawn from Sc_2O_3 (etc.) to CaF_2 the structures of substances $M_nO_{2n-2}\diamond_2$, discussed in Section VI, are found, c.q. must be found.

and less true as the radius (i.e., the polarizability) of an anion in the centre of the polyhedron increases and the charge of the surrounding cations increases and their radii decrease. This conforms to the electrostatic picture given in Section I. Nonisonomous cation polyhedra can usually be understood qualitatively as being caused by nonelectrostatic effects. Nonisonomous anion polyhedra that cause no obvious gain in polarization energy very rarely occur and never when surrounded by cations with s^2p^6 outer shell. We shall, therefore, assume that these anion coordination are due to cation–cation interactions, as is generally assumed for NbO, with both ions in square 4-coordination, and often, but not generally (*40*) for the $^{VI}Ni^{VI}As$ structure and its derivatives.

When we look at the surrounding of a cation by cations or anion by anions respectively, i.e., usually† by its next-nearest neighbours, this may be expected to be isonomous also, except for the cation coordination in double molecules, chain and sheet structures.

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† When poly-ions, caused by anion-anion or cation-cation bonding, are present the anion-anion or cation-cation distance may even become the smallest distance.

The usual representation of a crystal structure, the unit cell, is not the most suitable for showing the cation and anion polyhedra (cf. the structure of NiAs), so that several cells must be shown (*41*), or it may be that in a three-dimensional picture the coordination polyhedra are obscured by the many other ions present. In many textbooks the cation or anion polyhedra are shown in a part of the unit cell, without indication how the structure continues outside the picture, which often causes ambiguity. We, therefore, use a method of representation which we have described previously (*42*), in which a certain crystallographic site is the centre of a polyhedron, formed by midway planes between this site and its neighbouring crystallographic sites of the same type. This method can have certain advantages for representing all structures, including those of metals and organic compounds, but it is particularly useful for depicting inorganic ionic compounds, when an anion or a cation is placed on this crystallographic site.

We call the resulting polyhedra space-filling polyhedra (SFP), because they can be stacked with identical SFP to fill space without leaving any voids. Such SFP have been described already long ago (*43*) and (*44*), but the author has not seen any use made of them for describing structures.

Space-filling polyhedra, according to the above definition are brought in the position of the other SFP in the lattice by the operation of the symmetry elements of the space group.

Figure 8 shows the SFP for the simplest lattices, the simple cubic (s.c.), the body centred cubic (bcc), the cubic close-packed (ccp or fcc) and the hexagonal close-packed (hcp) lattices. When a metal atom is placed in each of these SFP, these polyhedra are a complete representation of the crystal structures, of α-Po, K, Cu, and Mg, respectively.

We shall now place an anion in the centre of each of these SFP. In Fig. 8a where the anion lies on a s.c. lattice, the vertices are shared by eight identical cubes, and are surrounded by a cube of anions. Eight 8-coordinated cations can be placed here, to give the structure of CsCl. The s.c. lattice is the only lattice for which the SFP can be identical to the unit cell. The edges are here shared by four cubes, the faces, of course, in all SFP by two SFP. Ions inside a SFP are not shared at all. The above case does not teach anything new, since everybody is familiar with the unit cell. In CaF_2 the F^- ion in the centre of the cube is surrounded by four Ca^{2+} ions on four vertices forming a tetrahedron. We use a formula $FCa_{\frac{4}{8}}$. This cube is one octant of the unit cell.

For an anion in a bcc lattice, (Fig. 8b), there is also only one type of vertex present on the SFP, which is surrounded by four anions forming a flattened tetrahedron. Since cations seldom occupy such a coordination polyhedron, structures with anions in an undistorted bcc lattice and cations in 4-coordination will not occur in binary ionic compounds. This SFP has edges shared by three SFP and faces, of course, shared by two. The structure of Cu_2O can be represented by placing the oxygen-ion in the centre and four Cu^+ ions in the centres of four of the hexagonal faces of this SFP, to form a tetrahedron. The formula is $OCu_{\frac{4}{2}}$.

The SFP for the ccp lattice is the well-known rhombic dodecahedron (Fig. 8c); that for the hcp lattice can be formed from it by cutting the rhombic dodecahedron in two halves by a horizontal cut and turning the bottom half over 180° around a vertical axis (Fig. 8d). In both SFP two kinds of vertices can be distinguished.

Those where four edges (or faces) meet are surrounded by six anions which form a regular octahedron. These six sites are the six octahedral sites surrounding the anion in a close-packed lattice. When these are filled, we have the NaCl structure for ccp ($ClNa_{6/6}$) and the NiAs structure for hcp ($AsNi_{6/6}$). (Fig. 9).

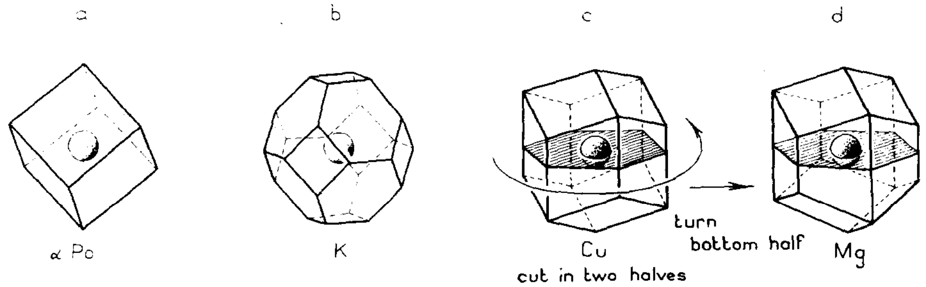

FIG. 8. Space filling blocks (SFP) for (a) a s.c. lattice, (b) a bcc lattice (c) a ccp lattice, (d) a hcp lattice. The hatched planes in (c) and (d) and the arrow in (c) indicate how the hcp SFP is obtained from the ccp SFP.

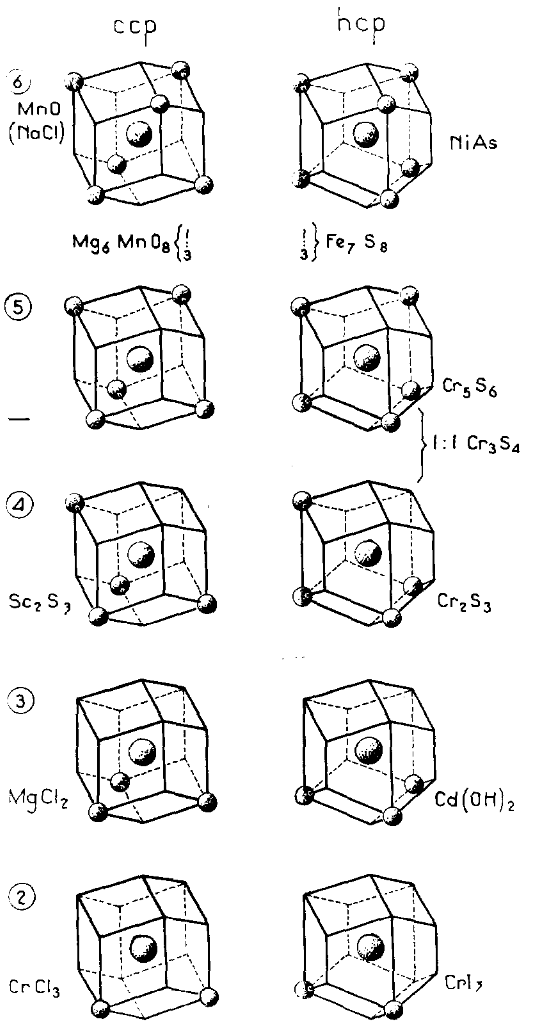

FIG. 9. SFP for ccp and hcp anion stackings, with ⑥, ⑤, ④, ③, and ② cation neighbours in octahedral sites. The sites above the anion are emptied first and then those below it.

The eight vertices where three edges (or faces) meet are surrounded by a regular tetrahedron of cations and represent the eight tetrahedral sites around each anion. When these are all filled, in the ccp lattice we have the structure of $Li_2O = OLi_{8/4}$, or, when the cation is in the centre, that of its antistructure CaF_2 ($=CaF_{8/4}$) (Fig. 12). In the hcp anion lattice the tetrahedral sites shown vertically above each other cannot be simultaneously filled without large distortions, since they are too near to each other.

When all octahedral and tetrahedral sites are filled in a ccp anion lattice, we obtain the formula $XM\frac{6}{6}+\frac{8}{4}=M_3X$. Originally BiF_3 was thought to have the antistructure $BiF\frac{6}{6}+\frac{8}{4}$, but it was later shown that only impure material, which contains O^{2-} ions and anion vacancies, shows this structure (*45*). It is the structure of, e.g., Li_3Bi, which has metallic properties. The shortest approach octahedral site–tetrahedral site, equal to the edge of the ccp SFP, seems to occur very rarely in ionic close-packed-anion structures, and, if so, not without a large distortion.

