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The Zintl–Klemm concept applied to cations in oxides. I. The structures of ternary aluminates

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The structures of 94 ternary aluminates are reinterpreted on the basis of the Zintl–Klemm concept and Pearson's generalized octet rule. In aluminates of highly electropositive metals such as alkali, alkaline-earth and rare-earth metals, the Al atoms form three-dimensional skeleta which can be interpreted as if the Al atoms were behaving as Zintl polyanions, adopting the structure of either main-group elements or Zintl polyanions showing the same connectivity. The O atoms are then located close to both the hypothetical two-electron bonds and the lone pairs, giving rise to a tetrahedral coordination. When more electronegative elements, such as W or Si, are present in the compound, the electron transfer towards the Al atoms does not take place. In this case, aluminium behaves as a base, transferring its electrons to the more electronegative atoms and the coordination sphere of aluminium becomes octahedral. In some compounds the Al atoms clearly show amphoteric character so that some Al atoms act as donors (bases) and hence are octahedrally coordinated, whereas others behave as acceptors (acids), adopting a tetrahedral coordination. From this it is concluded that the coordination sphere of aluminium is not a function of the ionic radius of the Al^{3+} cations, but it depends on the nature of the other cations accompanying them in the structure. The networks formed by these aluminates are, in many instances, similar to those of the binary oxides of the main-group elements. For this reason, a systematic survey of these oxides is also reported. Compounds such as stuffed cristobalites and trydimites and also perovskites are examples of this new interpretation. Perovskites are then reinterpreted as a stuffed pseudo-TeO_3 structure. Other families of compounds such as silicates and phosphates are susceptible to a similar interpretation. This study provides additional examples of how cations recognize themselves in spite of being embedded in an oxygen matrix.

1. Introduction

Aluminates, ternary and quaternary oxides of aluminium, have been widely studied. The Inorganic Crystal Structure Database (ICSD) contains 94 phases of ternary aluminates.

A structural characteristic of these aluminates is the variability in the coordination sphere of the Al atoms. In most cases, aluminium appears either tetrahedrally or octahedrally coordinated and only in a few compounds does aluminium appear as five-coordinated by O atoms. Moreover, in some compounds two types of coordination polyhedra coexist. This is the case for the mineral andalusite (Al_2SiO_5), where five- and six-coordinated Al atoms are found, or compounds such

as sillimanite (Al_2SiO_5), Al_5BO_3, $FeAlO_3$ and $Sr_4Al_{14}O_{25}$, where both $Al(O)_4$ tetrahedra and $Al(O)_6$ octahedra are present.

This variability in the coordination number of aluminium has not been explained satisfactorily since it is based on geometrical factors (the radius ratio r_+/r_-) and consequently it depends on the ionic radii set we use to calculate the ratio. Thus, if we take the radii of Shannon & Prewitt (1969), the r_+/r_- ratio has the values 0.2867 and 0.3897 for Al^{IV} and Al^{VI}, respectively. With these values, the Al atoms would necessarily occupy tetrahedral holes (limiting ratio for the tetrahedral coordination, 0.414). If the set of Pauling (1960) is considered, the r_+/r_- ratio (0.357) also predicts a tetrahedral coordination. Only if the univalent radii are used does the r_+/r_- ratio have a value of 0.41, which is close to the upper limit for tetrahedral coordination and which is the lower limit for octahedral coordination. Thus, these univalent radii (when applicable) should be the only geometrical support to the variable coordination of aluminium in their oxides. However, it should be pointed out that an r_+/r_- ratio of 0.40 (compared with 0.41) is considered to be an overwhelming argument to justify the tetrahedral coordination of Zn^{2+} cations in ZnS.

Another structural feature of aluminates is the constancy of the Al—Al distances. In recent work Isea *et al.* (1998) have shown that the distribution of the Al—Al distances in all aluminium oxides is not homogeneous, but it presents two maxima. The first is a sharp maximum which is centered at 2.86 Å, just the value of the Al—Al distance in *f.c.c.*-Al (face-centered cubic). This distance corresponds to the separation between two Al atoms which occupy edge-sharing octahedra. The structures of spinels ($A^{IV}M^{VI}{}_2O_4$) and delafossites ($A^{II}M^{VI}O_2$) were therefore interpreted as formed by fragments of a *f.c.c.*-Al net (Isea *et al.*, 1998). The same feature was observed in aluminium oxides, hydroxides and oxyhydroxides (Ramos-Gallardo & Vegas, 1995, 1996). The second maximum is broader and is centered at around 3.3 Å. It is coincident with the distribution of distances (Al—Al) between two Al atoms (normally tetra-coordinated) bridged by one single O atom, from which O'Keeffe & Hyde (1981) assigned a value of 1.62 Å to the non-bonded or 'one-angle' radius of Al^{3+}. An example of this behaviour is $NaAlO_2$ (Kaduk & Pei, 1995) in which the AlO_4 tetrahedra share corners to form a three-dimensional array where the Al—Al contacts are 3.21 Å.

From these studies (Ramos-Gallardo & Vegas, 1996; Isea *et al.*, 1998), it was concluded that the structures with hexa-coordinated Al atoms reproduce topology and distances of the elemental metal structure, and hence they could be related to it. However, in compounds with tetra-coordinated aluminium, the $Al(O)_4$ tetrahedra form networks which, in most cases, have been poorly described as complicated and capricious arrangements whose connectivity has not been understood and hence could not be related to any known elemental structure. Only in some compounds are these three-dimensional tetrahedral networks related to other $X(O)_4$ tetrahedral skeleta. This is the case for $KAlO_2$ (stuffed cristobalite structure), in which the KAl subarray is that of the Zintl phase LiAl (O'Keeffe & Hyde, 1985), and the above-mentioned $NaAlO_2$, which also adopts a distorted cristobalite structure. Other examples of stuffed quartz, trydimite, cristobalite and keatite structures are collected in chapter 23 of the treatise *Structural Inorganic Chemistry* (Wells, 1975).

These features, together with the structural similarity found between the Zintl phase $CaAl_2Si_2$ and the corresponding aluminosilicate $CaAl_2Si_2O_8$ (Vegas & Santamaría-Pérez, 2003), led us to think that the Zintl–Klemm concept could be maintained in the oxides and that its application to aluminates could help us to rationalize and explain the rather complicated networks found in this family of compounds which, on the other hand, cannot be explained in terms of the Pauling's r_+/r_- ratio.

The application of the Zintl–Klemm concept could be reasonable for the following reasons: on one hand because there are some main group elements whose structure is topologically maintained in their oxides. This occurs for example in two varieties of SiO_2 such as cristobalite and trydimite, where the Si atoms preserve the structures of elemental silicon (diamond-like and londsdaleite-like, respectively) and also in keatite whose silicon array is that of an HP phase of Ge (Wells, 1975). Other examples are provided by the P_4 molecules and the corresponding oxides P_4O_6, P_4O_8, P_4O_9 and P_4O_{10}, where the P_4 skeleton is preserved. This coincidence was already pointed out by Addison (1965). On the other hand, because aluminium is an element at the Zintl border (Miller, 1996) which is in the presence of very electropositive cations, it can behave as a Zintl polyanion (remember the case of LiAl mentioned above) and the polyanion networks could be maintained in the oxides.

As is well known, the Zintl concept (Zintl, 1939), later extended by Klemm (1958), is that in compounds A_xX_y, where A is a very electropositive element relative to a main-group element X, the structure can be thought of as if the A atoms transfer their valence electrons to the X atoms which use them to form X–X bonds. The number of bonds formed obey the $8-N$ rule. When heterogeneous X species are formed, then the X skeleton can be explained by the generalized octet rule (Pearson, 1964).

The first attempt to correlate the connection between tetrahedra with composition is due to Parthé & Engel (1986). Furthermore, the Zintl–Klemm concept was applied by Parthé & Chabot (1990) to deduce the connectivity in structures with anionic tetrahedron complexes of the general formula $C_mC'_{m'}A_n$. From valence-electron criteria they deduced expressions which allow the prediction of tetrahedral sharing numbers, as well as the formation of $C'-C'$ and $A-A$ bonds.

We report here a systematic study of the structures of all the ternary aluminates contained in the ICSD. The Al subarrays will be analysed in the light of both the Zintl concept and the generalized octet rule (Pearson, 1964). We will see that these two old concepts will help us to understand both the coordination sphere of the Al atoms and the three-dimensional array of these complicated frameworks. One of these old concepts, the Zintl concept, is *the single most important theoretical concept in solid state chemistry of this century*, in the opinion of Hoffmann (1988).

The study begins with a survey of the structures of all the oxides of the main group elements with which the aluminate networks could be related.

2. Discussion

2.1. Binary oxides of main-group elements

The known oxides of the main group elements (hereafter referred to as *X*) are collected in Table 1. Table 1 also contains both the elements and the Zintl polyanions with which the cationic *X* substructures are related.

For the group 14 elements, the similarity between the elemental structures and those of the oxides is straightforward. We have mentioned in §1 that the *X*-subarray in trydimite and cristobalite are topologically identical to hexagonal (wurtzite-like) and cubic (diamond-like) silicon, respectively. The cristobalite structure also exists for GeO_2. CO_2, which under normal conditions is a molecule, adopts the structure of quartz at very high pressures (above 40 GPa and 1800 K; Iota *et al.*, 1999). The same structure exists for SiO_2 and GeO_2. In quartz the *X* atoms adopt a structure formed by triangular and hexagonal helices which do not correspond to any structure of the Group 14 elements, but it is identical to that of the Si-rich compound $CrSi_2$ (Mattheiss, 1992) represented in Fig. 1. In addition, the subarray of *X* atoms in keatite corresponds to an HP (high-pressure) phase of Ge (Wells, 1975). More recently, O'Keeffe & Hyde (1985) reported the similarities between the Si array in both K_4Si_{23} and the silica-rich mineral melanophlogite. Other varieties of silica exist, such as ferrierite, moganite and chabazite, whose Si substructures do not correspond to any structure of the elements but where the four-connectivity is maintained.

