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A Framework for Analysing Relationships between Chemical Composition and Crystal Structure in Metal Oxides

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Abstract

A computer program has been written to characterize the coordination polyhedra of metal cations in terms of their volumes and polyhedral elements, *i.e.* corners, edges and faces. The sharing of these corners, edges and faces between polyhedra is also quantitatively monitored. In order to develop the methodology, attention is focused on ternary oxides containing the Al^{3+} ion, whose structures were retrieved from the Inorganic Crystal Structure Database (ICSD). This also permits an objective assessment of the applicability of Pauling's rules. The influence of ionic valence on the structures of these compounds is examined, by calculating electrostatic bond strengths. Although Pauling's second rule is not supported in detail, the calculation of oxygen-ion valences reveals a basic structural requirement, that the *average* calculated oxygen-ion valence in any ionic oxide structure is equal to 2. The analysis is further developed to define a general method for the prediction of novel chemical compositions likely to adopt a given desired structure. The polyhedral volumes of this structure are calculated, and use is made of standard ionic radii for cations in sixfold coordination. The electroneutrality principle is invoked to take valence considerations into account. This method can be used to guide the development of new compositions of ceramic materials with certain desirable physical properties.

Introduction

An understanding of the interplay between chemical composition, crystal structure and the physicochemical properties of crystalline ceramics is of fundamental interest in solid-state science. Naturally there are several legitimate approaches towards gaining such an understanding, but the method to be adopted here is based on *chemical*, rather than *physical* ideas. A starting point for the approach is given by the four rules postulated by Pauling (1960), in connection with the structure of complex ionic crystals.

(i) A coordinated polyhedron of anions is formed about each cation, the cation–anion distance being determined by the radius sum and the ligancy of the cation by the radius ratio.

(ii) In a stable ionic structure the valence of each anion, with changed sign, is exactly or nearly equal to the sum of the strengths of the electrostatic bonds to it from the adjacent cations.

(iii) The presence of shared edges and especially of shared faces in a coordinated structure decreases its stability; this effect is large for cations with large valence and small ligancy.

(iv) In a crystal containing different cations those with large valence and small coordination number tend not to share polyhedron elements with each other.

Fundamental to Pauling's rules are the ionic attributes of size, valence and charge. In a large number of cases, they give a satisfactory description of the relationship between chemical composition and crystal structure, in particular when the bonding is predominantly ionic in character. There are exceptions, however, in which the rules are not satisfied, and several authors have defined modifications to them. The first rule can only be regarded as qualitatively correct, since most cations are known to have a variety of coordination numbers, each with a different associated cationic radius (Shannon, 1976). The desire to refine the second rule has given rise to the bond-valence method (Brown, 1981), in which the valence of a metal–oxygen interaction depends

on the separation of the two ions. Although this refinement is helpful in dealing with asymmetric coordination polyhedra and the incidence of covalency in ionic systems, it also introduces an extra level of complexity into Pauling's formalism. Since the ionic valences no longer depend merely on topological considerations (*numbers* of coordinating ions), but rather on the *separations* of cations and their coordinating anions, it is arguable that the simplicity of Pauling's rules, in itself a major advantage, is lost in the bond-valence method. The third and fourth rules originate from the conception that metal oxides are stabilized largely by Coulombic forces. This is a useful starting point, but the assumption is inadequate for the whole range of metal oxide structures, in which covalency plays a role of varying importance.

Clearly if Pauling's rules are to be used as a *theory* to predict the crystal structures of metal oxides, they have serious deficiencies. However, their simplicity and ease of application suggest that they should, at least, be considered as a *framework* within which the crystal structures of metal oxides can sensibly be discussed. This viewpoint is developed in this paper, by characterizing the known room-temperature crystal structures of ternary oxides containing aluminium. This choice is made for several reasons. To describe the approach systematically, it is desirable to confine attention to a relatively small set of compounds, so that the treatment is well focussed. Aluminium is chosen as the cation common to all structures because it is well know to exist in both tetrahedral and octahedral coordination. The empty d and f shells in the aluminium ions also permit a fixed valence of $+3$ to be assigned to the ion in all the structures to be examined.

Method

A search was carried out for the structural data of all ternary oxides containing aluminium, $M_pAl_qO_r$, which are contained in the Inorganic Crystal Structure Database (ICSD) at the SERC Daresbury Laboratory. The structures obtained were subsequently divided into five families, depending on their chemical composition ($XAlO_3$, $X_3Al_5O_{12}$, XAl_2O_4, $XAlO_2$ and XAl_4O_7). Families containing only one structure were discarded, since this study is essentially comparative, and it is necessary to keep the amount of data analysed within manageable proportions. The data thus obtained were used as input to a Fortran77 computer program written specifically to characterize cation coordination polyhedra in ionic crystals (Thomas, 1989a). The program was run on an Apollo DN3000 workstation at the University of Leeds, and performs the following sequence of operations.

Step 1. Identification of the vertices of cation coordination polyhedra

These vertices correspond to the oxygen ions coordinating each cation in the unit cell. Translationally related unit cells are generated, in order to identify explicitly all the coordinating oxygen ions of each cation. Usually a consideration of cation–oxygen distances alone is sufficient to define unambiguous polyhedra. However in a few instances, asymmetry of coordination requires a more careful definition of coordination polyhedra.

Step 2. Identification of the faces of cation coordination polyhedra

Once the vertices are known from step 1, faces are identified by searching for planes of oxygen ions which form external surfaces of the polyhedron. The tolerance permitted in testing for the coplanarity of oxygen ions is an adjustable parameter, but a value of ± 0.03 Å is typical.

Step 3. Identification of the edges of cation coordination polyhedra

Once the faces are known from step 2, the edges of each face are identified by the following method. The centre of coordinates of a face is calculated by taking the mean of the x, y and z coordinates of each vertex. A vector is drawn from each vertex to this centre of coordinates, and the angles made by these vectors with a fixed direction in the plane of the face are calculated, in order to define a cyclic sequence of vertices. The edges of the face correspond to the lines joining the vertices, when taken in cyclic order.

Since each edge in a closed polyhedron is shared between two faces, each individual edge will be generated twice in this procedure. This feature is, in itself, a useful criterion to check that the generated polyhedron is closed. If a generated edge is not shared between two faces, then the generated polyhedron is in error.

Step 4. Calculation of the volumes of cation coordination polyhedra

The method employed has been described earlier (Thomas, 1989b), apart from a minor refinement in dealing with non-triangular faces where the constituent oxygen anions are not strictly coplanar. A problem can arise in calculating the volume contribution of such faces, particularly when they are shared between two adjacent cation coordination polyhedra. A successful way of dealing with this problem has been developed, whereby each face is divided into as many constituent triangles (subfaces) as there are edges in the face. Each triangle has an edge as its base, with its third vertex given by the

centre of coordinates of each face, as defined in step 3. The total volume contribution of the face is taken as the sum of the volume contributions of the constituent triangles. In the earlier method (Thomas, 1989b), a careful inspection of polyhedral volumes was necessary, in order to ensure that small regions of space were not counted as contributing to the volumes of *two* adjacent polyhedra. The present method removes the possibility of this occurring, since the subfaces of both adjacent polyhedral faces are identical to each other.

The algorithm used to calculate polyhedral volume is summarized in equations (1) and (2).

$$V_i = \sum_j V_j \tag{1}$$

where

$$V_j = \tfrac{1}{3}(A_j h_j). \tag{2}$$

In these equations, V_i is the volume of polyhedron i, V_j is the contribution to this volume from (sub)face j, A_j is the area of (sub)face j, and h_j is the perpendicular distance of the plane of (sub)face j from the centre of the polyhedron.

Step 5. Evaluation of the fraction of crystal space enclosed within cation coordination polyhedra

This fraction is denoted by f_{enc}, where

$$f_{enc} = \sum_i V_i/V_u, \tag{3}$$

V_i is the volume of the ith polyhedron, and V_u is the volume of the unit cell. The summation is performed over all the polyhedra in the unit cell. In the perovskite structure, for example, $f_{enc} = 1$ (Thomas, 1989b), indicating that there are no inter-polyhedral voids present.