Three-coordinated cations can occur on the edges, but have not been found in ccp structures. The idealized SFP for ${}^{III}B^{III}N$ is a hexagonal packing elongated along the vertical direction, with B in the middle of the three shorter vertical edges of the SFP. In BN, covalent bonding gives B three close anion neighbours, but B^{3+} ion has two next-nearest N neighbours above and below it. The fact that the two forms of graphite, when B and N are both replaced by C, do not have this arrangement, seems to indicate that ionic bonding does play a rôle in determining the structure of BN, as far as the bonding between the horizontal layers is concerned. A structure ${}^{V}M^{V}X$, with hexagonal close-packing, elongated in the horizontal directions to make all M–X distances equal, does not exist.

If we wish to compose a structure for a compound ${}^{VI}A^{III}BO_3$ with a ccp or hcp anion in an isonomous coordination (formula $OA\frac{3}{6}B\frac{1}{3}$), this can only be done by placing B on the middle of the long vertical edge of the hcp SFP and A in the two octahedral sites in such a way that the anion is surrounded by a flat triangle of one B and two A ions. This is approximately the calcite structure of $CaCO_3$ and, e.g., $MgCO_3$ and $LiNO_3$. In the idealized structure the distances ${}^{III}B$–O and ${}^{VI}A$–O have the ratio $\sqrt{6}/3 = 0.816$, which is within the ratios $2/3 = 0.667$ and $\sqrt{3}/2 = 0.866$ that are the limits for the radius ratio rule to hold.

When we use the ratio of the usual experimental C–O and Ca–O distances (=0.65, slightly below the lower limit), we see that the O ion should be displaced in the SFP towards the C ion to make the distance ratio perfect. This would be an example of a structure prediction, if the structure had not been determined in 1914.

The idea that one should look at the surrounding of the anion by cations is due to van Arkel, who explained this structure in almost the same way (*46*) without the use of SFP. The displacement of the anion, mentioned above, changes the shape of the SFP. We have assumed that the close-packed layer stacking is perfect, i.e., that the anion distances within the horizontal plane and between planes are equal. This need not be so, and also this distortion can be predicted (*46*).

In the following section we shall discuss the possible structures obtained by leaving out cations one by one from the octahedral sites in the NaCl-structure and in the NiAs structure. Similarly, cations will be taken out one by one from the tetrahedral sites in the Li_2O structure (or anions from the CaF_2-structure). A similar series of structures can be derived for hcp anions, but the cation positions joined by a short vertical edge of the SFP of Fig. 8d cannot be occupied simultaneously (*47*), which reduces the number of possibilities. This series is not discussed.

We shall disregard possible and really occurring distortions. This causes ambiguity for those cases where the SFP can be packed in more than one way, as e.g., for the SFP of $MgCl_2$ ($=CdCl_2$) (Fig. 9 ③, formula $ClMg\frac{3}{6}$), which in the idealized form shown can also represent the atacamite structure of $Cu_2(OH)_3Cl$ if we do not differentiate between OH^- and Cl^- (*48*). (Cf. also the two structures for Sc_2S_3 below). The real SFP will have different shape for different structures

We shall also make use of two (or more) SFP for describing one structure; this means the definition of SFP has to be changed accordingly. The same ambiguity can arise here, viz. when, e.g., one SFP of the $ClNa_{6/6}$ and one of the $AsNi_{6/6}$ structure are placed on top of each other, with one common face. These two SFP together represent the structure of TiP [$PTi_{6/6}(c) + PTi_{6/6}(h)$] with mixed *hc* anion stacking. In the horizontal directions they can be stacked in one way only, but if the combination of the two SFP is stacked differently in the vertical direction, viz., with the next pair of SFP upside down, a (hypothetical) *hhcc* MX structure can a.o. be obtained.

V. Derivation of Close-Packed-Anion Structures with Either Octahedral or Tetrahedral Sites or Both, Partly Filled

We shall now look at all SFP obtained when cations are taken out of the NaCl and NiAs SFP one by one.

In the NiAs structure the Madelung constant for all *c*/*a* ratios is lower than for the NaCl structure. It is often assumed that cation–cation interaction is the cause for the occurrence of this structure. The fact that sulfides, phosphides, etc., of metal ions with s^2p^6 outer shell do not occur in this structure, supports this assumption. When we take away cations from the NiAs SFP with As in the centre [(AsNi $\frac{6}{6}$) (Fig. 9 ⑥)], first those above the anions and then those below it, we obtain the stoichiometries $MX_{5/6} = M_5X_6$, $MX_{4/6} = M_2X_3$, $MX_{3/6} = MX_2$, $MX_{2/6} = MX_3$ and $MX_{1/6} = MX_6$. Because of the order in which we take the cations away, all structures formed can be described as a hexagonal anion stacking in which filled and partly filled cation layers alternate down to M_2S_3; in MX_2 filled and empty layers, and further to MX_6 partly filled and empty cation layer alternate.

In the SFP depicted the partly filled layers are for $\frac{2}{3}$ or $\frac{1}{3}$ filled. Ordered $\frac{3}{4}$ and $\frac{1}{4}$ filled layers are also known to occur, as well as two kinds of $\frac{1}{2}$ filled layers. These can be depicted by combining two SFP of Fig. 9. Thus, stoichiometries M_7X_8, M_3X_4, M_5X_8, and MX_4 are possible with the same type of structure. In the Cr–S system, between CrS and Cr_2S_3, which was formerly thought to be a solid-solution region, Jellinek (*49*) found Cr_7S_8, Cr_5S_6, Cr_3S_4, Cr_2S_3. In Cr_7S_8 the partly filled layer showed disorder, but Fe_7S_8 (*50*) has the expected ordered structure.† Cr_5S_8 was found afterwards (*51*) and has the structure fitting in this scheme.

Nb_3Cl_8 and $NbCl_4$ also fit into this structural series; distortions are caused by cation–cation interaction (*52*). The structures of $Cd(OH)_2$ and CrI_3($=BiI_3$) are shown in Fig. 9. WCl_6 and UCl_6 close the series.

Additional structures are obtained, when the cations are taken out from both layers at the same time. Several structures M_3X_4 with both layers $\frac{3}{4}$ filled result, with no example known to the author.

Both layers $\frac{2}{3}$ filled yields a.o. one M_2X_3 structure (Fig. 10 ④) with a fairly isonomous anion coordination, and this can be improved by moving the 2 M ions of the vertical M–M pairs apart and moving the anion towards them (*42*). This is possible since there are vacant cation sites above and below each such M–M pair. This structure is suitable for oxides, e.g., Al_2O_3 and for those sulfides where the cation is not too small, and, therefore does not polarize the S^{2-} ion too strongly (see below under Sc_2S_3). Yb_2S_3 and Lu_2S_3 have this structure (*53*).

For both layers $\frac{1}{3}$ filled both possible structures are known viz., that of PdF_3 (*54*) and that of TiI_3 (*55*).

The surrounding of the anion in PdF_3 is the most isonomous that can occur in a hcp lattice for MX_3 compounds. The angle Pd–F–Pd is, however, smaller than that of W–O–W in WO_3. The fluorides of Al^{3+} and all trivalent transition elements have an anion stacking between that of ReO_3 and PdF_3. Why the angle M–X–M is smallest for PdF_3 is difficult to fit into the picture. It has been suggested

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† We shall disregard the different structures obtained by the different ways of placing the partly filled layers above each other. These are of course predictable.

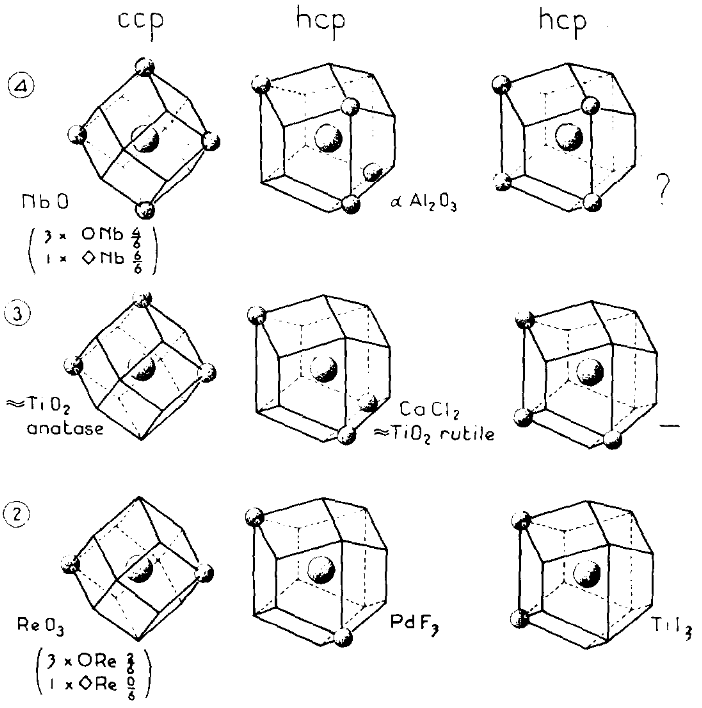

FIG. 10. The remaining SFP for ccp and hcp anion stacking with ④, ③, and ② cations in octahedral sites around an anion.

that PdF_3 is $Pd^{2+}Pd^{4+}F_6$ (*56*), but the charge difference for the ionic model would increase the angle.