Finally, the rutile-type structure is observed for HP-SiO_2 (stishovite), GeO_2, SnO_2 and β-PbO_2. In these structures, as in rutile, the cation array (body-centered tetragonal, b.c.t.) corresponds to an expansion of the b.c.t. structure of the HP γ-Sn (Barnett *et al.*, 1986). Thus, in all the Group 14 oxides the cation arrays correspond either to the structures of elements of the group or to structures of Si-rich compounds.

In Group 15 similar behaviour is observed. For phosphorus, five oxides are known, *i.e.* P_4O_6 (Jansen *et al.*, 1981), P_4O_7 (Jost & Schneider, 1981; Moebs & Jansen, 1984), P_4O_8 (Beagley *et al.*, 1969; Jansen & Strojek, 1997), P_4O_9 (Jost, 1964; Beagley *et al.*, 1967; Lueer & Jansen, 1991) and P_4O_{10} (Cruickshank, 1964; Arbib *et al.*, 1996). One unique phase is known for all of them except P_4O_{10}, of which three phases have been reported. All these oxides, except P_4O_7, maintain the skeleton of the P_4 molecule. In Fig. 2 the structures of P_4, P_4O_6 and P_4O_{10} are represented. As seen, when six O atoms are located close to the P—P bonds, the P_4O_6 molecule is formed. When more O atoms are added, close to the positions of the P lone pairs, the P_4O_8, P_4O_9 and P_4O_{10} oxides are formed. The exception to this rule is P_4O_7, in which the P_4 tetrahedron is broken in such a way that the apical P atom is displaced, breaking two P—P bonds. In the second phase of P_2O_5, phosphorus adopts the layer structure of elemental As and also that of the Si atoms (pseudo-phosphorus) in $CaSi_2$. In the third phase the P atoms arrange as the Si atoms (pseudo-phosphorus atoms) in the HP Zintl phase $SrSi_2$ (Evers *et al.*, 1983) or in $BaGe_2$ (Evers *et al.*, 1980). This structure is represented in Fig. 3 and consists of a three-connected net forming 12- and ten-membered rings.

Five phases have been reported for the arsenic oxides, *i.e.* two for As_2O_3, one for AsO_2 and two for As_2O_5. In the first phase of As_2O_3, the As atoms reproduce the topology of the layered three-connected net of the elemental As (Fig. 4;

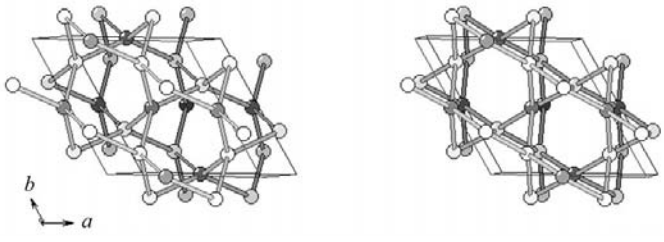

Figure 1
Stereopair of the structure of $CrSi_2$. Dark grey circles are Cr atoms. Medium grey circles are Si atoms. Both atoms form trigonal and hexagonal helices as the Si atoms in quartz. All figures were prepared using *DIAMOND* (Crystal Impact, 1998).

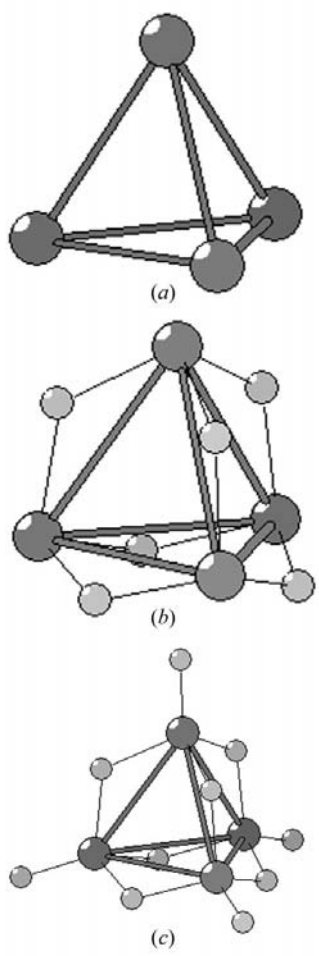

Figure 2
The molecules of (*a*) P_4, (*b*) P_4O_6 and (*c*) P_4O_{10}.

Table 1
The binary oxides of the main-group elements whose cation arrays are coincident with either the structure of the respective elements or simple binary compounds.

Oxides preserving the elemental structures	Elemental or alloy structures
SiO_2 (cristobalite), GeO_2 BPO_4, $BeSO_4$, $ZnSO_4$ (HT)	Si (diamond) BP, BeS, ZnS (blende)
SiO_2 (trydimite) BPO_4	C, Si (hexagonal)
SiO_2 (quartz), GeO_2, CO_2 BPO_4, $AlPO_4$	$CrSi_2$
SiO_2 (keatite)	Ge (HP)
SiO_2 (stishovite), GeO_2, SnO_2, β-PbO_2	Sn (HP)
Melanophlogite	K_4Si_{23}
$AlPO_4$ (metavariscite)	CrB_4, β-BeO
$AlPO_4$ (variscite)	Si (HP)-related
SnO (HP)	
P_4O_6, P_4O_8, P_4O_9, P_4O_{10}, As_2O_3,Sb_4O_6, Sb_4O_{10}	P_4 (molecules)
P_2O_5	$SrSi_2$ (HP), $BaGe_2$, $ThSi_2$
P_2O_5, As_2O_3	As (layers), $CaSi_2$
P_4O_7	
As_2O_5 (two phases)	$SrSi_2$ (ambient pressure)
As_2O_4	
Sb_2O_3	
Sb_2O_5, Sb_2O_4, Bi_2O_4	Bi, Sb (HP)
Bi_2O_3	
SO_3, SeO_2, Se_2O_5, γ-TeO_2	S (chains) asbestos-like
S_3O_9	S_3 (molecule)
Se_4O_{12}	S_4 (molecule)
TeO_3	Te (HP), Po
TeO_2	S_2 (molecule)

Frueh, 1951). In the second phase (Lihl, 1932), As_2O_3 adopts the structure of P_4O_6 where the As_4 molecules, as in P_4, are recognisable. It should be added that a variety of arsenic (yellow arsenic) is formed as a sublimation product. It is cubic and presumably consists of As_4 molecules, but structural data could not be obtained (Jung, 1926).

When additional O atoms are inserted in the first phase of As_2O_3, AsO_2 is obtained. The As skeleton is somewhat different, but maintains the layers of the elemental As. The additional O atoms are placed close to the lone pairs, but only in alternate As atoms so that the coordination of arsenic varies from 3 to 4.

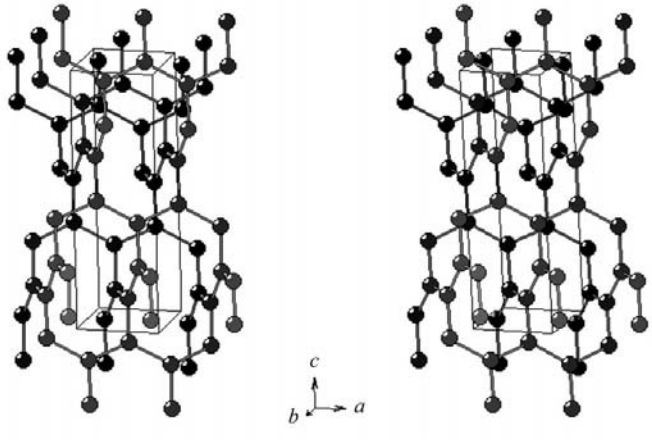

Figure 3
Stereopair showing the silicon partial structure of HP-$SrSi_2$. This array is similar to the third phase of P_2O_5.

The two phases of As_2O_5 are topologically related. The first, prepared under oxygen pressure (Jansen, 1978), has an As subarray similar to the Si array (pseudo-phosphorus) in the ambient pressure phase of $SrSi_2$ (Evers, 1978) and is formed by a three-connected net of both eight- and four-membered rings. This net is represented in Fig. 5. The second phase is stable above 578 K (Jansen, 1979*a*) and presents an arsenic subarray topologically related to the room-temperature phase. The difference is that in this case there is an As1 atom which is four-connected and the second one, As2, six-connected. It should be noted that in both phases of As_2O_5, one As atom (As1) is coordinated by six O atoms whereas As2 is only tetra-coordinated by four O atoms. This situation makes difficult the use of the principles applied to the other tetra-coordinated *X* atoms. Nevertheless, the skeleton of a pseudo-phosphorus atom as that existing in the Zintl phase $SrSi_2$ is observed in the oxides.

Antimony forms three oxides: Sb_2O_3, SbO_2 and Sb_2O_5. SbO_2 has one unique phase; the other two are stable in two phases. The first phase of Sb_2O_3 (Svensson, 1974) is formed by double chains of Sb atoms which are connected by additional interchain contacts. The final result is a band of zigzag puckered squares with the O atoms close to the midpoint of each square edge (see Fig. 6). In the second phase (Svensson, 1975), Sb_4O_6 forms a structure similar to P_4O_6 and As_4O_6 where Sb_4 tetrahedra are recognisable.

The same skeleton (Sb_4) is formed in one of the phases of Sb_4O_{10} (Dehlinger, 1927), whereas in the second phase of Sb_2O_5 (Jansen, 1979*b*) the Sb atoms form a network which is

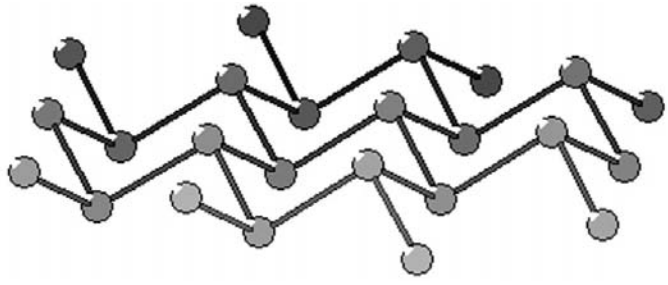

Figure 4
One layer of elemental As showing the chair conformation of the six-membered rings.