Step 6. Monitoring of faces shared by cation coordination polyhedra

A check is performed for faces of individual polyhedra indentified in step 2 which are shared with adjacent polyhedra. According to Pauling's third rule, shared faces destabilize a given structure, but the fourth rule implicitly allows face-sharing, provided that it does not take place between polyhedra of low coordination number and ions of high valence.

Step 7. Monitoring of edges shared by cation coordination polyhedra

A check is carried out for polyhedral edges shared between polyhedra. Although Pauling's third rule indicates that shared edges are destabilizing, the extent of this destabilization is less than that due to shared faces.

Step 8. Identification of vertices shared between adjacent polyhedra

A three-dimensional structure necessarily has shared polyhedral vertices, unlike the case for shared faces and edges. The manner in which vertices are shared is the structural characteristic to which Pauling's second rule refers. Since each polyhedral vertex is located at an oxygen ion, it follows, from Pauling's rule, that the number of polyhedra sharing a common vertex is directly related to the electrostatic bond strengths within those polyhedra.

For a cation coordination polyhedron, i, with cation valence $v_{c,i}$ and n_i vertices, each *intra-polyhdral* cation–oxygen bond has a strength of $v_{c,i}/n_i$. Pauling's second rule states that, for a metal oxide, the valence of an oxygen ion, v_O, shared between N_p polyhedra is equal, or nearly equal to 2, where

$$v_O = \sum_{i=1}^{N_p} v_{c,i}/n_i. \tag{4}$$

Thus the validity of Pauling's second rule can be staightforwardly tested by calculating the sum in equation (4) at each shared vertex.

Step 9. Evaluation of the total oxygen-ion valence of the unit cell

According to the electrostatic model of an ionic crystal, each ion is assigned an integral point charge, such that the sum of the magnitudes of the anionic charges (valences) in a unit cell is equal to the sum of the magnitudes of the cationic charges (valences) in that cell. This is a statement of the principle of electroneutrality. The *total* oxygen-ion valence of a unit cell, calculated from equation (4), is a summation over all adjacent cation–anion pair interactions, with the strength of each interaction determined by the valence and coordination number of the *cation*. Consequently, a given cation, i, contributes to n_i pair interactions, and the net contribution of that cation to the total oxygen-ion valence is $n_i \times v_{c,i}/n_i = v_{c,i}$. Thus the total calculated oxygen-ion valence, as well as the *actual* total oxygen-ion valence, is equal to the *sum* of the cationic valences. This result has two important consequences. First, a routine check that this total valence, calculated from equation (4), is equal to the sum of the cationic valences is a means of ensuring that the structural data being analysed are correct. Secondly, *any* ionic structure must satisfy the requirement that its total oxygen-ion valence, calculated from electrostatic bond strengths as defined in equation (4), is equal to the sum of the cationic valences. This is a concise method of articulating a basic structural requirement.

Table 1. *Crystallographic data and polyhedral volumes of compounds studied*

Chemical formula	$[O^{2-}]/[Al^{3+}]$	X	Space group	N_X	C_X	N_{Al}	C_{Al}	V_X(Å³)	V_{Al}(Å³)	V_X/V_{Al}	f_{enc}	r_X^{VI}(Å)	Ref.[a]
$XAlO_3$	3·0	La	$R\bar{3}m$	1	12	1	6	45·33	9·07	5·00	1·000	1·032	(1)
		La	$R\bar{3}m$	2	12	2	6	45·40	9·08	5·00	1·000	1·032	(2)
		Pr	$R\bar{3}m$	2	12	2	6	44·37	8·87	5·00	1·000	0·99	(2)
		Nd	$R\bar{3}c$	6	12	6	6	43·72	9·03	4·84	1·000	0·983	(3)
		Sm	$Pnma$	4	12	4	6	43·18	9·12	4·73	1·000	0·958	(4)
		Y	$Pnma$	4	12	4	6	41·60	9·30	4·47	1·000	0·90	(5)
		Y	$P6_3/mmc$	2	8	2	5	20·17	7·11	2·84	0·442	0·90	(6)
		Sc	$Pnma$	4	9	4	6	25·21	9·53	2·65	0·749	0·745	(7)
$X_3Al_5O_{12}$	2·4	Tb	$Ia\bar{3}d$	24	8	16	6	23·10	9·30	2·48	0·446*	0·92	(8)
						24	4		2·79	8·29			
		Ho	$Ia\bar{3}d$	24	8	16	6	22·80	9·72	2·35	0·444	0·901	(8)
						24	4		2·72	8·38			
		Y	$Ia\bar{3}d$	24	8	16	6	22·85	9·40	2·43	0·443	0·90	(9)
						24	4		2·81	8·13			
		Lu	$Ia\bar{3}d$	24	8	16	6	21·62	9·63	2·25	0·438	0·861	(10)
						24	4		2·73	7·92			
XAl_2O_4	2·0	Ba	$P6_3$	6	12	16	4	70·84	2·79[b]	25·39	0·722	1·35	(11)
				2	12			67·31		24·13			
		Ba	$P6_322$	2	9	4	4	41·76	2·81	14·86	0·455	1·35	(12)
		Pb	$P1$	2	6	4	4	21·61	2·75[b]	7·86	0·274	1·19	(13)
		Sr	$P2_1$	2	6	8	4	20·63	2·74[b]	7·53	0·266	1·18	(14)
				2	6			19·42		7·09			
		Ca	$P2_1/n$	4	12	24	4	60·06	2·74[b]	21·92	0·414	1·00	(15)
				4	6			17·53		6·40			
				4	6			16·75		6·11			
		Zn	$Fd\bar{3}m$	8	4	16	6	3·80	9·15	0·416	0·334	0·74	(16)
		Cu	$Fd\bar{3}m$	8	4	16	6	3·59[c]	9·45[c]	0·380	0·341	0·73	(17)
		Co	$Fd\bar{3}m$	8	4	16	6	3·77	9·24	0·408	0·336	0·725	(18)
		Mg	$Fd\bar{3}m$	8	4	16	6	3·64	9·38	0·388	0·340	0·72	(19)
		Ni	$Fd\bar{3}m$	8	4	16	6	3·04[c]	10·24[c]	0·297	0·361	0·69	(17)
		Be	$Pnma$	4	4	4	6	2·19	9·52	0·230	0·360	0·45	(20)
						4	6		8·84	0·248			
$XAlO_2$	2·0	Rb	$Fd\bar{3}m$	8	12	8	4	59·29	2·58	23·000	1·000	1·52	(21)
		Tl	$R\bar{3}m$	6	12	6	4	57·12	2·48	23·000	1·000	1·50	(22)
		Na	$R\bar{3}m$	3	6	3	6	15·88	9·25	1·717	0·667	1·02	(23)
		Cu	$P6_3/mmc$	2	2	2	6	–	9·15	–	–	0·77	(24)
		Cu	$R\bar{3}m$	3	2	3	6	–	9·08	–	–	0·77	(25)
		Li	$P4_12_12$	4	4	4	4	3·85	2·79	1·383	0·159	0·76	(26)
XAl_4O_7	1·75	Sr	$C2/c$	4	7	8	4	23·37	2·78	8·40	0·221	1·18	(27)
						8	4		2·74	8·54			
		Sr	$Cmma$	4	10	4	6	33·10	8·84	3·74	0·446	1·18	(28)
						4	4		1·72	19·19			
						8	4		1·68	19·65			
		Ca	$C2/c$	4	7	8	4	21·16	2·74	7·72	0·217	1·00	(29)
						8	4		2·73	7·75			
		Cu₂	$F\bar{4}3m$	4	12	16	4	55·13	2·87	19·21	0·580	0·77	(30)
				4	6			10·13		3·53			
Al_2O_3	1·5	–	$R\bar{3}c$	–	–	12	6	–	9·08	–	0·427	–	(31)

Notes: (a) The references, in CODEN form, are as follows: (1) KRISA 7 408 1962; (2) ACCRA 9 1019 1956; (3) ACSCE 39 673 1983; (4) JSSCB 4 11 1972; (5) MRBUA 10 85 1975; (6) COREA 257 867 1963; (7) JGREA 80 353 1975; (8) ACBCA 25 1853 1969; (9) KRISA 21 211 1976; (10) ACCRA 19 971 1965; (11) ZAACA 451 40 1979; (12) BUFCA 88 413 1965; (13) ZAACA 488 38 1982; (14) ZAACA 475 205 1981; (15) JINCA 38 983 1976; (16) ZEKGA 124 275 1967; (17) JSSCB 60 1 1985; (18) ACBCA 34 1093 1978; (19) KOBZA 16 77 1983; (20) PCMID 14 426 1987; (21) COREA 259 3769 1964; (22) ZENBA 27 1567 1972; (23) INOCA 7 443 1968; (24) ZEKRD 165 313 1983; (25) ASBSD 39 564 1983; (26) ACCRA 19 396 1965; (27) ACBCA 28 2625 1972; (28) ACBCA 38 889 1982; (29) ACBCA 26 1230 1970; (30) MOCMB 112 51 1981; (31) PSSAB 87 425 1985. (b) Average value taken in this structure of lower symmetry. (c) X and Al ions disordered.