We shall not discuss all possibilities, but mention the case of both layers one-half filled, for which there are two possibilities (*57*): (a) with ordering of cations along straight chains and (b) with ordering along zig zag chains, both within the cation layers.

The first is the structure of $CaCl_2$, in which the distortion is very small. The distortion must be greater in the rutile structure of, e.g., TiO_2 and MgF_2, since in $CaCl_2$ the Cl^- ion lies outside the plane of the triangle of cations. Ordering along zigzag chains occurs in α-PbO_2.

Turning to the cubic close-packed structures, we expect the same stoichiometries and corresponding structures. Taking out the cations first from the upper layer and then from the lower one (Fig. 9), we obtain nonisonomous anion coordinations in stoichiometries, e.g., M_7X_8, M_5X_6, M_3X_4, M_2X_3, (M_5X_8), MX_2, M_3X_8, MX_3, MX_4, MX_5, MX_6. We expect these not to occur for oxides and fluorides. It seems surprising at first sight that the M_7X_8 structure is shown by $Mg_6^{2+}Mn^{4+}O_8^{2-}$. The anion surroundings are: $1 \times OMg_{6/6}$ and $3 \times OMg_{4/6}Mn_{1/6}\square_{1/6}$. The small and highly charged Mn^{4+} ion and the cation vacancy are at opposite sides of the O^{2-} ion, which may cause sufficient anion polarization and displacement to make this structure stable even for an oxide. No M_5X_6 and M_3X_4 structures belonging to this series have been found so far.

Fig. 9 ④ gives a possible structure for $^{VI}M_2^{3+}S_3$; in 1959 (*42*) no structure was known containing this anion coordination. Considering that Al^{3+} was known to have structures $^{IV}Al_2S_3$ and that transition metal ion sulfides prefer the hcp structures, we thought that Sc_2S_3 should have this arrangement. Two structures were published in 1964 (*58*); the structure of one form, $Sc_{2.07}S_3$, has filled and $\frac{1}{3}$ (to be exact: 1.07/3) filled cation layers, as we predicted.

One might think that the other form, $Sc_{2.00}S_3$, would have all cation layers $\frac{2}{3}$ filled, with honeycomb ordering in each layer. This only leads to a structure $^{VI}M_2X_3$ in which one of the X ions has square coordination (Fig. 10 ④) and two that of Fig. 9 ④. Since a square anion coordination is impossible here, an antistructure containing Cu^{2+} or Pd^{2+} can have this structure. Scheer (*59*) in 1956 made Li_2PdO_2 and we predicted the structure before it was found by den Os (*60*) in 1961 for Li_2CuO_2. The way we arrived at this structure at that time was to order 2Li and Cu in the [110] direction of a NaCl lattice and then leave out the anions above and below the Cu^{2+} along the [001] axis to give it square

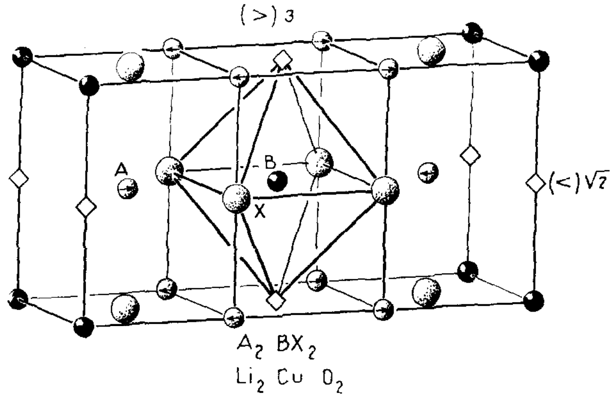

FIG. 11. The derivation of the structure of Li_2CuO_2. Small light circles: Li^+, dark small circles: Cu^{2+}, large circles: O^{2-}, ◇: anion vacancy. The arrows show the direction of the displacements needed to give Li^+ a surrounding more resembling a regular tetrahedron.

coordination. This leads to a structure with a unit cell with $a:b:c = 1:\sqrt{2}:3$ (Fig. 11). The coordination of the Li^+ is then distorted to make it more nearly a tetrahedron, making the axis ratios $1:<\sqrt{2}:>3$. The dimensions found were 1:1.27:3.27. Similarly one can order two vacancies and four Sc^{3+} ions in a row in a [110] direction of the NaCl lattice, but out of many possibilities we have found only one solution for which all S^{2-} ions have the coordination of Fig. 9 ④. This was indeed the structure of $Sc_{2.00}S_3$ *(58)*.

One modification of Al_2S_3 (γ) has 6-coordinated Al^{3+}, viz., in the Al_2O_3 structure. Since $r_{Al^{3+}} < r_{Sc^{3+}}$, we should expect to find an even less isonomous surrounding of S^{2-} for γ-Al_2S_3 than for Sc_2S_3, or the same. However, $^{VI}Al_2S_3$ probably is a metastable phase, which would resolve this paradox.

The anion coordination of Fig. 10 ③, is neither isonomous nor does it lead to a large polarization energy. When we elongate the pseudocubic lattice of the idealized structure, move the two equatorial cations downwards and the anion upwards, the anion obtains a fairly regular triangular coordination by cations. This is the structure of anatase (TiO_2). The elongation equal to $c/2a$ of the tetragonal unit cell, is 1.25 for anatase, but 1.08 for $LiFeO_2$, in which the vacancy positions are filled by Li^+ and the Ti^{4+} positions by Fe^{3+}, thus diminishing the charge difference. The structures of $MgCl_2$ and $CrCl_3$ are depicted in Fig. 9 ③ and ②. The structures of SnF_4 and α-UF_5, which have distorted ccp anion lattices can be written $2\times FSn_{2/6}+2\times FSn_{1/6}$ and $1\times FU_{2/6}$ and $4\times FU_{1/6}$; they fit into this picture. No structures for 6-coordinated cations with more isonomous F^- coordination can exist. Why such fluorides are stable at all is discussed by van Arkel *(61)*.

We shall more briefly discuss the SFP for close-packed anions with the eight tetrahedral sites around it partly filled, because the structures have been compared in a different way elsewhere *(62)*.

Figure 12 shows the structure of Li_2O ($=OLi_{8/4}$) or its antistructure CaF_2 ($=CaF_{8/4}$). We shall refer to derivatives of CaF_2 as antistructures. When one tetrahedral ion is taken out, we obtain the (anti)structure of $^{VII}Na_3{}^{VII}UF_7$ ◇, (◇ is an anion vacancy) in which not only the seven F^- and the anion vacancy are ordered, but the three Na^+ and the U^{4+} as well.

Figure 12 also shows the structure of Zn_3P_2 ($=ZnP\frac{6}{4}$) and an idealized picture of one of the structures that has been reported for Bi_2O_3 ($=BiO\frac{6}{4}$). These two figures together in the ratio 3:1 give the structure of, e.g., $Mg_3{}^{VI}N_2$ ($NMg\frac{6}{4}$) or its antistructure $^{VI}MX\frac{6}{4}$ of Sc_2O_3, Y_2O_3, In_2O_3 etc., often called after Mn_2O_3. Predictable distortions make the 6-coordination more nearly regular. In some structures the 5-coordination occurs in both ccp and hcp SFP, but in neither alone.

Four-coordination can have several shapes; that of ZnS (sfalerite) (Fig. 12) is not found for oxides. BeO and ZnO have the hcp ZnS (wurzite) structure with the same tetrahedral coordination. In this structure the next-nearest distance M–X is smaller, which gives it a higher Madelung constant.