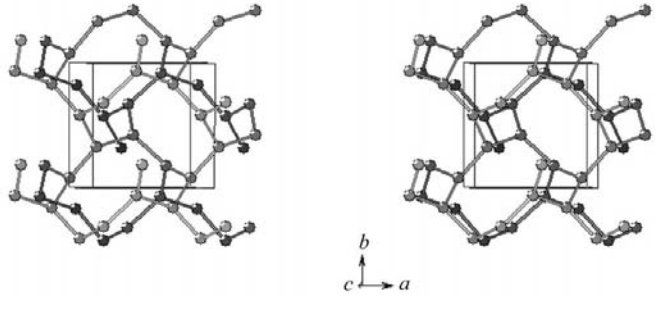

Figure 5
Stereopair showing the Si structure of the ambient pressure phase of $SrSi_2$. The Si atoms form a three-connected net formed by squares and octagonal helices as in As_2O_5.

close to the cubes present in the structure of Bi and in the HP phase of Sb. In this oxide all the Sb atoms appear octahedrally coordinated by six O atoms and the octahedra share corners in some directions and edges in other directions, as required by the stoichiometry X_2O_5.

In SbO_2 (Thornton, 1977) the Sb atoms show two types of coordination. The structure is represented in Fig. 7. It has layers of corner-connected $Sb(O)_6$ octahedra intercalated by layers of irregular $Sb(O)_4$ polyhedra, but owing to the lower O contents, these polyhedra share edges in one direction. The Sb substructure is formed by simple broken cubes, as seen in Fig. 7. This array is similar to that found in Sb_2O_5, which is also close to the Bi *s.c.* (simple cubic) structure.

The reported oxides of bismuth are Bi_2O_3 (stable in the varieties α, β, γ and δ; Harwig, 1978) and BiO_2 (Kumada *et al.*, 1995). With regard to Bi_2O_3 the α-phase contains very irregular cubes of bismuth, as in the element. The β and δ varieties are HT (high-temperature) phases in which the Bi atoms form *f.c.c.* arrays. The γ phase contains a very irregular array of Bi atoms in which connected tetrahedra can be identified. In BiO_4 the metal atoms form an array similar to that of SbO_2, which was discussed above.

From the Group 16 elements the following oxides have been reported: SO_3 (asbestos-like), S_3O_9, SeO_2, Se_2O_5, Se_4O_{12}, TeO_2, Te_2O_5 and TeO_3.

In SO_3 (Westrik & McGillavry, 1954), the SO_4 tetrahedra share two corners to form infinite chains, where the S atoms form helices as they do in fibrous or plastic sulfur and also in sulfur at high pressure (30–60 Kb; Sclar *et al.*, 1966). S_3O_9 consists of trimers in which the S atoms form triangles as in the S_3 molecules (Chen *et al.*, 2001).

In SeO_2 (Stahl *et al.*, 1992) the Se atoms form infinite chains (Se—Se—Se angle of 106.38°), resembling the structure of α-Se. The O atoms are situated close to the midpoint of the Se—Se bonds and close to one of the lone pairs attached to the Se atom. Se_2O_5 (Zak, 1980) also contains infinite chains of selenium, but where the angles are of the order 96°. Here, the additional O atoms are situated close to other lone pairs of Se. This leads to alternating coordination numbers of three and four. Se_4O_{12} is a tetramer. The Se atoms form squares which deviate from planarity as in the S_4 molecule, as deduced from theoretical calculations (Chen *et al.*, 2001). Se_4 molecules have also been reported.

For TeO_2 three phases were reported. The α-phase, synthesized by fusion (Leciejewicz, 1961), has been included in the rutile group. Its cation array is of the γ-Sn type. However, the Te atom has only four O atoms in its first coordination sphere. These O atoms form a polyhedron similar to that appearing in the SeO_2 structures discussed above. The HP γ-phase (Worlton & Beyerlein, 1975) contains zigzag chains of Te atoms, forming angles of 76°. The Te atoms are tetra-coordinated by four O atoms in a way similar to that of the α-phase. The third phase (the mineral tellurite) has been reported to be similar to the mineral brookite (TiO_2; Ito & Sawada, 1939). The Te atoms have the same coordination polyhedron in the other phases. The structure is represented in Fig. 8. However, the best way of describing the Te substructure

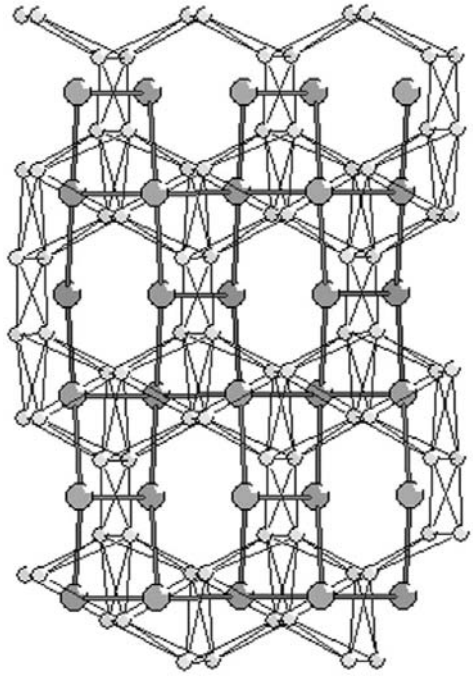

Figure 7
The structure of Sb_2O_4 projected on the *bc* plane. Large circles: Sb; small circles: O.

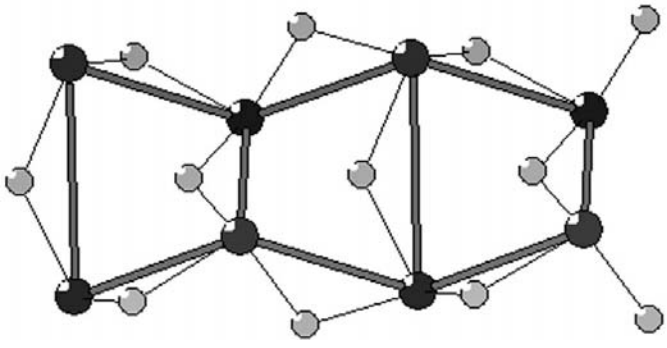

Figure 6
The structure of Sb_2O_3. Black circles: Sb; grey circles: O. The Sb atoms form puckered squares with the O atoms located close to the midpoint of the Sb—Sb bonds.

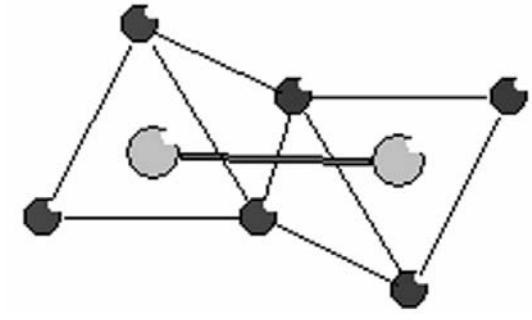

Figure 8
The structure of tellurite, III-TeO_2. The drawing shows a Te_2O_4 unit in which the Te atoms form dumbbells as in the S_2 molecules. The terminal O atoms are shared with adjacent Te_2O_4 units.

is to consider the existence of molecules of Te_2, as in S_2 (Spencer *et al.*, 2000). Two O atoms are situated midway between the two Te atoms as if they were to catch the four electrons forming the double bond. Another two O atoms are placed close to the expected position of the lone pairs. These O atoms, in turn, interact with adjacent Te_2 molecules. Considering these latter interactions the array of titanium in brookite is obtained.

The structure of Te_2O_5 (Lindqvist & Moret, 1973) can be related to that of Sb_2O_5. In this structure layers of hexa- and tetra-coordinated tellurium alternate, producing a cation array which cannot be related to any phase of the element.

In TeO_3 the Te atoms are octahedrally coordinated by six O atoms, each O atom being common to two octahedra. Thus, the Te atoms form a primitive rhombohedral network (α = 86.22°) similar to that existing in HP (high-pressure) γ-Te and almost similar to the simple cubic structure of β-Po.