Values of polyhedral volumes and volume ratios

Crystallographic and compositional data of the compounds are given in Table 1, together with polyhedral volumes and their ratios. The data are divided into compositional families, which are arranged in descending order of $[O^{2-}]/[Al^{3+}]$, *i.e.* the ratio of the molar concentration of oxygen ions to the molar concentration of aluminium ions. Considerations of charge neutrality dictate that this ratio decreases as the valence and/or relative concentration of the X cation decrease, until in alumina, Al_2O_3, where no X cation is present, $[O^{2-}]/[Al^{3+}] = 1·5$. Within each compositional family, the compounds are arranged in order of descending r_X^{VI}, which is the standard radius of the X cation when coordinated ocatahedrally (Shannon, 1976). This quantity is taken to represent 'relative ionic size' in a quantitative manner.

The columns headed N_X, C_X refer to the number of X cation coordination polyhedra in the unit cell and the number of corners (vertices) in each polyhedron. N_{Al}, C_{Al} refer likewise to aluminium coordination polyhedra. If a particular structure occupies

more than one row in the table, then either the X or the Al cations have more than one type of coordination polyhedron. For example, in all $X_3Al_5O_{12}$ compounds (garnets), of the 40 aluminium ions in the unit cell, 16 form octahedra and 24 form tetrahedra. And in $CaAl_2O_4$, the calcium ions have three types of coordination polyhedron, one with C_X equal to 12 and two with C_X equal to 6. Volumes of X and Al coordination polyhedra, calculated acoording to equations (1) and (2), are denoted by V_X and V_{Al} respectively. Of the eight XO_6 octahedra in $CaAl_2O_4$, four have a volume of $17 \cdot 53$ Å^3 and the other four a volume of $16 \cdot 75$ Å^3. Consequently, they are represented in two separate rows in the table. The quantity V_X/V_{Al} is simply the ratio of V_X to V_{Al}, with f_{enc} representing the quantity defined in equation (3).

It is immediately apparent that, apart from garnet ($X_3Al_5O_{12}$) and spinel (XAl_2O_4; X = Zn, Cu, Co, Mg, Ni) compounds, no simple correlation exists between space group and chemical composition. Five of the compounds, $LaAlO_3$, $YAlO_3$, $BaAl_2O_4$, $CuAlO_2$ and $SrAl_4O_7$, are bimorphic, with the differences between their two structures reflected by the data in the table. The difference between the two $LaAlO_3$ structures is very slight, the first being associated with the polar space group $R3m$, and the second having the centrosymmetric space group, $R\bar{3}m$.

In nearly all of the compounds, the cation coordination polyhedra can be assigned unambiguously, simply by considering the distances of oxygen ions (polyhedral corners) from the cations inside each polyhedron. This is not the case in the two structures of lowest symmetry, $PbAl_2O_4$ ($P1$) and $SrAl_2O_4$ ($P2_1$), in which the X ions (Pb and Sr) have a highly asymmetric coordination by oxygen ions. Thus the choice of *octahedra* in the table is only one of several possibilities. There is, however, a natural upper limit to the number of corners taken to define the coordination polyhedra, as the *overlapping* of polyhedra, a consequence of taking too high a value for C_X, is forbidden. It is appropriate to remark that a structural analysis based on Pauling's second rule cannot resolve this difficulty, since the total oxygen-ion valence of the unit cell, calculated from equation (4), is insensitive to changes in C_X. Although n_i increases as C_X increases, so that each term in the summation, $v_{c,i}/n_i$, is diminished, the *number* of terms in the summation increases in a compensatory manner. This reflects the structural feature that each oxygen ion is shared between a greater number of polyhedra as C_X is increased. A quantitative means of defining the coordination number of a cation is, in principle, provided by the bond-valence method, as has been discussed by Allmann (1975), but this lies outside the scope of the present study.

Within each family of compounds, it is seen that, for a given value of C_X, values of V_X generally decrease as the table is descended. This parallel decrease of V_X and r_X^{VI} suggests that the r_X^{VI} values are accurate general indicators of 'relative ionic size'. Values of V_{Al} depend on whether the polyhedron is a tetrahedron, a trigonal bipyramid or an octahedron, but they fall within narrow ranges: $(V_{Al})_{tetra} = 2 \cdot 741 \pm 0 \cdot 088$ Å^3 and $(V_{Al})_{octa} = 9 \cdot 237 \pm 0 \cdot 232$ Å^3. (In the evaluation of these ranges, the tetrahedral volumes for $SrAl_4O_7$ (ii) have been omitted, since their small values bring the accuracy of this structure into question. Octahedral volumes in $CuAl_2O_4$ and $NiAl_2O_4$ have also been omitted, since Al and X ions are disordered in these structures.)

V_X/V_{Al} and f_{enc} are discriminating structural parameters. As discussed previously (Thomas, 1989b), the ratio of cuboctahedral to octahedral polyhedral volume is exactly equal to 5 in all ferroelectric perovskites of general formula ABO_3. Of the perovskite structures examined here, only the first $LaAlO_3$ polymorph is capable of exhibiting ferroelectricity, owing to its polar space group. V_X/V_{Al} is also equal to 5 in the second polymorph of $LaAlO_3$ and in $PrAlO_3$, but as the size of the X ion decreases (expressed by r_X^{VI}), the cuboctahedral coordination polyhedron (Fig. 1b) becomes distorted, to assume a smaller volume and V_X/V_{Al} ratio, as in $NdAlO_3$ ($V_X/V_{Al} = 4 \cdot 84$). $SmAlO_3$ and the first polymorph of $YAlO_3$ have even smaller ratios, but the X-coordination polyhedron has now changed from a cuboctahedron into the octodecahedron shown in Fig. 1(c). Thus these structures are arguably no longer *perovskites*, but *perovskite-related* structures. The bimorphism of $YAlO_3$ suggests that the yttrium ion is only just big enough to be stabilized in this perovskite-related phase. The second $YAlO_3$ structure has C_X equal to 8 (Fig. 1h) and C_{Al} equal to 5 (Fig. 1j), corresponding to a completely different structural type. And in $ScAlO_3$, a further distinctive structure is observed.

The f_{enc} parameter has the value of unity in all perovskite and perovskite-related structures, which correspond to the first six entries in Table 1. Thus the X and Al coordination polyhedra mesh together completely, filling all available space. It is interesting to note that f_{enc} is also equal to unity in $RbAlO_2$ and $TlAlO_2$, where the Rb^+ and Tl^+ ions occupy truncated tetrahedra (Fig. 1d). In all the other structures, f_{enc} is considerably less than unity, indicating that there are voids between cation coordination polyhedra. The question naturally arises as to whether this void space can be used to accommodate guest ions in a given structure, a feature which may be important in phase-stabilization phenomena. These issues can only be resolved by a careful analysis of the voids in crystal structures, for which a computer algorithm has been expressly developed (Thomas, 1991).