The PdO structure, and not the NbO structure, is the one that is predicted when assuming the square Pd coordination to be dominant. In the idealized SFP of Fig. 12, this coordination is a rectangle of $\sqrt{2}$ by 1, and the tetrahedra around O^{2-} are regular. When the c axis is lengthened to make the Pd

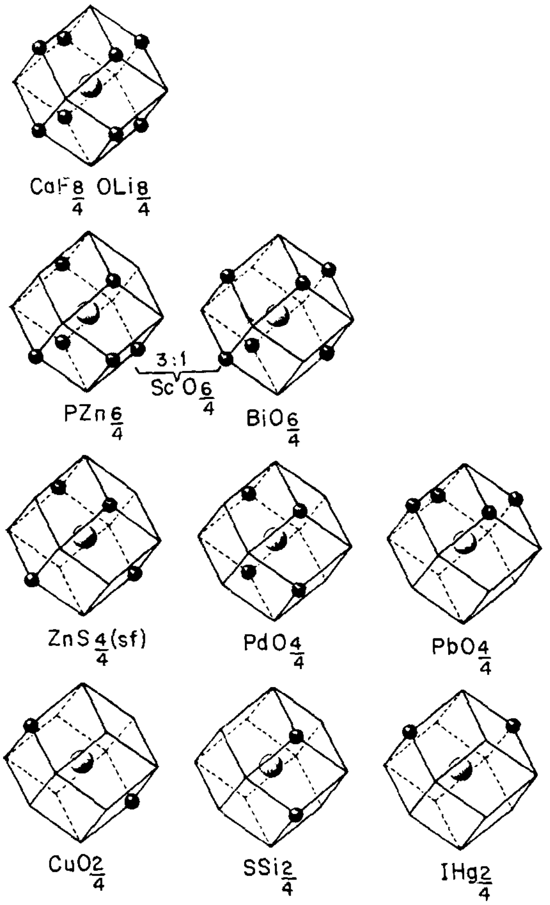

FIG. 12. SFP for ccp and hcp anion (c.q. cation) stacking, with 8, 6, 4, and 2 cation (c.q. anion) neighbours in tetrahedral sites.

coordination square, the tetrahedron around O^{2-} is lengthened by the same factor $\sqrt{2}$ .The real structure (*63*) is a compromise, with the *c* axis lengthened by a factor of 1.240.

Nonisonomous cation surrounding occurs in the PbO structure† with double Pb–Pb layers. For this structure various explanations have been given: polarizability of the cation, the free electron pair on Pb^{2+}, or a covalent model. The antistructure of PbO occurs in LiOH where the interaction between the permanent dipoles of OH^- plays a rôle, and in FeSe, where the polarizability of Se^{2-} may be held responsible.

A one-sided surrounding of the anion (Fig. 13) is also obtained by placing four cations on one side of the anion along a trigonal axis. This arrangement is found in Cu_3VS_4 (=$SCu\frac{3}{4}V\frac{1}{4}$) with the V^{5+} ion surrounded by the three Cu^+ ions, all on one side of the S^{2-} ion.

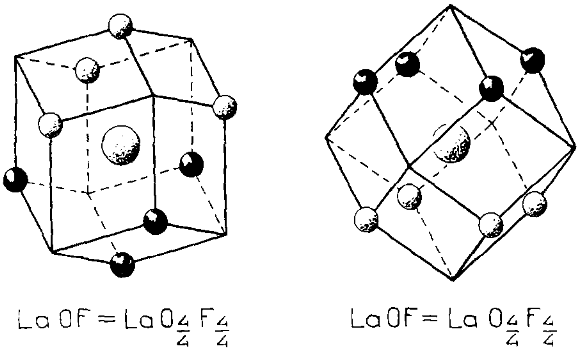

FIG. 13. The two types of order of O^{2-} and F^- around La^{3+} in rhombohedral and tetrahedral LaOF, respectively. When in the left figure the light small circles represent cation vacancies, the large circle S^{2-}, the three dark circles below the anion Cu^+ and the bottom dark circle V^{5+}, this is the structure of Cu_3VS_4.

The two last-named coordinations occur in the tetragonal and rhombohedral (anti)-structures of LaOF, respectively (Fig. 13). Here, the order is not between anions and vacancies, but between O^{2-} and F^- ions, whereby the charge difference is decreased. The gain in lattice energy by ordering is mainly due to the difference between the Ln–O and Ln–F distances (*64*). Three of the eight tetrahedral sites are filled in the different ordered $^{IV}M_3X_4$ ($XM\frac{3}{4}$) structures. Here, three of the four sites filled in ccp ZnS are occupied (*62*). Since this anion coordination is not isonomous, such structures are impossible for oxides and fluorides. Examples are the structures of β-Cu_2HgI_4, β-Ag_2HgI_4 and $CdIn_2Se_4$. In each of these the ordering of $3M + 1\square$ is different; the cations are also ordered.†

For filling two tetrahedral sites there are three possibilities in the ccp lattice, depicted in Fig. 12. They represent the framework (anti)-structure of Cu_2O, the layer structure of red HgI_2 and γ-$ZnCl_2$, and the chain structure of SiS_2, respectively. The structure of $^{II}Cu_2{}^{IV}O$ in our opinion only exists by the grace of the tendency of Cu^+ to have a linear 2-coordination. Any structure $^{IV}M^{II}X_2$ even when the anion is O^{2-} or F^-, as in SiO_2 c.q. BeF_2, has an angle M–X–M smaller than 180°, because the low X coordination and the small diameter of the M ion make the polarization energy gain high. If the central ion in Fig. 12 ($CuO\frac{2}{4}$) is an anion, it could be displaced horizontally to make the angle M–X–M smaller than 180°, but since the M–X distance is

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† In reality the *c* axis is shortened by a factor $\sim\sqrt{2}$ so that Pb lies on a bcc, not a fcc lattice.

† The structure of $^{IV}Ge_3N_4$ and $^{IV}Be_2{}^{IV}SiO_4$ are very different, with the anion in a more isonomous, i.e., a flat, 3-coordination.

fixed, this would bring the anions too close together, and other structures, which have no close-packed anion lattice, become more stable.

In the structure of red HgI_2 and γ-$ZnCl_2$ the angle M–X–M is already so small that no oxides or fluorides can have this structure. It is expected for polarizable anions with relatively large cations in 4-coordination.

Ionic bonding would, however, lead us to expect octahedral cation coordination in HgI_2; the fact that one form with 4-coordination occurs, is due to a covalent contribution to the bonding. When the cation is even smaller with respect to the anion, the cations can polarize the anion even more strongly by forming the chain structure of SiS_2 and $BeCl_2$ (Fig. 12), with even smaller angle M–X–M.

We now wish to mention a few close-packed-anion structures with both octahedral and tetrahedral sites filled. When we assume that tetrahedral and octahedral sites, joined by an edge in the cubic stacking cannot be occupied simultaneously, the largest number of metal neighbours around an anion then becomes seven, in the structure of Mg_3Sb_2; La_2O_3 (*65*)† has its antistructure. This can be regarded as $SbMg_{\frac{3}{6}} + \frac{4}{4}$, or $LaO_{\frac{3}{6}} + \frac{4}{4}$, respectively. When we take the antistructure, we cut the SFP of BaO ($BaO_{\frac{6}{6}}$) with NaCl structure and of ThO_2 ($ThO_{\frac{8}{4}}$) with CaF_2 structure, in two halves, perpendicular to a trigonal axis, and join them to form again a ccp SFP; we obtain a structure $MO_{\frac{3}{6}} + \frac{4}{4}$, but three distances between tetrahedral and octahedral sites are then too short. When we join the two halves after turning one around the trigonal axis over 180°, then the hcp structure of La_2O_3 is obtained (Fig. 13).

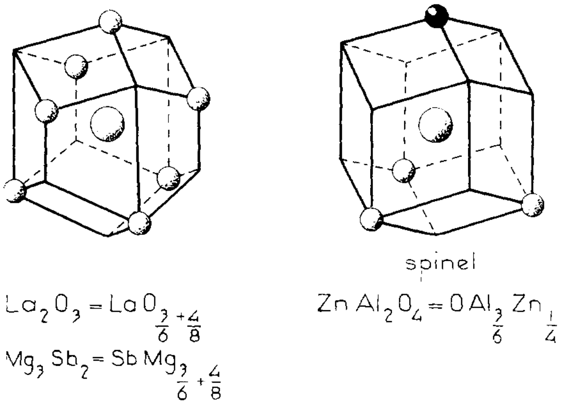

FIG. 14. SFP of (a) the La_2O_3 and Mg_3Sb_2 structure and (b) the spinel structure of, e.g., $ZnAl_2O_4$.

A derivation of the La_2O_3 structure from that of CsCl, by taking out every third cation layer perpendicular to the trigonal axis gives a structure $^{VIII}M_2{}^{V}X_2{}^{VI}X$, which has to be distorted much more severely to give the real La_2O_3 structure.