It is well known that III–V and II–VI compounds also reproduce the structures of the Group 14 (IVb) elements. This is the case for BN, which crystallizes in both graphite- and diamond-like structures, or BP, which adopts the zinc blende structure. For this reason we have also included in Table 1 some of these compounds and their corresponding oxides which, as occurred with the binary oxides, also maintain the structure of their respective III–V or II–VI binary compounds. Thus, BPO_4 (cristobalite-like structure) reproduces the zinc-blende network of BP. This compound also crystallizes with the quartz- and trydimite-like structures which have not been observed in BP, but which can be related to structures of the Group 14 elements. The same can be said of $AlPO_4$ (quartz-like) which is related, as mentioned above, to $CrSi_2$. We have also included dihydrates of $AlPO_4$, *i.e.* the minerals variscite and metavariscite ($AlPO_4{\cdot}2H_2O$), because, even being quaternary compounds, the AlP subarrays are intimately related either to structures of the Group 14 or to plausible structures of this group. In metavariscite (Kniep & Mootz, 1973) the AlP subarray forms a three-dimensional four-connected net with octagons and squares (Fig. 9) This array is similar to the boron network in CrB_4 and also presents similarities with the Al–Si array in paracelsian (Kniep, 1978). Moreover, this network is also identical to the structure of β-BeO, a II–VI compound which is also represented in Fig. 9. Although no element of Group 14 presents this structure it is surprising that both a Zintl phase such as CrB_4, in which the B atom could be structurally converted into a pseudo-carbon, as well as a II–VI binary oxide as in β-BeO adopt this structure. In variscite (Kniep *et al.*, 1977), the second variety of $AlPO_4{\cdot}2H_2O$, the AlP subarray also forms a network composed of $\mathbf{4.8^2}$ layers, which alternate in the third direction in such a way that squares of the upper layers lie on the octagons of lower layers. This network is very similar to a variety of silicon compounds at HP (110–160 Kb; Crain *et al.*, 1994). In fact, in projection, both structures are identical. The differences appear only in the third dimension. Thus, whereas in variscite there are $\mathbf{4.8^2}$ layers, in HP-Si the octagons and squares convert into octagonal and squares helices. Both structures are represented in Fig. 10. Finally, BeS, another II–VI compound with the diamond structure, preserves this

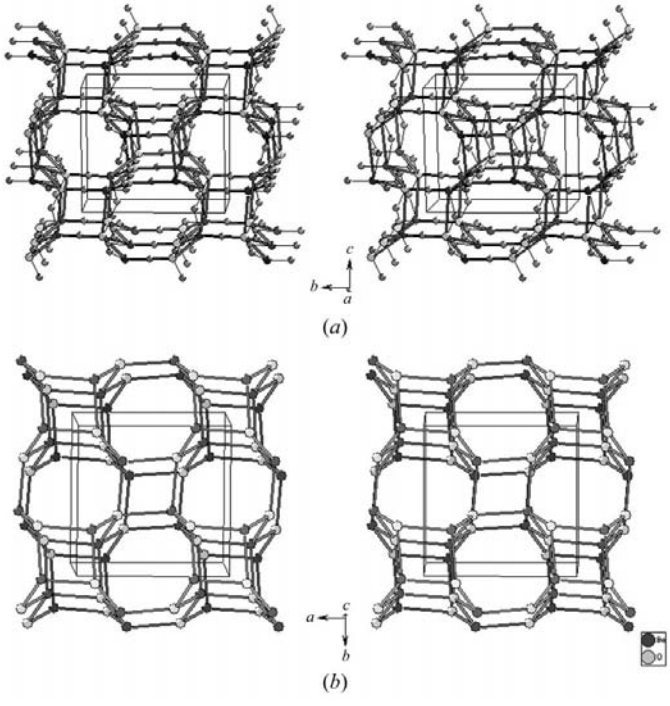

Figure 9
(*a*) Stereopair showing the $AlPO_4$ skeleton in metavariscite, $AlPO_4{\cdot}2H_2O$. The P and Al atoms are bonded by contacts to show its similarity with the structure of β-BeO. (*b*) The structure of β-BeO.

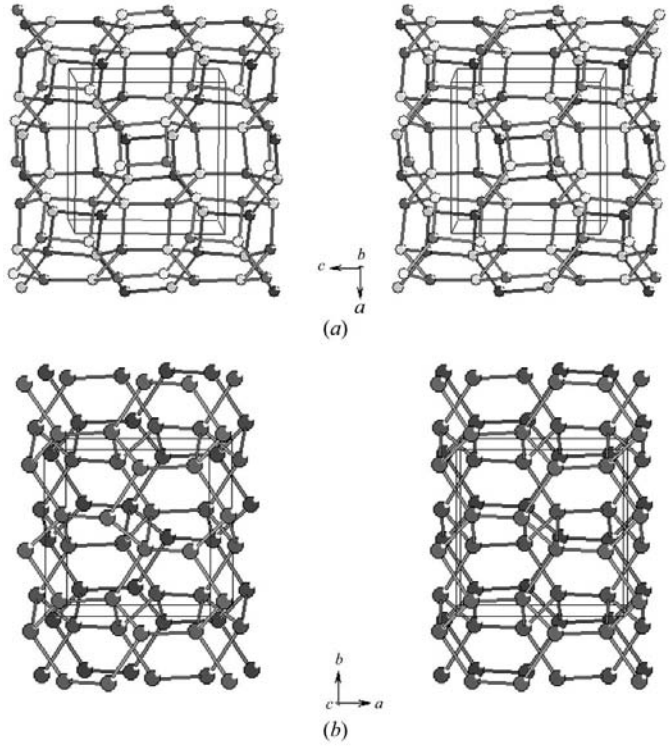

Figure 10
(*a*) Stereopair showing the four-connected AlP-skeleton in variscite, $AlPO_4{\cdot}2H_2O$. (*b*) The structure of HP-Si to show the similarity with variscite.

Table 2
The alkali metal aluminates.

X = halogen.

Compounds	Space group	Al network
$LiAlO_2$	$P4_12_12$, $R\bar{3}m$	Diamond-like
$LiAl_5O_8$	$Pmmn$	Spinel $(Al)_2(LiAl_3)O_8$
Li_5AlO_4	$P4_332$	Discrete AlO_4^{5-} anions
$NaAlO_2$	$Pna2_1$, $R\bar{3}m$	Diamond-like
$NaAl_{11}O_{17}$	$P6_3/mmc$	β-Alumina
$NaAl_{23}O_{35}$	$P6_3/mmc$	β-Alumina
Na_5AlO_4	$Pbca$	Discrete AlO_4^{5-} anions
$Na_7Al_3O_8$	$P\bar{1}$	Pseudo-P_2S
$Na_{14}Al_4O_{13}$	$P2_1/c$	Pseudo-SX
$Na_{17}Al_5O_{16}$	Cm	Pseudo-S_3X_2
$KAlO_2$	$Pbca$	Diamond-like
$K_6Al_2O_6$	$C2/m$	Pseudo-S (S_2 molecules)
$RbAlO_2$	$Fd\bar{3}m$	Diamond-like
$Rb_6Al_2O_6$	$C2/m$	Pseudo-S (S_2 molecules)
$CsAlO_2$	$Fd\bar{3}m$	Diamond-like
$Cs_6Al_2O_6$	$P2_1/c$	Pseudo-S (S_2 molecules)

network when it forms the oxide $BeSO_4$, as occurs with ZnS and HT $ZnSO_4$ (Vegas & Jansen, 2002).

As seen, the similarity between the elemental structures and those of the oxides is almost complete. As is well known, the structures of the main-group elements can be understood in the light of the $(8 - N)$ rule. They form $(8 - N)$ two-center, two-electrons bonds, the non-bonding electrons remaining as lone pairs. Consequently, it seems reasonable to think of the structures as oxides, just as if the O atoms had occupied positions close to the regions of maximal electron density, in the structure of the elements, such as the bonding pairs and the lone pairs. These regions of maximal electron density have been observed in S_8 molecules in an electron density study (Coppens *et al.*, 1977). If this were so, the tetrahedral coordination of the X atoms would be justified because in most of these elemental structures the number of bonds and lone pairs is always four. This is particularly true in the compounds with the highest oxidation state, such as X_2O_5 (X = P, As, Sb), XO_3 (X = S, Se) and X_2O_7 (X = halogen).

2.2. Alkali metal aluminates

All the alkali metal aluminates are collected in Table 2. Their structures will be interpreted in the light of the Zintl–Klemm concept as if the alkali metal atoms would donate electrons to the Al atoms, converting them into main-group pseudo-atoms. The skeleta formed by the Al atoms will then be compared either with the structures of the *p*-block elements or with those of pseudo-atoms formed in Zintl phases.

We will begin with the compounds of stoichiometry $MAlO_2$ (M = Li, Na, K, Rb, Cs; Marezio, 1965; Kaduk & Pei, 1995; Husheer *et al.*, 1999; Langlet, 1964). All these compounds crystallize as stuffed cristobalites in which the Al array adopts the structure of elemental Si (diamond-like). The compounds can be thought of as if the valence electrons of the alkali metal would have been transferred to the Al atoms, transforming it into a pseudo-silicon, thus forming four tetrahedral bonds with the four neighbours. If we consider the existence of these bonds, the O atoms would be inserted close to the midpoint between the two Al atoms just as if they would play the role of an electron pair forming the hypothetical Al—Al bonds. Two of these compounds, $LiAlO_2$ (Marezio & Remeika, 1966) and $NaAlO_2$ (Reid & Ringwood, 1968), transform at high pressures into the α-$NaFeO_2$-type structure in which Al^{3+} cations are inserted into the octahedral holes of an *f.c.c.* array of O atoms. In this structure the Al atoms form $\mathbf{3^6}$ layers with an Al—Al distance of 2.86 Å, just the shortest distance in elemental aluminium as it occurs in other Al oxides (Ramos-Gallardo & Vegas, 1995; Isea *et al.*, 1998; Vegas, 2000).

Li_5AlO_4 and Na_5AlO_4 present the same structural features. They are composed of M^+ cations and isolated AlO_4^{5-} anions, similar to SiO_4^{4-}, PO_4^{3-}, SO_4^{2-} and ClO_4^- anions. All of these are isoelectronic and can be interpreted as if the X central atom had adopted a noble gas configuration, with eight electrons in the outer valence shell. The eight electrons would be arranged in four pairs at the corners of a tetrahedron, which are the positions of the four O atoms. Also here, the Zintl–Klemm concept is maintained, with a formal transfer of five electrons from the alkali metal atoms to the Al atom.

The compounds $M_6Al_2O_6$ (M = K, Rb, Cs) have the same structural principles. Those of K and Rb are isostructural. They are formed by $Al_2O_6^{6-}$ anions, which consist of two AlO_4 tetrahedra joined by a common edge, as seen in Fig. 11. Considering the Al subarray it can be said that the anion is formed by $(Al = Al)^{6-}$ molecules, as if the six M atoms had donated six electrons to the two Al atoms, converting them into two pseudo-sulfur atoms which adopt the structure of a S_2 molecule. In this molecule, the S atoms would be connected by a double bond (S═S), with two additional lone pairs on each S atom. Four O atoms would be situated on the lone pairs with two additional ones catching the four electrons involved in the Al═Al double bond. The S_2 molecule has been observed in the gas phase (Spencer *et al.*, 2000), but it also exists as a pseudo-atom in the Zintl compound Li_2Si where the electrons from lithium convert the Si atoms in pseudo-sulfur in the form of $(Si{=}Si)^{4-}$ anions (Axel *et al.*, 1990). We have seen how these $X{=}X$ molecules could also exist in TeO_2.