Amongst the garnet compounds, $X_3Al_5O_{12}$, values of V_X generally reflect the corresponding values of r_X, with typical values for V_{Al} in four- and sixfold coordination. Values of f_{enc} indicate the presence of voids in the garnet structure. XAl_2O_4 compounds can be divided into two broad categories, depending on whether the aluminium ions have a coordination number of four or six. The former category is associated with larger X ions (X = Ba, Pb, Sr, Ca), and the latter with smaller ions. Bimorphic $BaAl_2O_4$ has the barium ion in either 12- or ninefold coordination, with the aluminium ion in fourfold coordination. Note that in structures of lower symmetry, V_{Al} is quoted as an average value, since there are several symmetry-independent Al sites, with coordination tetrahedra of slightly differing volumes. If the volumes of the X coordination octahedra are considered in the X = Pb, Sr, Ca systems, it is seen that their magnitudes decrease as the table is descended, in parallel with values of r_X^{VI}.

All compounds in this family with Al in sixfold coordination have the spinel structure, apart from $BeAl_2O_4$, after which the chrysoberyl structure is named. In two of the spinel structures (X = Cu, Ni), X and Al ions form both tetrahedra and octahedra, in a disordered fashion. Further evidence is found that V_X/V_{Al} is a discriminating structural parameter: in spinels, this ratio has values between 0·297 (X = Ni) and 0·416 (X = Zn), whereas in chrysoberyl (X = Be), V_X/V_{Al} falls to the two values of 0·248 and 0·230, corresponding to the two different aluminium

octahedral volumes in this structure. Thus a changeover between spinel and chrysoberyl structures can be anticipated at some intermediate ratio in the range $0·248 < V_X/V_{Al} < 0·297$.

The six $XAlO_2$ compounds all have different structures, although the difference between $RbAlO_2$ and $TlAlO_2$ is concerned only with changes in symmetry. In both these compounds, the types of coordination polyhedra and the manner in which they fill space are identical. Note that V_X/V_{Al} is integral, with a value of 23. This is due to fixed geometrical constraints, by analogy with the situation obtaining in perovskites. As r_X^{VI} falls, a structural change to that of $NaAlO_2$ is observed, and finally the $LiAlO_2$ structure is obtained. Again V_X/V_{Al} is a useful structural indicator. In the case of the bimorphs of $CuAlO_2$, values of V_X cannot be assigned, since layered 'sandwich' structures are present, in which the Cu^+ ions lie between monolayers of connected AlO_6 octahedra, of composition AlO_2^-. The coordination number of the Cu^+ ions is two, thus precluding the definition of a cation coordination polyhedron.

Amongst the compounds of composition XAl_4O_7, the first polymorph of $SrAl_4O_7$ and $CaAl_4O_7$ adopt similar structures, with V_X/V_{Al} ratios of 0·221 and 0·217 respectively. Despite this similarity, r_X^{VI} is significantly smaller for Ca^{2+} than it is for Sr^{2+}, suggesting that this structure may have a wide compositional stability range. However, the bimorphism of $SrAl_4O_7$ indicates that ions larger than Sr^{2+} are unlikely to be stabilized in this structure. In
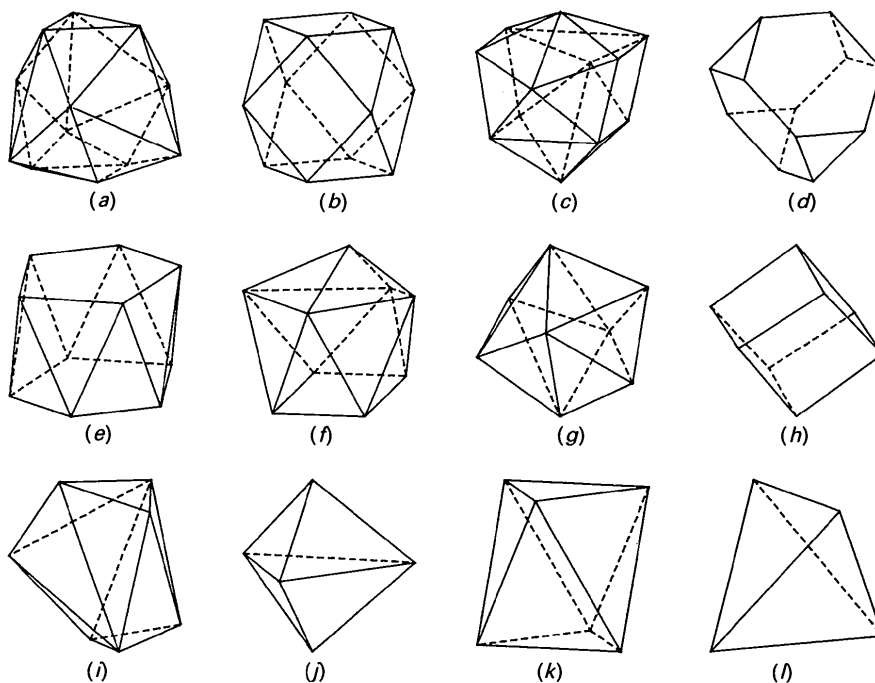

Fig. 1. Cation coordination polyhedra defined in Table 2, in clinographic projection.

$Cu_2Al_4O_7$, the Cu^+ ions have 12- and sixfold coordination, unlike the twofold layer coordination found in $CuAlO_2$ compounds.

Al_2O_3 has been included only for comparative purposes: its V_{Al} value of 9·08 Å^3 is below the average V_{Al} value of the compounds studied.

Characteristics of the cation coordination polyhedra

Table 2 lists the characteristics of the cation coordination polyhedra in these compounds. The shape of a given polyhedron can be described in terms of the numbers of its corners (vertices), edges and faces, represented in the table as C_X, E_X, F_X for X-cation polyhedra and as C_{Al}, E_{Al}, F_{Al} for Al-coordination polyhedra. Polyhedral types are stated in the table, and Fig. 1 shows all the different coordination polyhedra encountered in these compounds. The letters in the column of the table headed 'Fig'. indicate that part of Fig. 1 in which a particular polyhedral type is to be found. Note that each letter (a) to (l) is to be found against one structure only: it is the data of this structure which have been used to draw the relevant part of Fig. 1.

It can be seen that all the X- and Al-coordination polyhedra obey Euler's law (Wells, 1956):

$$C + F = E + 2, \tag{5}$$

i.e. the sum of the numbers of corners and faces in any polyhedron is equal to two more than the number of edges.

The columns headed C_X^s, E_X^s and F_X^s give the numbers of *shared* corners, edges and faces in X polyhedra, with a corresponding function for the columns headed C_{Al}^s, E_{Al}^s and F_{Al}^s. Notice that each non-zero entry in these E and F columns has an extra code letter, a, x or m, adjacent to the number. These letters, indicate whether the edges and faces are shared with Al-coordination polyhedra, X-coordination polyhedra, or a mixture of Al- and X-polyhedra, respectively. The entries in these columns permit an objective assessment of the validity of Pauling's third and fourth rules, which are concerned with the broad principles governing the sharing of polyhedral elements. The fourth rule deals specifically with crystals containing different cations, such as all the compounds here, apart from Al_2O_3. A strict observance of this rule for all coordination polyhedra would imply that X-polyhedral edges and faces are shared only with Al edges and faces, and that Al edges and faces are shared only with X edges and faces. However, this is only the case in XO_4, AlO_4 tetrahedra, and in the AlO_5 trigonal bipyramid found in the second polymorph of $YAlO_3$. In coordination polyhedra with a coordination number greater than five, the sharing of edges between *like* polyhedra is relatively common: for example, in the

spinel structure (XAl_2O_4; X = Zn, Cu, Co, Mg, Ni) six of the 12 Al-octahedral edges are shared with other AlO_6 octahedra. And in all the larger X polyhedra, no particular tendency towards sharing with Al polyhedra is observed.