For the spinel structure $^{IV}A^{VI}B_2O_4$ ($=OB_{3/6}A_{1/4}$) of, e.g., $ZnAl_2O_4$, the SFP is depicted in Fig. 14. The anion is surrounded by a slightly elongated tetrahedron; the anion–cation distances become more equal when the anion moves away from the tetrahedral site, as is most often found. This structure is found for a great many compounds of widely different valencies and in solid solutions, in which also more than two valencies can occur. The structure is stable because of the isonomous surrounding of the anion, but also because a close-packed structure $^{VI}M_3O_4$ with isonomous anion coordination cannot be constructed, as we have seen above. Thus, a compound with spinel structure is often formed from oxides that have six-fold cation coordination themselves.

The factors governing the distribution of the cations among the two sites and the existence—or nonexistence—of spinels as it depends on the composition has been intensively studied. We shall not discuss these investigations here but refer to some papers that include a review of the literature (*67*), (*68*), and (*69*).

The nonexistence of close-packed structures $^{VI}M_3O_4$ leads to another conclusion, which is corroborated by experiment. Oxides with spinel structure under high pressure will not transform into a $^{VI}M_3O_4$ structure, but either decompose, like $Li_{0.5}Fe_{2.5}O_4$ (*70*), or give the $^{VII}Sr_2{}^{VI}PbO_4$ structure, like Mn_2GeO_4 (*71*). Sulfides with spinel structure like MCr_2S_4 (M = Fe, Co, or Mn) under high pressure assume the Cr_3S_4 structure (*72*), $NiCr_2S_4$ has this structure already at normal pressure (*73*). Some sulfoscandates with spinel structure under pressure may give one of the $^{VI}M_3S_4$ structures with ccp anion stacking, mentioned above.

When we try to construct a structure $^{IV}A^{VI}BX_2$, we do not find any that will have isonomous close-packed anion coordination. This means that β-$NaFeO_2$ ($^{IV}Na^{IV}FeO_2$) under pressure will not transform to the α form, $^{VI}Na^{VI}FeO_2$ via a hypothetical $^{VI}Na^{IV}FeO_2$ form.

Structures for $^{IV}A^{VI}BX_2$ with nonisonomous close-packed anion coordination can be constructed, and one has indeed been found for $CuCrS_2$ (*74*). This is shown in Fig. 15, in a more conventional way, by drawing only those ions that lie in the [110] plane of a hexagonal unit cell. It is seen that the Cu–Cr distance is much shorter than is necessary because,

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† Recently Müller-Buschbaum (*66*) suggested the structure is more complicated.

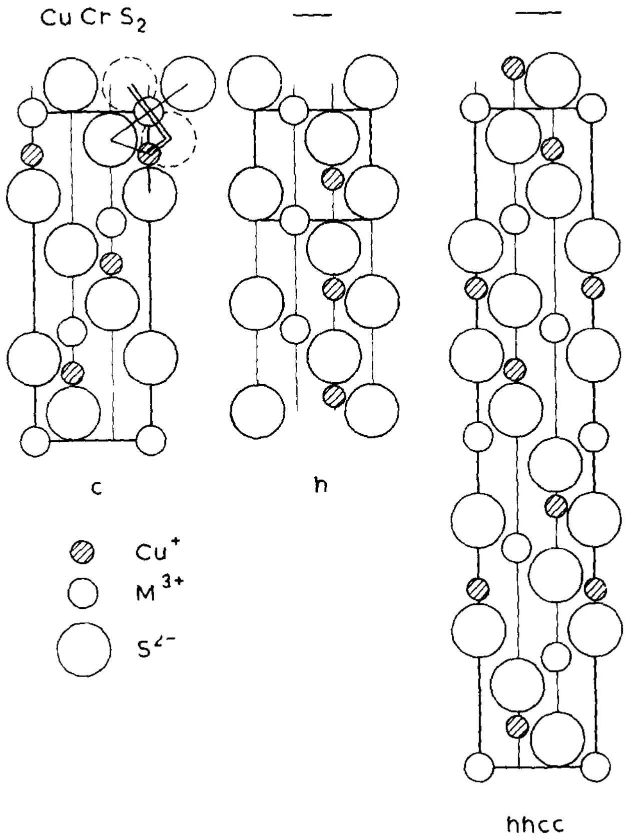

FIG. 15. The structures of $^{IV}A^{VI}BS_2$ drawn as hexagonal cells. Only the ions in the [110] plane are drawn. Thick outlines indicate the unit cells. All vertical lines represent trigonal axes. In the left figure some of the anions above and below the plane of the paper are indicated by broken circles, and the octahedral and tetrahedral coordinations shown. From left to right: *c* anion stacking occurring in $CuCrS_2$, *h* stacking and *hhcc* stacking (both hypothetical structures, see text).

if the stacking of the sulphur ions would be hexagonal (*h*) instead of cubic (*c*), the Cu and Cr ions would move further apart (Fig. 15).

It is thought that this is due to a Cu^+–Cr^{3+} "bond" or interaction. We are now trying to prepare $CuScS_2$, which, if it can be made, presumably will give the *hhcc* structure (Fig. 15) for which the electrostatic repulsion for second-nearest-neighbours would probably be smaller than in the *h* structure. It is also possible that the shortest distance ^{IV}A–^{VI}B in the *h* and *hhcc* structures is still too small when no interaction between these ions can occur. In that case, $CuScS_2$ would not form.

A structure very similar to this hypothetical *hhcc* structure, where this short ^{IV}A–^{VI}B distance is not present, because the ^{VI}B for which this occurs is absent, is known. It is that of $^{VI}In^{IV}In^{IV}ZnS_4$ (*75*). Ydo and co-workers in our laboratory found that also $MgAl_2S_4$ and $MnAl_2S_4$ have this structure, in which Mg and Mn, at least mainly, occupy the octahedral sites (Fig. 16) (*76*). $FeAl_2S_4$ has a *h* anion stacking (*76*) and $MgGa_2S_4$ a complicated structure, derived from the hypothetical *c* stacking (Fig. 16), by introducing a plane, very roughly parallel to the paper, at which the whole structure is moved upward by $\frac{1}{6}$ times the cell height (*77*).

It may at first sight seem strange that $MgAl_2S_4$ has such a layer structure with even an empty cation layer in it, whereas $MgAl_2O_4$ and several sulfoindates MIn_2S_4 have the spinel structure. When we look at the anion surrounding for all structures MAl_2S_4 we see the spinel arrangement for two layers and the $^{IV}M_3S_4$ arrangement in the two other layers (disregarding the anion stacking). The nonisonomous anion-surrounding of $^{IV}M_3S_4$ cannot occur in oxides, and Al^{3+} is smaller than In^{3+} and therefore prefers 4-coordination. The structure of $MgGa_2S_4$ cannot be simply explained. Other sulfogallates are being investigated in our laboratory. Under high pressure these materials M_3S_4 are all expected to transform to the spinel structure.

One of the predictions we could not make was for

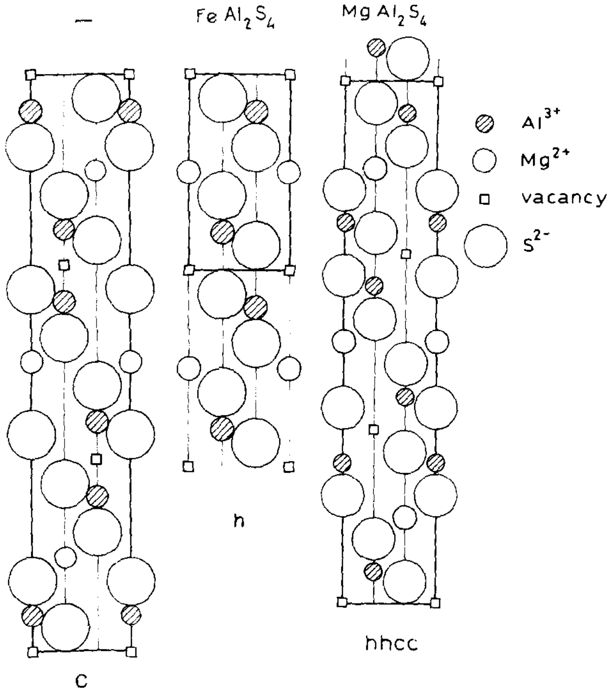

FIG. 16. Three structures of compounds $^{IV}A_2{}^{VI}BS_4$ drawn as described for Fig. 15. The *hhcc* structure on the right, that of $MgAl_2S_4$, corresponds to the hypothetical structure of Fig. 15, with every other octahedral cation layer empty. The *h* structure in the middle, of $FeAl_2S_4$ does not correspond to the middle figure in Fig. 15, when every other octahedral cation layer is empty. The *c* structure on the left does not occur. The structure of $MgGa_2S_4$ is derived from it (see text).