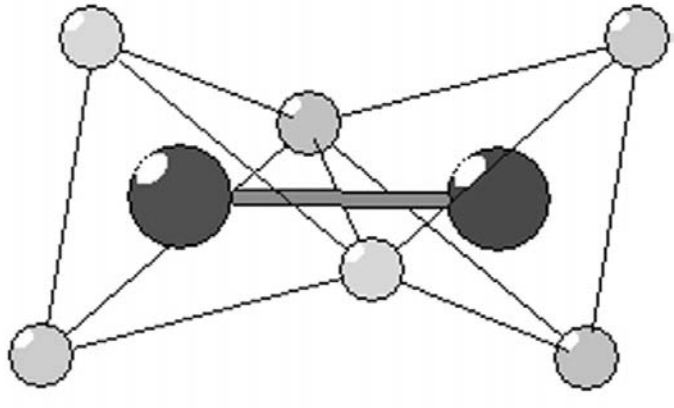

Figure 11
The structure of the $(Al_2O_6)^{6-}$ anion in $K_6Al_2O_6$. It is formed by two edge-sharing tetrahedra in which the Al atoms form dumbbells as in the S_2 molecule.

Table 3
The alkaline-earth aluminates.

Compounds	Space group	Al network
$BeAl_2O_4$	*Pnma*	Ni_2In
$MgAl_{26}O_{40}$	*P*2/*m*	β-Alumina
$MgAl_2O_4$	$F\bar{4}3m$	Spinel ($MgCu_2$)
$CaO(Al_2O_3)_6$	$P6_3/mmc$	β-Alumina
$CaAl_4O_7$	*C*2/*c*	
$CaAl_2O_4$	$P2_1/n$, $P2_1/c$	Diamond hexagonal HP – hexagons and squares
$Ca_2Al_2O_5$	$I\bar{2}mb$	Brownmillerite (Sb_2O_4 and Sb_2O_5)
$Ca_4Al_6O_{13}$	$I\bar{4}3m$	Pseudo-Si (sodalite)
$Ca_5Al_6O_{14}$	$Cmc2_1$	As_2Ge
$Ca_9Al_6O_{18}$	$Pa\bar{3}$	Pseudo-S (S_6 molecules)
$Ca_{12}Al_{14}O_{33}$	$I\bar{4}3d$	Pseudo-P_4Si_3
$SrO(Al_2O_3)_6$	$P6_3/mmc$	β-Alumina
$SrAl_2O_4$	$P2_1$	Diamond hexagonal
$SrAl_4O_7$	*C*2/*c*, *Cmma*	
$Sr_4Al_{14}O_{25}$	*Pmma*	
$Sr_7Al_{12}O_{25}$	*P*3	Pseudo-Si
$Sr_9Al_6O_{18}$	$Pa\bar{3}$	Pseudo-S (S_6 molecules)
$BaAl_2O_4$	$P6_322$	Diamond hexagonal
$Ba_3Al_2O_6$	$P2_12_12_1$, $Pa\bar{3}$	Pseudo-S (S_{12} molecule)
$Ba_{17}Al_3O_7$	$P4_2/mcm$	Two Al as pseudo-X_2

In $Na_7Al_3O_8$ all the Al atoms appear in the tetrahedral coordination. The Al network is represented in Fig. 12 and consists of infinite chains of alternate six and four rings, in which two Al atoms are three-connected and one Al atom is two-connected. Even if this skeleton does not correspond to any main-group element nor to any Zintl polyanion, its connectivity conforms to the Zintl–Klemm concept if we assume that two Al atoms are converted into pseudo-phosphorus (transfer of two electrons per atom) and one into pseudo-sulfur (transfer of three electrons), giving rise to two three-connected atoms (pseudo-phosphorus) and one two-connected atom (pseudo-sulfur). As seen in other oxides, O atoms are located on bonding pairs and lone-pair regions thus producing a tetrahedral coordination of the Al atoms.

Another two compounds which conform to this concept are $Na_{14}Al_4O_{13}$ and $Na_{17}Al_5O_{16}$. The former contains isolated $(Al_4O_{13})^{14-}$ polyanions, such as those represented in Fig. 13. The Al subarray consists of four Al atoms which form Al—Al—Al angles of 114° and is also consistent with the Zintl–Klemm concept. The two central Al atoms are two-connected as if they were pseudo-sulfur and two terminal ones are one-connected as if they were pseudo-halogen. To achieve this, a total of 6 + 8 electrons need to be transferred, which is just the number of Na^+ cations forming the structure. It is worth mentioning that the same polyanion is formed in the Zintl phase Ba_3P_4 (von Schnering *et al.*, 1984), where two P atoms convert into pseudo-sulfur and two into pseudo-chlorine with a total transfer of 2 + 4 electrons.

The same can be said of $Na_{17}Al_5O_{16}$. The structure contains $(Al_5O_{16})^{17-}$ polyanions formed by five corner-sharing $Al(O)_4$ tetrahedra in which the Al atoms adopt a zigzag conformation with angles ranging from 113 to 114°. This polyaluminate anion is represented in Fig. 14 and can also be understood in the light of the Zintl–Klemm concept. With a formal transfer of nine electrons, the three central atoms of Fig. 14 are converted into pseudo-sulfur and by a formal transfer of eight electrons the two terminal Al atoms convert into pseudo-chlorine (the total number of transferred electrons is 17). As in the other polyaluminates, O atoms are also located at the lone pairs and bonding pairs. Surprisingly, this Al-array is just that formed by the S atoms in the Zintl phase K_2S_5 (Kelly & Woodward, 1976), where two S atoms behave as pseudo-chlorine by the transfer of two electrons.

Finally, in $LiAl_5O_8$ with the spinel structure, the Al atoms present two types of coordination spheres. The Li atoms and the three Al atoms are located at the octahedral sites, whereas two Al atoms occupy the tetrahedral interstices. This structure can be considered as a filled variant of γ-Al_2O_3, which is a

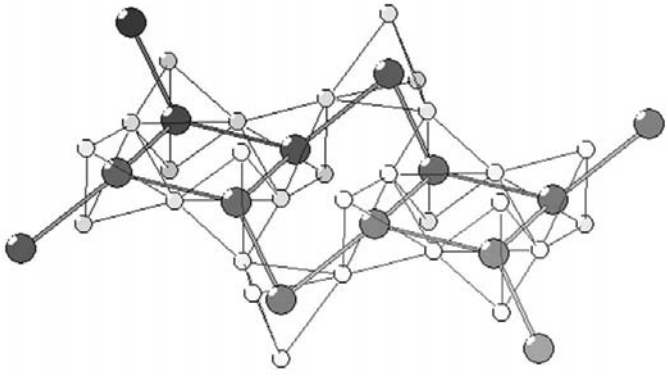

Figure 12
The tetrahedral Al network in $Na_7Al_3O_8$, showing the pseudo-phosphorus and pseudo-sulfur atoms.

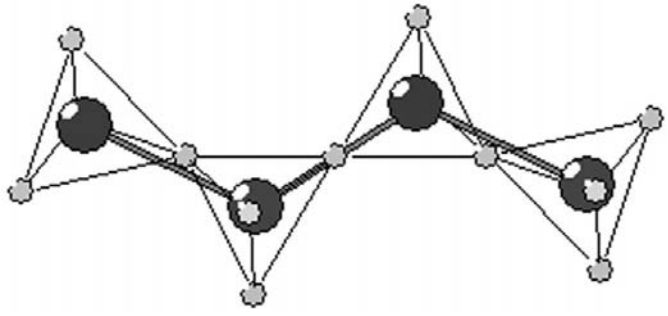

Figure 13
The $(Al_4O_{13})^{14-}$ anion in $Na_{14}Al_4O_{13}$. The two central Al atoms are pseudo-sulfur and the two terminal are pseudo-halogen. The Al-array is similar to the P-array in Ba_3P_4.

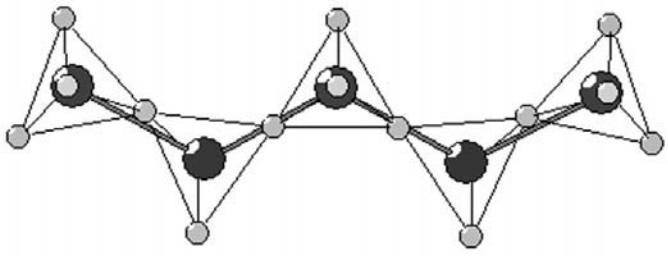

Figure 14
The $(Al_5O_{16})^{17-}$ anion in $Na_{17}Al_5O_{16}$. It is formed by discrete units of five corner-connected tetrahedra. It consists of three pseudo-sulfur and two pseudo-halogens as the S-array in K_2S_5.

defect spinel. As has been reported for spinel itself ($MgAl_2O_4$; Isea *et al.*, 1998; Vegas, 2000), the octahedral Al atoms form an array which is one half of an f.c.c. array in which the Al—Al distance is 2.86 Å, just the value of the same distance in Al metal. Consequently, the unit-cell parameter of the spinel structure becomes twice the unit cell of *f.c.c.*-Al. In $LiAl_5O_8$, however, owing to the partial insertion of Li, the unit-cell parameter is somewhat contracted (compare the values of 7.903 Å in $LiAl_5O_8$ with 4.04 Å in aluminium metal). It seems that a small proportion of the alkali metal in the aluminates does not produce the effect of transforming aluminium into other main group element structures unless we admit that aluminium has an amphoteric character and that the three Al atoms at the octahedral sites, together with the Li atom, convert the two tetrahedral Al atoms into a pseudo-argon, giving rise to the existence of AlO_4^{5-} anions. This was discussed above when we described the structures of the M_5AlO_4 compounds. In this case, the spinel could be formulated as $LiAl_3(AlO_4)_2$.