The sharing of *faces* of polyhedra is, as suggested by Pauling's third rule, comparatively uncommon. However, it is unavoidable in structures where f_{enc} is equal to unity. Particularly worthy of note is the presence of shared edges and faces in alumina, Al_2O_3. This is rather surprising in view of Pauling's third rule, but the reason for this is discussed in the following section.

Calculation of electrostatic oxygen-ion valences

Table 3 gives the valences of each oxygen ion in the unit cell for all the structures. These valences are the so-called electrostatic valences, calculated from equation (4). The column headed N_O gives the number of oxygen ions in the unit cell, with the column headed 'oxygen-ion valences, v_O' giving the valences of each oxygen ion. These are represented as a valence, multiplied by its frequency of occurrence. For example in the second polymorph of $BaAl_2O_4$ [hereafter written as $BaAl_2O_4$ (ii), with a similar notation for other bimorphs], two oxygen ions have a calculated valence of 2·1667 and six have a calculated valence of 1·9444. The column headed $v_{O,tot}$ gives the *total* calculated oxygen-ion valence for the unit cell, which is obtained by summing all the calculated oxygen valences. Thus in $BaAl_2O_4$ (ii), for example, 2·1667 × 2 + 1·9444 × 6 = 16. As discussed in step 9 of the method, the definition of electostatic valence requires that $v_{O,tot}$ is equal to the sum of the cationic valences. Since, by the electroneutrality principle, this sum is also equal to the sum of anionic valences, $v_{O,tot} = 2N_O$. The right-hand column gives the workings of calculating v_O from equation (4), which permit the manner in which polyhedral corners are shared to be inferred. For example, in $YAlO_3$ (ii), the two oxygen ions with v_O equal to 2·55 are shared between two X polyhedra with C_X equal to 8 and three Al polyhedron with C_{Al} equal to 5. Similarly the four oxygen ions with v_O equal to 1·725 are shared between three X polyhedra with C_X equal to 8 and one Al polyhedron with C_{Al} equal to 5.

For structures in which every oxygen ion has an identical topological coordination, in the sense that identical numbers and types of cation coordination polyhedra share a corner at each oxygen ion, v_O is equal to 2 for each oxygen ion. This is a corollary of the electroneutrality principle, which requires that $v_{O,tot} = 2N_O$. Since, in this case, each oxygen ion is topologically equivalent, $v_{O,tot} = N_O v_O$, so $v_O = 2$. It follows also that the valence condition [equation (4)] applying at each oxygen ion is identical to a state-

Table 2. *Attributes of the cation coordination polyhedra*

Chemical formula	X	C_X	E_X	F_X	Polyhedral type*	Fig.	C_X^{λ}	E_X^{λ}	F_X^{λ}	C_{Al}	E_{Al}	F_{Al}	Polyhedral type*	Fig.	C_{Al}^{λ}	E_{Al}^{λ}	F_{Al}^{λ}
XAlO$_3$	La	12	24	14	co	(b)	12	24m	14m	6	12	8	o		6	12x	8x
	La	12	24	14	co		12	24m	14m	6	12	8	o		6	12x	8x
	Pr	12	24	14	co		12	24m	14m	6	12	8	o		6	12x	8x
	Nd	12	24	14	co		12	24m	14m	6	12	8	o		6	12x	8x
	Sm	12	28	18	od	(c)	12	28m	18m	6	12	8	o		6	12x	8x
	Y	12	28	18	od		12	28m	18m	6	12	8	o		6	12x	8x
	Y	8	12	6	cu	(h)	8	12m	0	5	9	6	tbp	(j)	5	6x	0
	Sc	9	20	13	ap4c	(f)	9	18m	2a	6	12	8	o		6	12x	2x
X_3Al$_5$O$_{12}$	Tb	8	18	12	tdd		8	10m	0	6	12	8	o		6	6x	0
										4	6	4	t		4	2x	0
	Ho	8	18	12	tdd		8	10m	0	6	12	8	o		6	6x	0
										4	6	4	t		4	2x	0
	Y	8	18	12	tdd	(g)	8	10m	o	6	12	8	o		6	6x	0
										4	6	4	t		4	2x	0
	Lu	8	18	12	tdd		8	10m	0	6	12	8	o		6	6x	0
										4	6	4	t		4	2x	0
XAl$_2$O$_4$	Ba	12	30	20	ic	(a)	12	20m	8m	4	6	4	t		4	6x	2x†
		12	30	20	ic		12	23m	4m								
	Ba	9	20	13	ap4c		9	12m	2x	4	6	4	t		4	3x	0
	Pb	6	12	8	o		6	2a	0	4	6	4	t		4	1x	0
	Sr	6	12	8	o		6	4m	1x	4	6	4	t		4	0·5x†	0
		6	12	8	o		6	5m	1x								
	Ca	12	30	20	co		12	21m	5m	4	6	4	t		4	3x†	0·5x†
		6	12	8	o		6	4m	1x								
		6	12	8	o		6	5m	1x								
	Zn	4	6	4	t	(l)	4	0	0	6	12	8	o		6	6a	0
	Cu	4	6	4	t		4	0	0	6	12	8	o		6	6a	0
	Co	4	6	4	t		4	0	0	6	12	8	o		6	6a	0
	Mg	4	6	4	t		4	0	0	6	12	8	o		6	6a	0
	Ni	4	6	4	t		4	0	0	6	12	8	o		6	6a	0
	Be	4	6	4	t		4	3a	0	6	12	8	o		6	6m	0
										6	12	8	o		6	3m	0
XAlO$_2$	Rb	12	18	8	tt	(d)	12	18m	8m	4	6	4	t		4	6x	4x
	Tl	12	18	8	tt		12	18m	8m	4	6	4	t		4	6x	4x
	Na	6	12	8	o	(k)	6	12m	0	6	12	8	o		6	12m	0
	Cu	2	–	–	ls		2	–	–	6	12	8	o		6	6a	0
	Cu	2	–	–	ls		2	–	–	6	12	8	o		6	6a	0
	Li	4	6	4	t		4	1a	0	4	6	4	t		4	1x	0
XAl$_4$O$_7$	Sr	7	15	10	td		7	6m	0	4	6	4	t		4	0	0
										4	6	4	t		4	2x	0
	Sr	10	20	12	ap5	(e)	10	14m	2x	6	12	8	o		6	6m	0
										4	6	4	t		4	0	0
										4	6	4	t		4	3x	0
	Ca	7	14	10	td	(i)	7	6m	0	4	6	4	t		4	2x	0
										4	6	4	t		4	0	0
	Cu$_2$	12	24	14	co		12	24m	4	4	6	4	t		4	3x	0
		6	12	8	o		6	12x	4								
Al$_2$O$_3$	–	–	–	–	–		–	–	–	6	12	8	o		6	6a	1a

* Abbreviations used are: ap4c capped quadrilateral antiprism, ap5 pentagonal antiprism, co cuboctahedron, cu distorted cube, ic icosahedron, ls layer structure, o octahedron, od octodecahedron, t tetrahedron, tbp trigonal biprism, td trigonal decahedron, tdd trigonal dodecahedron, tt truncated tetrahedron.
† Average value.

ment of the electroneutrality principle. For example, in X_3Al$_5$O$_{12}$ compounds, the condition $2v_X/8 + v_{Al}/6 + v_{Al}/4 = 2$ can be rearranged to give $3v_X + 5v_{Al} = 24$. This is identical to the equation which can be derived at sight from the chemical formula, merely by applying the electroneutrality principle. In structures where non-equivalent oxygen ions exist, however, individual values of v_O deviate from 2, subject to the overall constraint imposed by the principle of electroneutrality, that $v_{O,tot} = 2N_O$. These conclusions may be summarized by stating that the *average* oxygen-ion valence, when calculated from equation (4), must be equal to 2.

Pauling's second rule applied to oxides states that each value of v_O is *equal*, or *nearly equal* to 2.

However, Table 3 shows significant deviations from 2 in structures with non-equivalent oxygen ions. The largest deviation is found in Cu$_2$Al$_4$O$_7$, where four oxygen ions have a value of v_O equal to 3. So, as is well known, the second rule is to be applied with caution.