a close-packed structure $^{VI}B_2{}^{IV}A_3O_{12}$. We heard (*78*) that Wilhelmi was finishing the structure of Cr_5O_{12} and that it was a close-packed anion-lattice. Presuming this would be $^{VI}Cr_2^{3+}{}^{IV}Cr_3^{6+}O_{12}$, the prediction of the structure seemed easy since one has only to surround every O^{2-} by one tetrahedral ion and one octahedral ion (formula $OB_{1/6}A_{1/4}$). This arrangement occurs in the garnet structure of, e.g., $^{VIII}Y_3{}^{VI}Fe_2{}^{IV}Fe_3O_{12}$. The angle $^{VI}Fe\text{–}O\text{–}{}^{IV}Fe$ is 126.6°, because O^{2-} has two more cation neighbours, $(OC_{2/8}B_{1/6}A_{1/4})$, giving it four neighbours with interbond M–O–M angles roughly as expected for isonomy. Try as we might, we could not construct an hcp or ccp or mixed anion lattice with only the coordination $OB_{1/6}A_{1/4}$ with a large angle A–O–B. This was especially vexing because it had seemed easy to take out two out of three octahedral sites from the spinel or olivine structures in an ordered manner. When the structure of Cr_5O_{12} was published (*79*), we saw that this problem had baffled nature too. This does not prove, however, that it cannot be done. Then the structure of $^{VI}Al_2{}^{IV}W_3O_{12}$ was published (*80*). This proves indeed to be of the type $OB_{1/6}A_{1/4}$, but the holes occupied by the large ions in the garnet structure are still there. It can be regarded as a garnet structure without the large ions, distorted in such a way that the angles $^{IV}M\text{–}O\text{–}{}^{VI}M$ become larger (viz., between 143 and 175°). We believe that our negative result, viz., that a close-packed structure $OB_{1/6}A_{1/4}$ does not exist, was probably correct.

VI. Structure Predictions on Oxides

We wish to discuss also some structure work that is currently done in our laboratory on oxides, to check predictions made. It was thought that in the perovskite and K_2NiF_4 structures of $SrTiO_3$ and Sr_2TiO_4, respectively, the Ti^{4+} ions could be replaced by Cu^{2+} or Pd^{2+}, at the same taking out one O^{2-} ion, to give Cu^{2+} or Pd^{2+} a square coordination. Sr–Cu oxides were prepared previously (*81*), but no structures were known. The first compound that was prepared by G. Ytsma, $SrCuO_2$, did not show the expected tetragonally deformed structure derived from cubic $SrTiO_3$ (Fig. 17a), but the second, Sr_2CuO_3 (*82*), and also Ba_2CuO_3, Cu_2CuO_3, Ba_2PdO_3, and Sr_2PdO_3 did show the orthorhombically distorted structure derived from Sr_2TiO_4 (Fig. 17c).

The structure found for $SrCuO_2$ (*82*) is shown in Fig. 17b. The layer sequence is SrO–SrO–CuO–CuO;

the Sr^{2+} ion has 7-coordination, the Cu^{2+} ion a square 4-coordination.

$BaPdO_2$ showed two modifications, one of which (β) has a structure (*83*) between $BaNiO_2$ (*84*) and our hypothetical $SrCuO_2$.

A series of oxides is known (*85*) between $BaNiO_3$, with *h*-stacked BaO_3 layers and the cubic perovskite $SrTiO_3$, with *c*-stacked SrO_3 layers: $BaNiO_3$ (*h*), $BaRuO_3$ (*hhc*), $BaMnO_3$ (*hc*), $BaTiO_3$ (hex.) (*hcc*), $SrTiO_3$ (*c*).

By taking out one oxygen ion per layer one obtains: $BaNiO_2$ (*h*), —— (*hcc*), $BaPdO_2$ (*hc*), —— (*hcc*), —— (*c*).

Kafalas and Longo (*86*) report that the structures ABO_3 under high pressure transform to a structure with a larger part of *c*-stacked AO_3 layers, and that the same transformation is obtained by gradually replacing Ba^{2+} by Sr^{2+}.

Similarly G. Ytsma is at present attempting to find the missing structures by solid-solution formation, and under high pressure.† Also $^{VII}SrCuO_2$ will be put under high pressure to see whether it transforms into the hypothetical $^{VIII}SrCuO_2$ of Fig. 17a.

Another compound investigated by G. Ytsma was $Sr^{2+}Cu_2^{+}O_2^{2-}$. Here also, the structure was predicted before it was known. We assumed that Cu^+ should have a linear 2-coordination, so that O^{2-} should also have two Cu^+ neighbours, which points to a chain Cu–O–Cu . . ., and further only that O^{2-} should have isonomous coordination.

A structure having a ccp O^{2-} lattice with Sr^{2+} in 6-coordination was chosen as the most likely one, and was confirmed by experiment (*82*). In this structure each O^{2-} has three Sr^{2+} neighbours, arranged as Ti in TiO_2 (anatase) (Fig. 10 ③), and the two Cu^+ ions, situated in a plane perpendicular to that of the three Sr^{2+} ions, completing the 5-coordination ($OSr_{3/6}Cu_{2/2}$) of the O^{2-} (Fig. 18). Here, the elongation, mentioned for TiO_2 (anatase) in Section V, need not take place. In fact there is a slight compression, (or better, a elongation in the perpendicular directions) viz., by 10%, probably in order to make the Cu–Cu distance not too small.

Finally, we wish to mention the possible structures that can occur in a series of oxides M_nO_{2n-2}, which can be derived from CaF_2 or ThO_2 by taking anions out of the s.c. lattice in an ordered manner. Many compounds have been described that seem to belong to this series (*87*) and (*88*), but for many the structures are unknown. The structure of $Zr_5Sc_2O_{13}$ with $n = 14$ has recently been determined (*89*).

Table II shows the compositions of this series, their average cation coordination (known since the anion coordination is always tetrahedral), some of the possible combinations of cation coordinations, and compounds for which the structures have been solved. Since cations with coordination higher than six cannot be found in a close-packed lattice, one would for such compounds first look at the simplest lattice in which 8- to 6-coordination can occur by taking away anions in an ordered way, which is the s.c. lattice, even if the existence of this series had not been known. The general formula is M_nX_{2n-p} in which p is any positive integer.

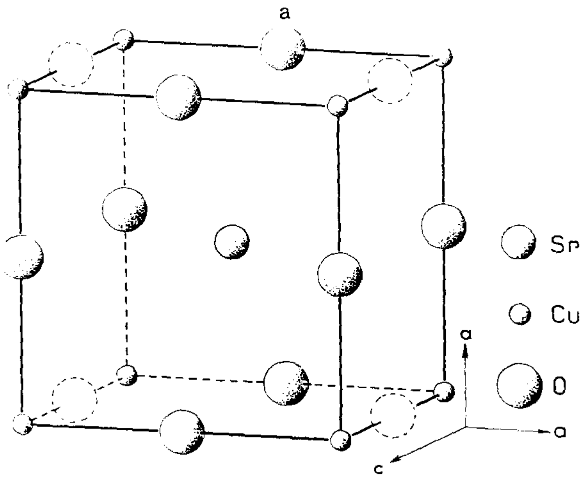

FIG. 17. (a) Unit cell of hypothetical tetragonal structure for $SrCuO_2$.

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† Dr. C. J. M. Rooymans of the Philips Research Laboratories has kindly offered to perform these experiments.

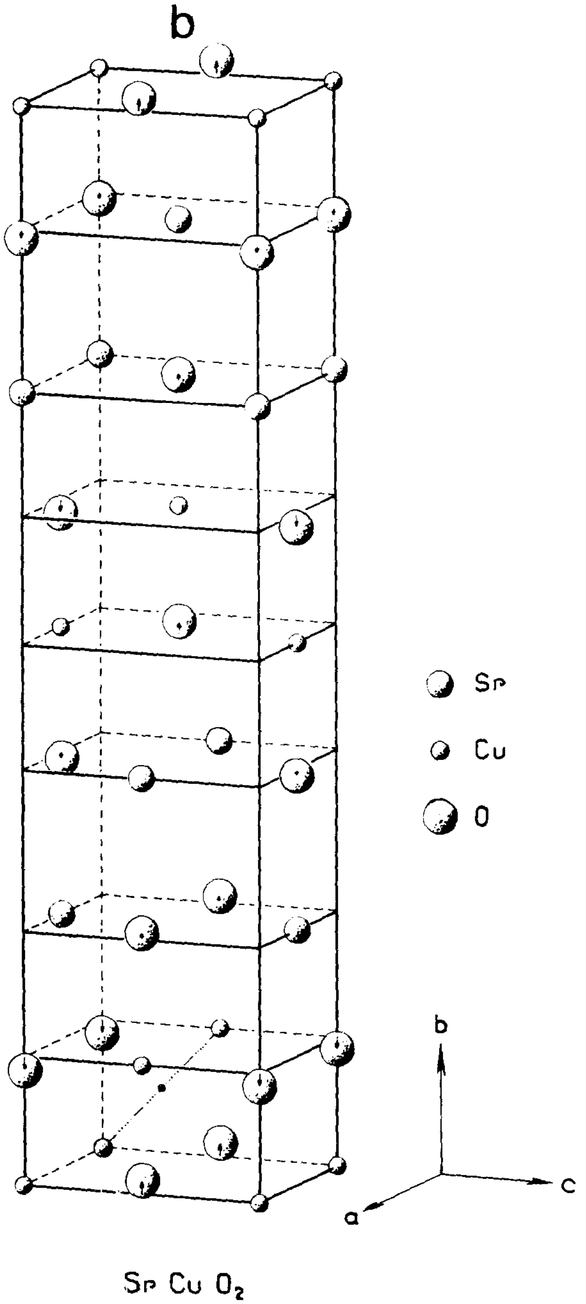

FIG. 17. (b) real unit cell of $SrCuO_2$. Layer sequence SrO–SrO–CuO–CuO.