What has been discussed for the spinel structure is also applicable to the two β-alumina structures $NaAl_{11}O_{17}$ and $NaAl_{23}O_{35}$. Here the Al atoms dominate the structures owing to the small amounts of Na taking part in the compounds. This type of Al array has previously been discussed (Ramos-Gallardo & Vegas, 1996). As occurs with other skeleta in which Al is hexa-coordinated, the Al^{3+} cations reproduce the topology and distances of elemental Al.

2.3. Alkaline-earth aluminates

The alkaline-earth aluminates are collected in Table 3. $MgAl_{26}O_{40}$, $CaO(Al_2O_3)_6$ and $SrO(Al_2O_3)_6$ have the structure of β-alumina, which has been described above.

$BeAl_2O_4$ (crysoberyl; Pilati *et al.*, 1993) belongs to the olivine-group structures. In it, the Al atoms are octahedrally coordinated and the Be atoms are at the center of the O_4 tetrahedra. The cation subarray, as in olivine, is of the Ni_2In-type (O'Keeffe & Hyde, 1985), and the Al subarray can be described as fragments of the f.c.c. aluminium structure (Vegas *et al.*, 1991). As in other aluminates containing Al^{3+} cations, the Al—Al distances (2.737 × 2, 2.907 × 2, mean value 2.82 Å) reproduce those of the pure metal (2.86 Å; Isea *et al.*, 1998). This compound could then be formally formulated as composed of formal Al^{3+} cations and BeO_4^{6-} anions.

$MgAl_2O_4$, the mineral spinel, has also been described above, when we discussed the structure of $LiAl_5O_8$. There, we supposed the existence of AlO_4^{5-} anions, but if we apply the same principles here we must assume the existence of MgO_4^{6-} anions which could justify the existence of a tetrahedrally cordinated Mg^{2+} cation. However, this interpretation does not seem plausible and probably the best way of understanding this cation array should be to consider the $MgAl_2$ subarray as a possible high-pressure phase of the $MgAl_2$ alloy. This plausible alloy would be a Laves phase similar to the analogous $CaAl_2$. All this discussion mentions is the difficulty of interpreting all the structural features of the spinel structure, especially when we take into account that the high-pressure phase of Si_3N_4 also adopts this type of structure. In the nitride the Si subnet has the structure of a Laves phase. Is this array typical of a main group element? In this sense, must we interpret the $MgAl_2$ subarray as if Mg donates two electrons to the two Al atoms converting them into pseudo-silicon? It should be pointed out that the truncated tetrahedra which are the basis of the Al-skeleton in the Laves phases also appear as components of the Samson polyhedra in Zintl phases as $K_{49}Tl_{108}$ (Eisenmann & Cordier, 1996).

Another compound, listed in Table 3, which is difficult to interpret is $Ba_{17}Al_3O_7$ (Rohr & George, 1995). The oxygen content here is not enough to accept all the electrons from the Ba atoms. There are two crystallographically independent Al atoms, one is not coordinated by O atoms but only by Ba atoms, forming a sort of alloy. The second Al atom forms groups of $Al_2O_7^{8-}$, which consist of two $Al(O)_4$ tetrahedra sharing a corner. It can be interpreted as if part of the Ba electrons were transferred to the two Al atoms (4 e^- per atom) giving rise to a pseudo-halogen molecule which forms an X_2O_7 group as it does with Cl_2O_7.

The structures of the remaining compounds can be satisfactorily explained by applying the Zintl–Klemm concept. Thus, MAl_2O_4 (M = Ca, Sr, Ba), even crystallizing in three different space groups, have the same structure. The Al atoms form four-connected nets similar to wurtzite or hexagonal silicon (Jennings & Richman, 1976). This can be achieved by assuming that the two valence electrons of the AE atom are transferred to the Al atoms converting them into pseudo-silicon. The O atoms would be located in the vicinity of the midpoint of each Al—Al bond. One of these compounds, $CaAl_2O_4$, has an additional high-pressure phase with a different structure (Ito *et al.*, 1980). The Al subarray is also four-connected but instead of being formed only by six-membered rings, as in the silicon-like network, it is formed by octagons, squares and hexagons which are arranged as the P and Al atoms in variscite, $AlPO_4{\cdot}2H_2O$ (Kniep, 1978), as has been discussed above. It is surprising that the pseudo-silicon atoms in $CaAl_2O_4$ adopts the same structure as either Si itself or an III–V array, as in AlP.

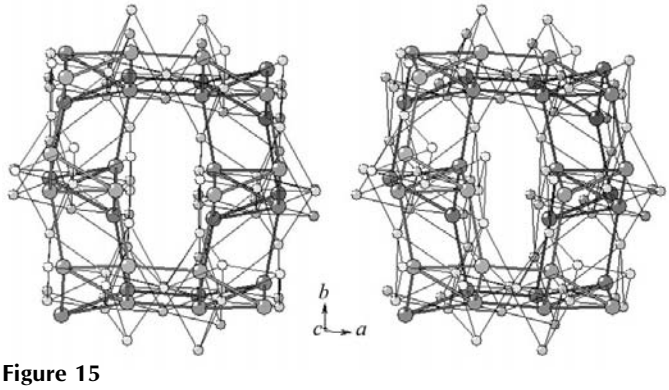

Figure 15
Stereopair showing the tetrahedral skeleton in $CaAl_4O_7$ at normal pressure. The Al—Al contacts are drawn to show the five-connectivity of the Al atoms. The O atoms lying at the center of Al_3 triangles are also seen.

$CaAl_4O_7$ and $SrAl_4O_7$ are also isostructural (Boyko & Wisnyl, 1958; see Table 3) with four formulae in the unit cell. In these compounds, all the Al atoms are tetrahedrally coordinated, with all O_4 tetrahedra sharing corners. The structure is represented in Fig. 15. Looking at the Al array, it appears that half of the Al atoms (the eight Al1 atoms) are five-connected, whereas the other half (the eight Al2 atoms) are six-connected. Since calcium can only transfer eight e^-, not all the Al atoms can be converted into pseudo-elements of the main group. This is the reason why, in this compound, the Al atoms show a higher and unusual connectivity which could be explained looking at the location of the O atoms. In the environment of Al1, we see that three O atoms are situated close to the midpoint of three Al–Al contacts, as if the three valence electrons of aluminium would have formed three directed, two-center, two-electron bonds. It is clear that the other two contacts do not originate from this type of bond because the central Al atom would have ten electrons, thus violating the octet rule. Therefore, the two remaining bonds are formed with two Al atoms belonging to a triangle which has only one O atom at its center, just as if the Al_3 triangle corresponded to a three-center, two-electron bond. These two electrons would complete the octet of the central Al atom. In the case of Al2, which is six-connected, the Al—Al bonding scheme can be explained in the same way. Here, there are two Al—Al contacts which have the O atom midway between them. This seems to indicate that Al2 has used two valence electrons to form these two-center, two-electron bonds. The remaining four contacts take place with four Al atoms belonging to two different Al_3 triangles than those described above. In this way the Al2 atoms also complete their octet. Thus there are eight electrons from calcium plus eight electrons from Al2 which are involved in these three-center, two-electron bonds. This would lead to eight bonding pairs, which is just the number of such $O(Al)_3$ triangles in the unit cell.

$SrAl_4O_7$ (Machida *et al.*, 1982) has a second phase, which is synthesized at high pressures. In this phase there are three crystallographically independent Al atoms. Of these one (four atoms in the cell) is hexa-coordinated and the other two (12 atoms in the cell) are tetra-coordinated. These 12 atoms form planar nets composed of hexagons and squares in which three- and four-connected Al atoms coexist. This layer is represented in Fig. 16 and can also be interpreted by means of the Zintl–Klemm concept as if the Ca atoms and the hexa-coordinated Al atoms would donate electrons to the tetrahedrally coordinated Al atoms, converting them into pseudo-silicon and pseudo-phosphorus. As seen in Fig. 16, the O atoms are located midway between the Al—Al contacts and also on the lone pair existing on the pseudo-phosphorus atom. These layers are held together by the Al^{3+} (hexa-coordinated) cations.

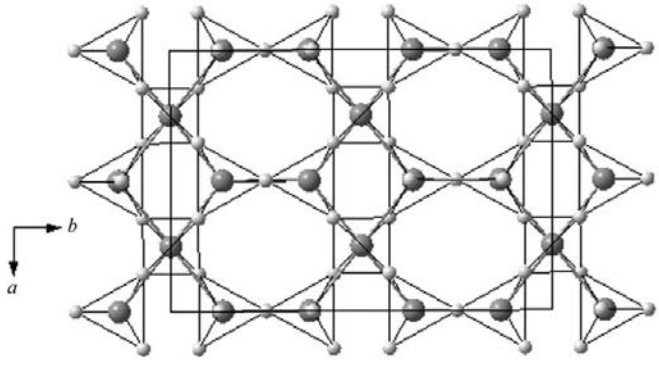

Figure 16
One layer of $Al(O)_4$ tetrahedra in the high-pressure phase of $SrAl_4O_7$. The Al—Al contacts show the four- and three-connectivity of the net.