A further investigation into the validity of this rule can be made by monitoring the effect on calculated values of v_O of substituting cations of different valences into the structures with non-equivalent oxygen ions. (In all structures with topologically equivalent oxygen ions, any set of valences satisfying the electroneutrality principle will automatically satisfy Pauling's second rule exactly.) The results of this investigation are given in Table 4. A structure of

Table 3. *Oxygen-ion valences calculated from equation* (4)

Chemical formula	X	v_X	v_{Al}	N_O	Oxygen-ion valences, v_O	$v_{O,tot}$	Valence conditions at oxygen ions [equation (4)]
$XAlO_3$	La	3	3	3	2.0000×3	6	$4v_X/12 + 2v_{Al}/6 = 2$
	La	3	3	6	2.0000×6	12	$4v_X/12 + 2v_{Al}/6 = 2$
	Pr	3	3	6	2.0000×6	12	$4v_X/12 + 2v_{Al}/6 = 2$
	Nd	3	3	18	2.0000×18	36	$4v_X/12 + 2v_{Al}/6 = 2$
	Sm	3	3	12	2.0000×12	24	$4v_X/12 + 2v_{Al}/6 = 2$
	Y	3	3	12	2.0000×12	24	$4v_X/12 + 2v_{Al}/6 = 2$
	Y	3	3	6	2.5500×2	12	$2v_X/8 + 3v_{Al}/5 = 2.55$
					1.7250×4		$3v_X/8 + v_{Al}/5 = 1.725$
	Sc	3	3	12	2.0000×12	24	$3v_X/9 + 2v_{Al}/6 = 2$
$X_3Al_5O_{12}$	Tb,Ho} Y,Lu}	3	3	96	2.0000×96	192	$2v_X/8 + v_{Al}/6 + v_{Al}/4 = 2$
XAl_2O_4	Ba	2	3	32	2.0000×32	64	$3v_X/12 + 2v_{Al}/4 = 2$
	Ba	2	3	8	2.1667×2	16	$3v_X/9 + 2v_{Al}/4 = 2.1667$
					1.9444×6		$2v_X/9 + 2v_{Al}/4 = 1.9444$
	Pb	2	3	8	2.1667×4	16	$2v_X/6 + 2v_{Al}/4 = 2.1667$
					1.8333×4		$v_X/6 + 2v_{Al}/4 = 1.8333$
	Sr	2	3	16	2.1667×8	32	$2v_X/6 + 2v_{Al}/4 = 2.1667$
					1.8333×8		$v_X/6 + 2v_{Al}/4 = 1.8333$
	Ca	2	3	48	2.1667×12	96	$2v_X/6 + 2v_{Al}/4 = 2.1667$
					2.0000×24		$v_X/12 + v_X/6 + 2v_{Al}/4 = 2$
					1.8333×12		$v_X/6 + 2v_{Al}/4 = 1.8333$
	Zn, Cu} Co, Mg, Ni}	2	3	32	2.0000×32	64	$v_X/4 + 3v_{Al}/6 = 2$
	Be	2	3	16	2.0000×16	32	$v_X/4 + 3v_{Al}/6 = 2$
$XAlO_2$	Rb	1	3	16	2.0000×16	32	$6v_X/12 + 2v_{Al}/4 = 2$
	Tl	1	3	12	2.0000×12	24	$6v_X/12 + 2v_{Al}/4 = 2$
	Na	1	3	6	2.0000×6	12	$3v_X/6 + 3v_{Al}/6 = 2$
	Cu	1	3	4	2.0000×4	8	$v_X/2 + 3v_{Al}/6 = 2$
	Cu	1	3	6	2.0000×6	12	$v_X/2 + 3v_{Al}/6 = 2$
	Li	1	3	8	2.0000×8	16	$2v_X/4 + 2v_{Al}/4 = 2$
XAl_4O_7	Sr	2	3	28	2.2500×8	56	$3v_{Al}/4 = 2.25$
					2.0714×8		$2v_X/7 + 2v_{Al}/4 = 2.0714$
					1.7857×12		$v_X/7 + 2v_{Al}/4 = 1.7857$
	Sr	2	3	28	2.2000×16	56	$v_X/10 + v_{Al}/6 + 2v_{Al}/4 = 2.2$
					1.6500×8		$2v_X/10 + v_{Al}/6 + v_{Al}/4 = 1.65$
					1.9000×4		$2v_X/10 + 2v_{Al}/4 = 1.9$
	Ca	2	3	28	2.2500×8	56	$3v_{Al}/4 = 2.25$
					2.0714×8		$2v_X/7 + 2v_{Al}/4 = 2.0714$
					1.7857×12		$v_X/7 + 2v_{Al}/4 = 1.7857$
	Cu_2	1	3	28	3.0000×4	56	$4v_{Al}/4 = 3$
					1.8333×24		$2v_X/12 + v_X/6 + 2v_{Al}/4 = 1.8333$
Al_2O_3	–	–	3	18	2.0000×18	36	$4v_{Al}/6 = 2$

formula $X_pAl_qO_r$ may be generalized to one of formula $X_pY_qO_r$, in which X and Y are allowed to take on any integral valences which are consistent with the electroneutrality principle. Thus $BaAl_2O_4$ (ii) is generalized to XY_2O_4, such that $v_X + 2v_Y = 8$. Four pairs of valences are permitted: $(v_X, v_Y) = (6,1)$, (4,2) (2,3), (0,4), where the assignment of $v_X = 0$ implies that the X-coordination polyhedron is vacant, i.e. the composition is YO_2.

For each pair of (v_X, v_Y) values in the table, the r.m.s. deviation of v_O values from the ideal Pauling value of 2 is quoted. The deviation corresponding to the actual chemical composition, where Y corresponds to Al and v_Y is equal to 3, is denoted by an asterisk. It is seen that this deviation is not always the smallest one, i.e. substitution of ions of different valences into the structure can give a closer agreement with Pauling's second rule than the actual

values associated with the composition in the left-hand column. In the $YAlO_3$ (ii) structure, for example, the closest agreement with Pauling's rule is to be found for a composition $X^{5+}Y^+O_3$. Similarly in the $Cu_2Al_4O_7$ structure, the actual composition is associated with a deviation of 0.717, although *exact* agreement with the rule would be obtained for a composition $X_2^{3+}Y_4^{2+}O_7$.

These findings reinforce the conclusion that Pauling's second rule should be treated with caution in analysing the structures of ionic oxides. It appears that the maintenance of electroneutrality, together with the requirement for cations to be coordinated by anions, and *vice versa*, are the minimum requirements to be satisfied by ionic oxides. Whereas the calculation of oxygen-ion valences according to equation (4) is a useful analytical technique, the requirement that each oxygen-ion valence is equal, or

Table 4. *Root-mean-square deviations of oxygen-ion valences from the ideal value of 2, for different combinations of cations satisfying the electroneutrality condition*

Deviations are non-zero only in structures containing topologically non-equivalent oxygen ions.

Structure and electroneutrality condition	X	Y	R.m.s deviation of oxygen-ion valences, ν_O, for different pairs of cationic valences, ν_X and ν_Y (ν_X, ν_Y, r.m.s. deviation)			
YAlO₃ (ii) $\nu_X + \nu_Y = 6$	Y	Al	(6,0, 0·395) (2,4, 0·712)	(5,1, 0·119) (1,5, 0·988)	(4,2, 0·158) (0·6, 1·265)	(3,3, 0·435)*
BaAl₂O₄ (ii) $\nu_X + 2\nu_Y = 8$	Ba	Al	(6,1, 0·373)	(4,2, 0·248)	(2,3, 0·124)*	(0,4, 0·000)
PbAl₂O₄ $\nu_X + 2\nu_Y = 8$	Pb	Al	(6,1, 0·500)	(4,2 0·333)	(2,3, 0·167)*	(0,4, 0·000)
CaAl₂O₄ $\nu_X + 2\nu_Y = 8$	Ca	Al	(6,1, 0·408)	(4,2, 0·272)	(2,3, 0·136)*	(0,4, 0·000)
SrAl₂O₄ $\nu_X + 2\nu_Y = 8$	Sr	Al	(6,1, 0·500)	(4,2, 0·333)	(2,3, 0·167)*	(0,4, 0·000)
SrAl₄O₇ (i) $\nu_X + 4\nu_Y = 14$	Sr	Al	(6,2, 0·510)	(2,3, 0·195)*		
SrAl₄O₇ (ii) $\nu_X + 4\nu_Y = 14$	Sr	Al	(6,2, 0·123)	(2,3, 0·240)*		
CaAl₄O₇ $\nu_X + 4\nu_Y = 14$	Ca	Al	(6,2, 0·510)	(2,3, 0·195)*		
Cu₂Al₄O₇ $\nu_X + 2\nu_Y = 7$	Cu	Al	(5,1, 0·717)	(3,2, 0·000)	(1,3, 0·717)*	

* Values of (ν_X, ν_Y, r.m.s. deviation) for composition in left-hand column.

is nearly equal to 2 is too tight a constraint. Thus Pauling's second rule is routinely violated in metal oxides.