In the Figs. 19 and 20 the anion–anion vacancy order is indicated by two types of squares (one hatched, the other white), representing respectively the cubes $\diamond MX_{4/8}$ and $XM_{4/8}$. The cation coordination is read off from every other corner where eight cubes meet. The number of possible ways of ordering vacancies becomes very large, if no limitations are

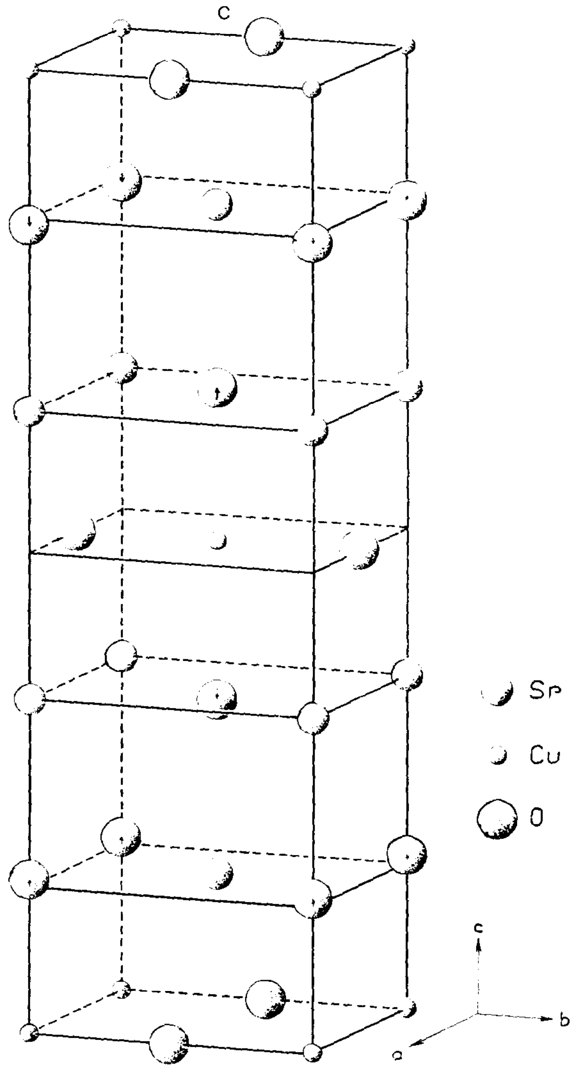

FIG. 17. (c) Unit cell of Sr_2CuO_3.

used.† For MX one finds a.o. three possibilities already derived from the SFP of the other ion, which is ccp, viz., the structures of ZnS, PdO, and PbO. (Section V). The structures of Bi_2O_3, Sc_2O_3 and Zn_3P_2 have also been derived from the SFP of the other ion, viz. of Bi^{3+}, Sc^{3+}, and P^{3-}. A simple

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† For the prediction of possible and likely structures of this type that A. B. A. Schippers is trying to make, types of ordering in which more than three types of cation coordinations occur, and patterns that are repeated after long distances are excluded.

Schippers is preparing a computer program that will determine the space-group for simple structures from which anions or cations are taken out in an ordered manner. It is hoped that this will facilitate the solving of this type of structures from X-ray powder data.

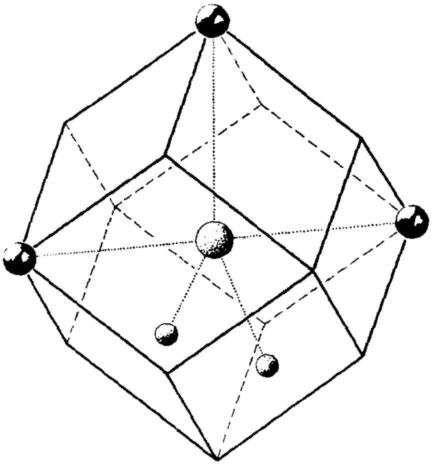

FIG. 18. SFP of $SrCu_2O_2$ with the O^{2-} ion in the centre. Unit cell is tetragonal.

structure can be derived for M_3X_4 with cations in 6,6 and 4-coordination. In this structure two half-filled anion layers with chequerboard pattern like in ZnS alternate with one filled layer like in CaF_2. It, therefore, is a combination of ZnS and the Zn_3P_2 structure, where one chequerboard layer alternates with one full one. An oxide ${}^{IV}M{}^{VI}M_2{}^{IV}O_4$ will prefer the spinel structure, however, because in the hypothetical structure described above the ${}^{VI}M$ cation has far from isonomous coordination. The anti-structure ${}^{IV}M_4{}^{VI}X_2{}^{IV}X$ seems possible; we are at present trying to prepare Zn_4As_2Se, in order to see whether this will have this combination-structure of ZnSe and Zn_3As_2.

For the stoichiometry M_3X_5 we at first placed the anions in layers in which the vacancies are far apart in order to avoid clustering of vacancies, i.e., to obtain a possible structure for ${}^{VII}M_2{}^{VI}MX_5$. The three simplest patterns (Fig. 19a, c, d) when stacked with themselves can give one and the same structure, for which A. B. A. Schippers determined the space-

TABLE II

$M_nX_{2n-2}\diamond_2$

n	Formula	Average cation coordination	Some combinations of cation coordinations	Structures found
2	MX	4	4	ZnS, (PbO) (PdO)
3	M_3X_4	$5\frac{1}{3}$	664	
			655	
			844	
4	M_2X_3	6	66	Zn_3P_2, Sc_2O_3, Ag_2O_3(?), Bi_2O_3(?)
			75	
			84	
			8664	
5	M_5X_8	$6\frac{2}{5}$	86666	
			88844	
			77666	
6	M_3X_5	$6\frac{2}{3}$	884	
			776	$Sr_2UO_5 = Cd_2UO_5$ *(90)* *(91)*
			866	
			875	La_2TiO_5 *(16)*
7	M_7X_{12}	$6\frac{6}{7}$	7777776	$UY_6O_{12} = Zr_3Sc_4O_{12}$ *(92, 89)*
			8888844	
			8886666	
8	M_4X_7	7	7777	Na_3UF_7
			8866	$La_2Ti_2O_7$ (=pyrochlorite structure)
	⋮		8776	
14	M_7X_{13}	$7\frac{3}{7}$		$Zr_5Sc_2O_{13}$ *(89)*
∞	MX_2	8	8	ThO_2

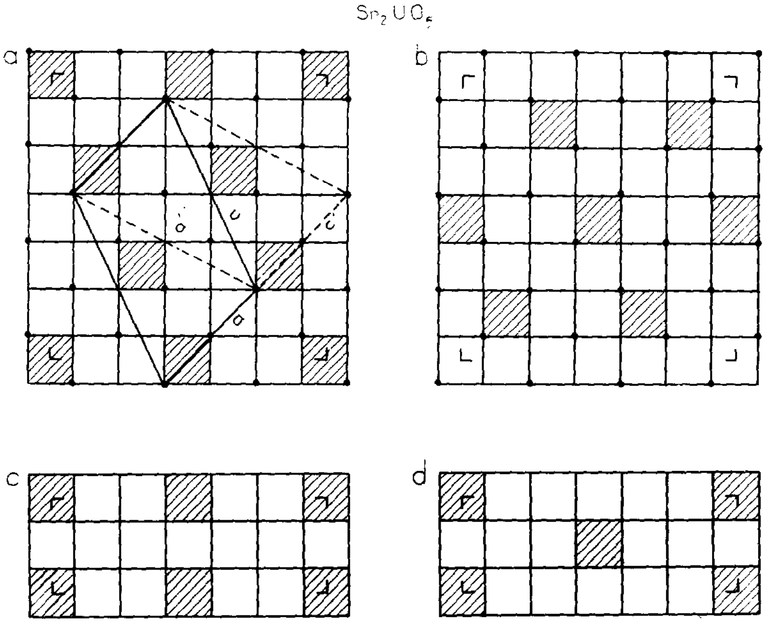

FIG. 19. a, c, and d represent three simple patterns of order between anions and anion vacancies in A_2BX_5. □ represents a cube $XM\frac{4}{8}$, ▨ a cube, ◇ $M\frac{4}{8}$ (◇ = anion vacancy) ● represents M ions above the plane of the anions when a and b are stacked c and d are the patterns on the side faces. This is the simplest structure for ${}^{VII}A_2{}^{VI}BO_5$; it has been found for Sr_2UO_5. The drawn lines represent the *a* and *c* axis in the space group $P^2{}_1/c$ the dashed lines those in space group C^2/c.

group and the monoclinic cell dimensions expressed in the CaF_2 cell edge, and the angle β. We then heard that Dr. Loopstra et al. (*90*) had determined the crystal structure of Sr_2UO_5 by X-ray and neutron diffraction, and he kindly sent us the manuscript. The coordinations are ${}^{VII}Sr_2{}^{VI}UO_5$. Table III compares the coordinates predicted, before distorting the structure, e.g., to make the 6-coordination of U^{6+} like a regular octahedron. It is seen that even at that stage the similarity was striking.† A. B. A.