The next compound to be discussed is $Ca_2Al_2O_5$ (Kahlenberg *et al.*, 2000). It is a high-pressure phase and has a brownmillerite-type structure. Brownmillerite has traditionally been described as an O-defect perovskite in which layers of corner-sharing $Al(O)_6$ octahedra alternate with layers of $Al(O)_4$ tetrahedra. These tetrahedra share two corners with the upper and lower octahedral layers and one additional corner with one neighbouring tetrahedron within the same layer. It is well known that the cation array in perovskites is of the CsCl type. Consequently, in brownmillerite the CaAl subarray has a similar structure but which is distorted, in principle, owing to the lower O contents and by the need to fit both the octahedral and tetrahedral geometries. An alternative description of this structure arises if we apply the Zintl–Klemm concept. By assuming an electron transfer from Ca towards Al, the latter would behave as pseudo-phosphorus and although there is no phase of phosphorus with

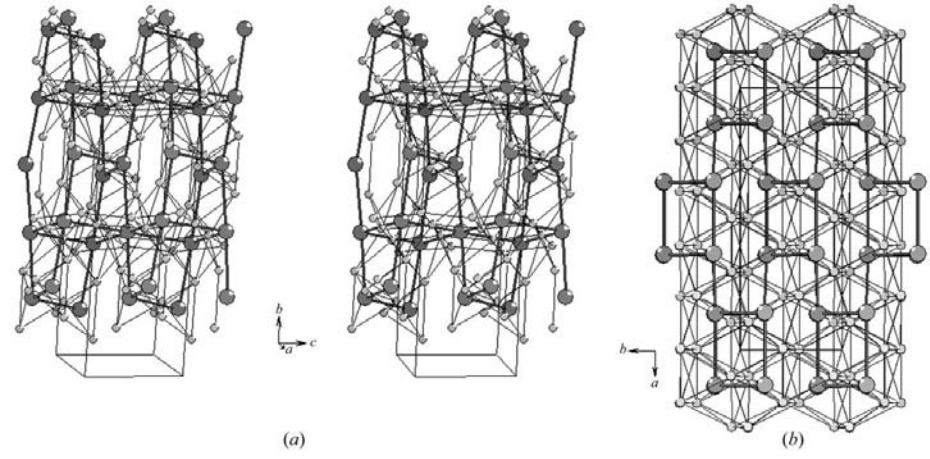

Figure 17
(*a*) Stereopair of the structure of the brownmillerite $Ca_2Al_2O_5$. The Al—Al contacts are drawn to show the similarity with the cubes of elemental Bi. (*b*) The structure of Sb_2O_5 to show its similarity with (*a*).

this structure, the Al array in brownmillerite is similar to the Sb array in the second phase of Sb_2O_5 (Jansen, 1979*b*; see §2.1), in which the Sb atoms also form distorted cubes similar to those of the high-pressure phase of antimony and also to those of bismuth. It should also be pointed out that a difference exists between the $Al_2O_5^{4-}$ skeleton and the Sb_2O_5 structure. In the former octahedra and tetrahedra coexist, whereas in the latter all the Sb atoms are octahedrally coordinated, although stoichiometry requires that these octahedra share corners in some directions and edges in others. However, both skeleta are similar (see Fig. 17). It should be added that the $Al_2O_5^{4-}$ skeleton of the brownmillerite structure also shows strong similarities with the structure of the α form of Sb_2O_4 (Thornton, 1977). Thus, the structure of the $Al_2O_5^{4-}$ net could be formed by notionally inserting one additional O atom into the tetrahedral layers of SbO_2, breaking the edge-sharing connection and leading to a corner-connected framework. However, the Sb subarray in both Sb_2O_5 and SbO_2 is quite similar and, at the same time, similar to the Al subarray in $Ca_2Al_2O_5$.

$Ca_4Al_6O_{13}$ is cubic. The Al subarray forms a four-connected net similar to that of sodalite. In agreement with the Zintl–Klemm concept, three Ca atoms would donate 6 e^- to the six Al atoms converting them into pseudo-silicon atoms, so justifying the four-connected net. In this compound there is a fourth Ca atom which does not transfer charge to the Al atoms. It transfers the two valence electrons to an O atom which is not bonded to aluminium, but only to the Ca atoms. The compound should then be formulated as $Ca_3(Al_6O_{12})\cdot CaO$.

$Ca_5Al_6O_{14}$ can be interpreted in a similar way. The ten valence electrons of the Ca atoms are transferred to the Al atoms. Four Al atoms each receive two electrons to become pseudo-phosphorus and two Al atoms each receive one electron to become pseudo-silicon. The Al subarray can be considered as a pseudo-compound of stoichiometry P_2Si, which consequently has two atoms which are three-connected (P) and one atom which is a four-connected atom (Si). These atoms form an almost planar McMahon net which is represented in Fig. 18. This net is present in the structure of marcasite (FeS_2) and surprisingly also exists in P_2Si itself!

The three compounds $M_9Al_6O_{18}$ (M = Ca, Sr, Ba) will be discussed together (Mondal & Jeffery, 1975; Alonso *et al.*, 1990; Walz *et al.*, 1994; Antipov *et al.*, 1987). The Ca and Sr compounds are isostructural and different from the Ba compound. In the three compounds the Al atoms are tetracoordinated. In the Ca and Sr compounds the $Al(O)_4$ tetrahedra form isolated six-membered rings which have the chair conformation, such as the S_6 molecules (see Fig. 19). However, in the Ba compounds the $Al(O)_4$ tetrahedra form isolated rings of 12 $Al(O)_4$ tetrahedra, in which the Al atoms adopt the structure of the S_{12} molecule (see Fig. 20). This relationship between the $Al_{12}O_{36}$ group and the S_{12} molecule was pointed out by Walz *et al.* (1994). These structural coincidences can be

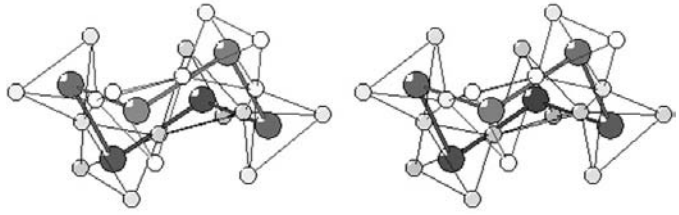

Figure 19
Stereopair of the six-membered ring $(Al_6O_{18})^{18-}$ in $M_9Al_6O_{18}$ (M = Ca,Sr). The Al atoms adopt a chair conformation as in the S_6 molecule.

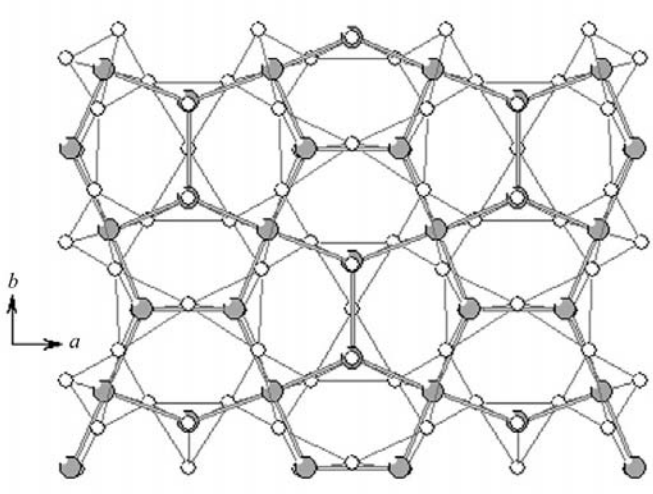

Figure 18
One layer of AlO_4 tetrahedra in $Ca_5Al_6O_{18}$. The Al—Al contacts show the existence of four- and three-connected Al atoms, corresponding to pseudo-silicon and pseudo-phosphorus, respectively. This net is similar to those existing in $GeAs_2$.

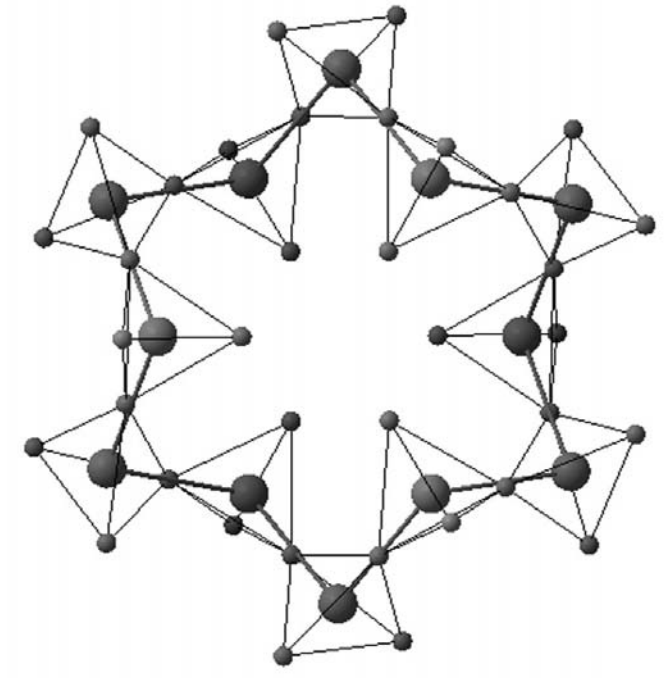

Figure 20
The anionic ring $(Al_{12}O_{36})^{36-}$ existing in $Ba_{18}Al_{12}O_{36}$. The Al atoms, bonded by contacts, adopt the structure of the S_{12} molecules.

adequately explained following the Zintl–Klemm concept. Thus, the nine alkaline-earth atoms convert the six Al atoms into pseudo-sulfur and the structures of the existing S_6 and S_{12} molecules are adopted!

The connectivity of the Al atoms in $Ca_{12}Al_{14}O_{33}$ (Bartl & Scheller, 1970) can be interpreted in the same way. The 24 Ca atoms contained in the unit cell donate 48 e^- to the Al atoms. Of these 16 are converted into pseudo-phosphorus (32 e^-) and 12 are converted into pseudo-silicon. The remaining four electrons are given to two O atoms which bond uniquely to the Ca atoms. The Al atoms then form a rather complicated framework with three- and four-connected atoms, which are in the ratio 4:3 as if it was a compound with stoichiometry P_4Si_3. Unfortunately, we have not found any analogous compound with this stoichiometry which could present this type of framework.