Despite this limitation, the concept of electrostatic bond strengths, embodied in equation (4), can be invoked to consider the reasons for the existence of shared edges and faces in alumina, Al_2O_3. According to Pauling's rules, these would be associated with a relatively unstable structure. However, this is not the case, as the Al_2O_3 (corundum) structure is stable over a wide range of temperature and pressure.

In the case of AlO_6 octahedra, the strength of each Al—O bond is $3/6 = 0·5$. Thus, if each oxygen ion is to be equivalent, as is the case in alumina, four octahedra must meet at each oxygen ion. It is the requirement of these *four* octahedra meeting which results in the presence of shared edges and faces. Clearly, fewer polyhedra would be required to meet at common vertices if the bond strength of each Al—O interaction were greater. This can only be achieved through the adoption of coordination polyhedra with fewer vertices, *e.g.* tetrahedra. However, if AlO_4 tetrahedra were to be adopted in the crystal structure of Al_2O_3, the strength of each Al—O bond would be $3/4 = 0·75$. This is incompatible with each oxygen ion being topologically equivalent, since $2/0·75$ is non-integral. Thus the octahedron is adopted as the coordination polyhedron in alumina, even though this results in shared edges and faces.

If the requirement that each oxygen ion be topologically equivalent were waived, it is possible to conceive of an Al_2O_3 structure based on AlO_4 tetra-

hedra. This would consist of some oxygen ions ('type-1 ions') shared between three tetrahedra, and others ('type-2 ions') shared between two. Since the valence of type-1 ions would be 2·25, and that of type-2 ions would be 1·5, an average oxygen-ion valence of 2 would be obtained from a 2:1 ratio of the number of type-1 oxygen ions to the number of type-2 oxygen ions.

The electroneutrality principle itself can provide helpful insight into the structural principles of these, and other compounds. In the above example of $BaAl_2O_4$ (ii), the valence pair $(\nu_X, \nu_Y) = (0,4)$ is consistent with the condition that $\nu_X + 2\nu_Y = 8$. Thus this structure can be regarded as a derivative of a binary oxide, which, from Table 2, consists of YO_4 tetrahedra sharing corners. When the valence of the Y ion falls below 4, an X ion of the appropriate valence is accommodated in a polyhedron with C_X equal to 9, in order to preserve neutrality. Similarly, $YAlO_3$ (ii) can be regarded as a derivative either of an $X^{6+}O_3$ or of a $Y^{6+}O_3$ structure, corresponding to the (ν_X, ν_Y) pairs (6,0) and (0,6). However, these two binary oxides are quite dissimilar, the former consisting of corner- and edge-linked XO_8 cubes, and the latter made up of corner- and edge-linked YO_5 trigonal bipyramids (see Table 2).

By comparison, all the compounds of formula XAl_4O_7 cannot be regarded as structural derivatives of a parent binary oxide, since the appropriate electroneutrality condition does not permit a (ν_X, ν_Y) combination in which either ν_X or ν_Y is equal to zero. However, these compounds themselves may be 'parents' of structural derivatives of complex, quaternary oxides of general formula $X_p Y_q Z_r O_s$. In order to make a final judgement on this matter, a closer examination of their void space is required.

Other compositions in Table 3, with equivalent oxygen ions, can be analysed in this manner. The electroneutrality condition of the garnet structure, $X_3Al_5O_{12}$, which is given by $3\nu_X + 5\nu_{Al} = 24$, is satisfied only by $(\nu_X, \nu_Y) = (3,3)$. Thus this structure cannot be regarded as a derivative of a binary oxide. This contrasts with the situation in the spinel structure, where the less restrictive condition, $\nu_X + 2\nu_Y = 8$, permits the values $(\nu_X, \nu_Y) = (0,4)$. Thus this structure can be regarded as a structural derivative of a binary oxide of composition YO_2, which, according to Table 2, consists of corner- and edge-shared octahedra.

Predicting the existence of isostructural compositions

The above analysis permits the following basic conclusions to be drawn.

(i) The calculation of polyhedral volumes and their ratios is a discriminating method of characterizing different structures.

(ii) The ionic radii of Shannon (1976) for octahedrally coordinated cations are reliable and useful indicators of 'relative ionic size.'

(iii) In any ionic structure, the total oxygen-ion valence of a unit cell, calculated from equation (4), is always equal to the total cationic valence.

(iv) The electroneutrality principle restricts the valences of the ions which may be found in a given type of structure.

Conclusions (i), (ii) and (iv) may be used to define a general method for predicting hypothetical compositions most likely to adopt structures identical to known crystal structures, such as the ternary oxides studied here. This method is based on the fact that the volume of any regular polyhedron can be expressed in terms of the distance, r, from its centre to each of the (equidistant) vertices. In general this volume, V_{poly}, is equal to $N_{poly}r^3$, where, for example, N_{poly} has the value of 4/3 for a regular octahedron, $8(3)^{1/2}/27$ for a regular tetrahedron and $10/3(2)^{1/2}$ for a regular cuboctahedron.

This dependence of polyhedral volume on r can be generalized to a semi-empirical expression of the form of equation (6):

$$V_{poly} = N_{poly}(K_n r_C^{VI} + r_O)^3. \qquad (6)$$

In this expression, V_{poly} is the actual volume of a cation coordination polyhedron with n vertices in a given structure (as given, for example, by V_X, V_{Al} in Table 1). r_C^{VI} is the radius given by Shannon for a cation in sixfold coordination, and K_n is a factor used to convert from a sixfold to an n-fold coordinated ionic radius, $r_{C,n}$. r_O is the appropriate radius for an oxygen ion, which is weakly dependent on the number of its coordinating cations (Shannon, 1976). N_{poly}, however, no longer has a fixed value, but it is treated as a semi-empirical parameter given by $V_{poly}/(K_n r_C^{VI} + r_O)^3$. The variation in values of N_{poly} for a given type of polyhedron and cation from one structure to another reflects subtle changes in its size and shape, i.e. whether the coordination polyhedron is expanded, compressed or distorted.

Values of K_n correspond to mean values of the ratio $r_{C,n}/r_C^{VI}$ over all cations whose n-fold coordinated radii have been quoted by Shannon. The following values have been adopted: K_4 0·75760, K_5 0·91147, K_6 1·00000, K_7 1·07001, K_8 1·14242, K_9 1·16611, K_{10} 1·17771, K_{11} 1·17128, K_{12} 1·26287. This definition of n-fold coordinated ionic radii is more general than one based on the actual n-fold coordinated radii given by Shannon, since these are not quoted for all ions. It also embodies the principle that the r_C^{VI} ionic radii are to be used as parameters representing relative ionic size.

The values of N_{poly} calculated are characteristic of a given structure. The other parameters characteristic of the different structures are the polyhedral volume

ratios, e.g. V_X/V_{Al} in Table 1. In a structure with n different polyhedra, $(n-1)$ independent polyhedral volume ratios may be defined.