TABLE III

Sr_2UO_5

Rietveld-Loopstra (neutrons) March 1968 Acta Cryst. **B25** (4) 787 (1969)				Predicted structure unrefined			
Space-group $P^2{}_1/c$				$P^2{}_1/c$			
a = 8.1043 (13) Å				$a = x\sqrt{2}$	$a =$ 7.64 ± 0.42 Å		
b = 5.6614 (8) Å				$b = x$	$b =$ 5.4 ± 0.3 Å		
c = 11.9185 (18) Å				$c = x\sqrt{5}$	$c =$ 12.07 ± 0.67 Å		
β = 108.985 (10)°				$\cos\beta = 1/10\sqrt{10}$	β = 108° 26′		
Z = 4				Z = 4			
U (1) (2a)	0	0	0	U (1) (2a)	0	0	0
U (2) (2b)	½	0	0	U (2) (2b)	½	0	0
4*e*:				4*e*:			
Sr (1)	0.1571 (13)	0.0747 (13)	0.3181 (7)	Sr (1)	0.1667	0.0	0.3333
Sr (2)	0.3359 (10)	0.4926 (14)	0.1379 (6)	Sr (2)	0.3333	0.5	0.1667
O (1)	0.4501 (13)	0.3215 (18)	0.3354 (8)	O (1)	0.4167	0.2500	0.3333
O (2)	0.8912 (12)	0.2959 (16)	0.3579 (8)	O (2)	0.9167	0.2500	0.3333
O (3)	0.6017 (12)	0.2978 (17)	0.0731 (8)	O (3)	0.5833	0.2500	0.1667
O (4)	0.0153 (12)	0.2573 (17)	0.1176 (8)	O (4)	0.0833	0.2500	0.1667
O (5)	0.2499 (15)	0.1552 (13)	0.9956 (10)	O (5)	0.2500	0.2500	0.0
Cell volume: 517.1				Cell volume: 476.0 ± 70.8			

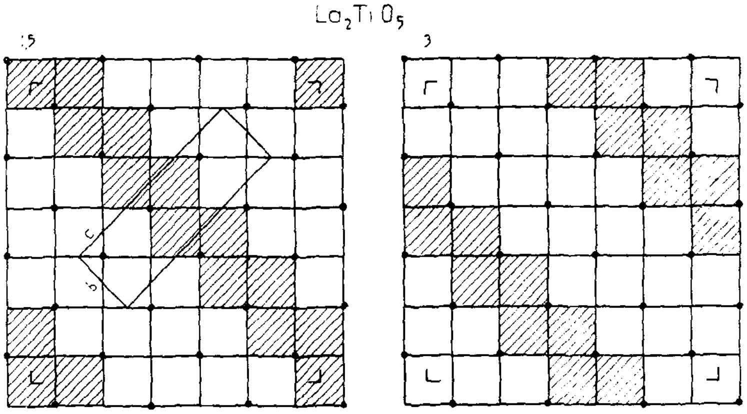

FIG. 20. Representation of anion and anion-vacancy patterns occurring in the idealized structure of La_2TiO_5. The layer sequence in La_2TiO_5 is: 1 (left); 2 full (=white); 3 (right); 4 (full); 5 (left) etc.

Schippers showed there is another possibility that might have given the same structure by applying larger distortions (*93*).

He also found that the structure of $^{\text{VII}}La_2{}^{\text{V}}TiO_5$, reported by Bertaut et al. (*16*), can be derived from another type of anion vacancy order, the layer patterns of which are shown in Fig. 20. The idealized structure shown has the coordinations $^{\text{VIII}}La^{\text{VII}}La^{\text{V}}Ti^{\text{IV}}O_5$, and the distortion, which is predictable in a qualitative way, moves one anion away from the $^{\text{VIII}}La^{3+}$ ion. The monoclinic cell for Gd_2TiO_5 proposed by Collongues (*94*) is wrong; correct indexing of his X-ray data (*95*) gives it the same orthorhombic structure as that of La_2TiO_5, published by Bertaut et al.

Collongues also mentions another form of Gd_2TiO_5 with a hexagonal unit cell with $a = 3.672$ Å and $c = 11.907$ Å (*88*). We could predict a structure having such a hexagonal cell as follows. The length of the *a* axis suggests a structure with one oxygen per layer, and with the A ion in a cubic 8-coordination. This can give a cell such as has been reported for α-UO_3. In the plane of the top and bottom apices of the cube, cations (B) can be placed in 5-coordination. In order to make the vertical B–O distance about equal to the horizontal one, the adjacent O^{2-} layers must be moved away from the BO layer, making the two vertical AO distances much longer than the other six. This gives a idealized picture of the structure of $^{\text{VIII}}Y^{\text{V}}AlO_3$ reported by Bertaut et al. (*96*) (Fig. 21). If we now wish to find a possible structure for Gd_2TiO_5, we have to put in another A-ion and two oxygen ions. This can be done in the way shown in Fig. 21. This gives both Gd ions 7-coordination with another anion farther away.

This 8-th neighbour can be removed altogether from the coordination of one Gd^{3+} ion by moving the O^{2-} in the BO layer over $\frac{1}{3}$ of the horizontal distance, i.e., over $\frac{1}{3}a\sqrt{3}$ in the [110] direction. This halves the length of the unit cell, making it more nearly corresponding to that reported by Collongues. This alternative structure can also be derived from an idealized $^{\text{VIII}}M^{\text{VII}}M^{\text{V}}MO_5$ structure, which is a derivative of the CaF_2 structure (*93*).

In September 1968, Wadsley told us that the structures of two forms of Gd_2TiO_5 had been determined in his laboratory. One was equal (*97*) to that of La_2TiO_5 (*16*), the publication of which he had not seen, the other seemed to correspond to one of the two hexagonal structures described above (*98*).

Acknowledgments

The fact that so much work done by Wadsley and his co-workers is mentioned in this paper is not caused by the aim of this memorial issue of this journal. Although not so extensive, the lecture given at Atlantic City in 1968 covered very much the same ground. Wadsley's results and his way of thinking have been a challenge to us, and discussions with him were among the most stimulating experiences we have known. We miss the scientist and critic Wadsley as much as we miss David as a very good friend.

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† The structure of Cd_2UO_5, which is the same, was published earlier (*91*). We had seen it, but at that time did not recognize the relationship with the CaF_2 structure.

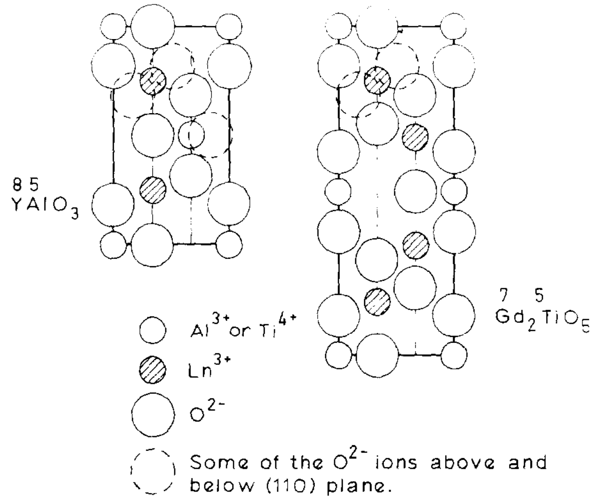

FIG. 21. The structure of $YAlO_3$ (Bertaut) and Gd_2TiO_5 as predicted, in the representation of hexagonal unit cells as in Fig. 15. The layer distances are idealized, also in the left figure.

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