In searching for other compositions which can adopt a given structure, the so-called 'generating structure', the volume of the unit cell should be capable of being increased or decreased, as the volumes of cation coordination polyhedra change. This is implicitly accommodated by employing a search/match procedure based on polyhedral volume ratios. Once N_{poly} values have been calculated for every different polyhedron in the generating structure, the volumes, V_{poly}, all cations of known r_C^{VI} would adopt in these polyhedra are calculated, using equation (6). Since the generating structure has fixed polyhedral volume ratios, only combinations of cations with simlar volume ratios may have the same structure. Two further considerations limit the number of isostructural compositions generated: first, the electroneutrality condition of the generating structure must be obeyed by the cations; and secondly, no generated structure with a minimum O—O separation below a certain limit, taken as 2·5 Å, is allowed.

The search/match procedure evaluates the polyhedral volume ratios, $[V_2/V_1]_{calc}$, $[V_3/V_1]_{calc}$, etc. for every cation with a known r_C^{VI} value. V_1, V_2, V_3 refer to the volumes of different polyhedra, V_{poly}, which are calculated from equation (6) using the $(N_{poly})_X$ and $(N_{poly})_Y$ values of the generating structure. The closest fit is determined by evaluating the ratios of the calculated V_2/V_1, V_3/V_1 values to the corresponding V_2/V_1 and V_3/V_1 values in the generating structure, denoted by $[V_2/V_1]_{gs}$, etc. in Table 5. The better the fit, the closer these ratios are to unity. Thus the criterion used to monitor closeness of fitting is the r.m.s. deviation of these values from unity, quoted in the column headed 'R.m.s.d.' in Table 5. Clearly, a deviation of zero is associated with ions corresponding to the generating structure itself.

In this table, the column headed 'd_{O-O}^{min}' gives the minimum O—O separation in the generated structure. The five closest fits are given for each generating structure. Thus the YAlO₃ (i) structure can also be adopted by $Nd^{3+}Cr^{3+}O_3$, $Pa^{3+}Ti^{3+}O_3$, $Tm^{2+}W^{4+}O_3$ and $Eu^{3+}As^{3+}O_3$. Similar interpretations can be given for the other generating structures.

It is interesting to note that the numbers of generated compositions with an r.m.s. deviation smaller than 0·02 vary widely. The chrysoberyl structure gives rise to no fewer than 125 compositions, whereas the $BaAl_2O_4$ (ii) structure generates only four. Thus the former structure is expected to be much more common.

A brief comparison of the results for $RbAlO_2$ and $TlAlO_2$ is also interesting. As discussed above, these two structures are topologically identical, yet they

Table 5. *A selection of the structures studied, with some of the hypothetical compositions most likely to adopt identical structures*

LS denotes low-spin state of cation.

Generating structure, electroneutrality condition and N_{poly} value	Ions substituted into structure (1)	(2)	(3)	$\dfrac{[V_2/V_1]_{calc}}{[V_2/V_1]_{gs}}$	$\dfrac{[V_3/V_1]_{calc}}{[V_3/V_1]_{gs}}$	d_{O-O}^{min} (Å)	R.m.s.d.
$YAlO_3$(i)	Al^{3+}	Y^{3+}	–	1·00000	–	2·666	0·00000
$v_x + v_y = 6$	Cr^{3+}	Nd^{3+}	–	0·99994	–	2·776	0·00006
$(N_{poly})_x = 2·5488$	Ti^{3+}	Pa^{3+}	–	0·99981	–	2·852	0·00019
$(N_{poly})_Y = 1·2836$	W^{4+}	Tm^{2+}	–	1·00035	–	2·839	0·00035
	As^{3+}	Eu^{3+}	–	1·00042	–	2·728	0·00042

Total number of compositions indentified with R.m.s.d. < 0·02: 105

$YAlO_3$(ii)	Al^{3+}	Y^{3+}	–	1·00000	–	2·672	0·00000
$v_x + v_y = 6$	Ag^{3+}	Ac^{3+}	–	0·99916	–	2·948	0·00084
$(N_{poly})_x = 1·4088$	As^{3+}	Eu^{3+}	–	1·00113	–	2·731	0·00113
$(N_{poly})_Y = 1·0571$	Mn^{3+}(LS)	Eu^{3+}	–	1·00113	–	2·731	0·00113
	Cr^{3+}	Nd^{3+}	–	1·00122	–	2·776	0·00122

Total number of compositions identified with R.m.s.d. < 0·02: 109

$BeAl_2O_4$	Al^{3+}	Al^{3+}	Be^{2+}	1·00000	1·00000	2·517	0·00000
$v_y + 2v_y = 8$	Ti^{3+}	Ti^{3+}	Fe^{2+}(LS)	1·00000	0·99983	2·694	0·00012
$(N_{poly})_x = 0·4291$	Nb^{3+}	Nb^{3+}	Mn^{2+}(LS)	1·00067	1·00067	2·760	0·00047
$(N_{poly})_Y = 1·2593, 1·3562$	Ta^{3+}	Ta^{3+}	Mn^{2+}(LS)	1·00000	1·00067	2·760	0·00047
	Tm^{3+}	Tm^{3+}	Pd^{2+}	1·00000	1·00086	2·970	0·00061

Total number of compositions identified with R.m.s.d. < 0·02: 125

$RbAlO_2$	Al^{3+}	Rb^+	–	1·00000	–	2·797	0·00000
$v_x + v_y = 4$	Rh^{3+}	Cs^+	–	1·00095	–	2·947	0·00095
$(N_{poly})_x = 1·8852$	Ti^{3+}	Cs^+	–	0·99506	–	2·948	0·00494
$(N_{poly})_Y = 0·4239$	Cu^{3+}(LS)	Rb^+	–	0·99380	–	2·797	0·00620
	Co^{3+}(LS)	Rb^+	–	0·98675	–	2·797	0·01235

Total number of compositions identified with R.m.s.d. < 0·02: 8

$TlAlO_2$	Al^{3+}	Tl^+	–	1·00000	–	2·716	0·00000
$v_x + v_y = 4$	In^{3+}	Fr^+	–	0·99833	–	3·012	0·00167
$(N_{poly})_x = 1·8563$	Fe^{3+}(LS)	Rb^+	–	1·00318	–	2·732	0·00318
$(N_{poly})_Y = 0·4084$	Ir^{3+}	Cs^+	–	1·00509	–	2·879	0·00509
	Ru^{3+}	Cs^+	–	1·00509	–	2·879	0·00509

Total number of compositions indentified with R.m.s.d. < 0·02: 14

$BaAl_2O_4$(ii)	Al^{3+}	Ba^{2+}	–	1·00000	–	2·792	0·00000
$v_x + 2v_y = 8$	Cu^{3+}(LS)	Ba^{2+}	–	0·99366	–	2·792	0·00634
$(N_{poly})_x = 1·6229$	Co^{3+}(LS)	Ba^{2+}	–	0·98738	–	2·792	0·01262
$(N_{poly})_Y = 0·4940$	Fe^{3+}(LS)	Ba^{2+}	–	0·98114	–	2·792	0·01886

Total number of compositions identified with R.m.s.d. < 0·02: 4

have different space groups. None of the generated compositions listed in the table are common to the $RbAlO_2$ and $TlAlO_2$ structures, although these do exist, with larger r.m.s. deviations. Thus the composition $TlAlO_2$ can be generated in the $RbAlO_2$ structure with a deviation of 0·02156, and the composition $RbAlO_2$ can be generated in the $TlAlO_2$ structure with a deviation of 0·02203. It is possible that those compositions which fit the $RbAlO_2$ structure most closely will have the space group $Fd3m$, and those closest to the $TlAlO_2$ structure will have space group $R\overline{3}m$, but this remains to be proven.

In more general terms, the sensitivity of the method to subtle changes in polyhedral coordination makes it potentially useful in identifying further compositions with a particular, desired structure. This structure may be specific to a given type of physical property, e.g. ferroelectricity or piezoelectricity, in which the space-group symmetry may also play an important role (Thomas, 1989b; Abrahams, 1989). The framework described, incorporating polyhedral volumes, standard ionic radii and electrostatic bond strengths, is a useful tool for the systematic exploration of new compositions for materials with certain desirable physical properties.

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