The structure of $Sr_4Al_{14}O_{25}$ is rather complicated. The unit cell contains two formula units and there are six crystallographically independent Al atoms. Three of them, Al4, Al5 and Al6, a total of eight atoms in the unit cell, are octahedrally coordinated, whereas Al1, Al2 and Al3 are located at the center of the O_4 tetrahedra. When these tetrahedral atoms are bonded by contacts (up to 3.46 Å), it appears as the skeleton depicted in Fig. 21. As seen, there are 12 Al atoms which are five-connected (Al1 and Al3), and eight Al atoms which are two-connected (Al2). To interpret this network we need to again assume the amphoteric character of aluminium and suppose that the octahedrally coordinated Al atoms donate electrons which are accepted by the Al atoms which form the tetrahedral framework. Thus, the total number of transferred electrons is 24 from the eight Al atoms (Al4, Al5 and Al6) plus 16 from the eight Sr atoms. Of these electrons, eight are transferred to O5, which does not take part in the tetrahedral skeleton but bonds only to the octahedrally coordinated Al atoms and to strontium. The total amount of 32 e^- can be donated to the tetrahedral framework. This amount is distributed in the following way: the eight Al2 atoms which show a twofold connectivity are assumed to be pseudo-sulfur, thus accepting 3 e^- per atom (24 electrons). The remaining 8 e^- must be transferred to both Al1 and Al3. As these two atoms are five-connected, the first impression is that they behave as a main-group element, forming $8 - N$ bonds. However, to form five two-center, two-electron bonds the Al atoms would need five electrons and this situation would violate both the octet rule and the $(8 - N)$ rule. For this reason, if we assume that each Al atom retains its three valence electrons it would form only three bonds. The additional electrons needed to form the other two bonds must be provided by the donor cations (octahedral Al and Sr). We have seen that there were eight remaining electrons. If they are transferred to Al1 and Al3 (12 atoms), each would accept 0.666 e^-. The only way of sharing this fractional charge is to assume the existence of three-center, two-electron bonds. In this way, the octet rule is maintained and the Al atoms are able to form five bonds. Looking at the oxygen positions we see that there are three O atoms which are situated midway between the Al atoms connected by two-center, two-electron bonds and one additional O atom which is situated just at the center of a Al_3 triangle as if it had accepted the two electrons common to the three Al centers. This O atom is then common to three $Al(O)_4$ tetrahedra. Two of these three-center, two-electron bonds should be added to the central Al atom, thus completing the fivefold connectivity.

Finally, $Sr_7Al_{12}O_{25}$ (Nevskii *et al.*, 1978), is also a very complicated structure. A projection of the Al array is represented in Fig. 22. The drawing reveals the existence of very puckered layers of the Kagomé type, which are components of the spinel structure. This seems reasonable because the compound has an O atom which is not bonded to any Al atom, in such a way that it could be formulated as $Sr_6Al_{12}O_{24}{\cdot}SrO$. Thus, it could be seen as an intergrowth of a compound with the spinel stoichiometry ($SrAl2O_4$) and SrO. In fact, when the Al array is observed from the projection in Fig. 22, one can recognize structural elements of the spinel structure and where all the Al atoms are four-connected, as if behaving as pseudo-silicon. This is consistent with the transfer of two

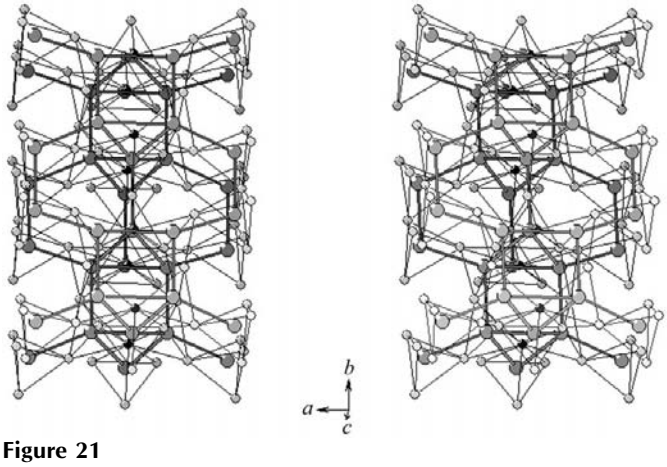

Figure 21
The structure of $Sr_4Al_{14}O_{25}$ showing the connectivity of the Al atoms (five- and two-connected). The O atoms which lie at the center of Al_3 triangles are drawn as small black circles.

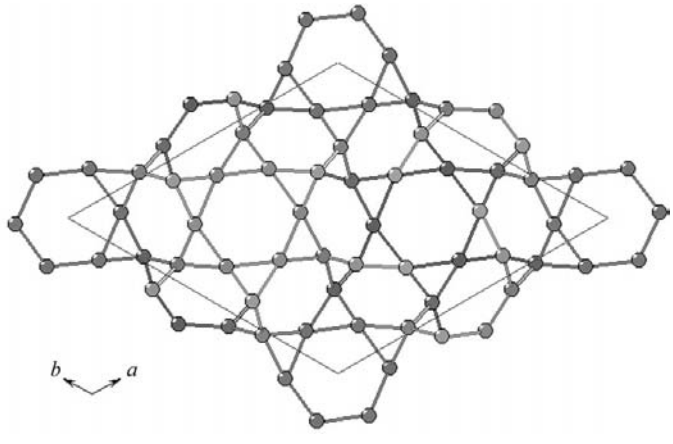

Figure 22
One layer of a four-connected net in $Sr_7Al_{12}O_{25}$. This net, formed by the Al atoms, is a puckered Kagomé net typical of the spinel structure.

Table 4
Aluminates of the transition metals.

Compound	Space group	Al skeleton
$AgAlO_2$	$P6_3/mmc$	3^6 planar nets
$AgAl_{11}O_{17}$	$P6_3/mmc$	β-Alumina
$CuAlO_2$	$P6_3/mmc$	3^6 planar nets
$Cu_2^{I}Al_4O_7$	$F\bar{4}3m$	Variant of spinel
$TiAl_2O_5$	$Cmcm$	Pseudo-P (P_2O_5 layers)
$Ti_7Al_2O_{15}$	$C2/m$	Pseudo-S; linear chains of tetrahedra
AlV_2O_4	$Fd\bar{3}m$	Direct spinel
$TaAlO_4$	$P4_2/mnm$, $C2/m$	Al and Ta localized in rutile sites; Al and Ta in octahedral holes
$FeAl_2O_4$	$Fd\bar{3}m$	Spinel
$FeAlO_3$	$Pna2_1$ (hcp-O)	Chains of pseudo-S (111 and 116°)
$AlWO_4$	$C2/m$	Fragments of Al metal
$Al_2(WO_4)_3$	$Pbcn$, $P2_1$	Isolated $Al(O)_6$ octahedra
$Al_2(WO_4)_3$	$Pbcn$, $P2_1/a$	Isolated $Al(O)_6$ octahedra

electrons from strontium to the two Al atoms, converting them into pseudo-silicon. The other Sr atom gives charge directly to the free oxygen. It is interesting to see how the spinel structure, which should not be stable because strontium should occupy tetrahedral sites, is not completely lost, producing at the same time, an AlO_2 framework which is consistent with the Zintl–Klemm concept.

2.4. The rare-earth aluminates

Most of these compounds belong to two great families of structures, *i.e.* compounds of the general formula $(RE)AlO_3$ and the garnets of the general formula $(RE)_3Al_5O_{12}$. In addition, two compounds with the formula $(RE)_4Al_2O_9$ (RE = Y, Eu) have been reported (Brandle & Steinfink, 1969).

The $(RE)AlO_3$ compounds exist as two different phases. A high-temperature phase, obtained over 1273 K with the perovskite structure has been reported for (RE) = Sc, Y, La, Ce, Pr, Nd, Sm, Tb, Dy and Ho. Among these there are tetragonal and rhombohedral distortions of the perovskite structure, although the most frequent structure is the orthorhombic distortion (*Pnma*; Diehl & Brandt, 1975), isostructural to the $(RE)FeO_3$ oxides. The second phase reported is hexagonal (space group $P6_3/mmc$; Bertaut & Mareschal, 1963). It has been synthesized below 1173 K and could be considered as an intermediate step in the formation of the perovskite structure. The cation array of the perovskite-type phases has been previously studied. The (RE)Al substructure is of the CsCl type and has the same topology and dimensions as the (RE)Al alloy itself (Ramos-Gallardo & Vegas, 1997; Vegas & Jansen, 2002). Although the perovskite structure has been widely studied and it is believed to be well understood, no satisfactory explanation of its skeleton, formed by corner-sharing octahedra, exists. We believe that a more rational description of this structure type can be achieved by applying the Zintl–Klemm concept. In $(RE)AlO_3$ the Al atoms form a simple cubic net. If we assume that the RE atoms can donate three electrons to the Al atoms, they would become pseudo-sulfur adopting so the structure becomes that of a Group 16 element. Although there is no phase of sulfur with this *s.c.* net, it is similar to the rhombohedral structure of the HP phase of Te, which is also the structure of β-Po. This structure, with the angle $\alpha = 77°$, is not far from the structure of α-Po which is really simple cubic. Moreover, the AlO_3 network is exactly the structure of TeO_3 (see Fig. 23) discussed above. Other perovskites such as $MSnO_3$ (M = Ca, Sr, Ba) can also be considered as real stuffed pseudo-TeO_3. The perovskite structure is then formed when the B cations are susceptible to transformation into pseudo-tellurium or a pseudo-element of Group 16.

The second family of rare-earth aluminates belongs to the garnet group, corresponding to the formula $(RE)_3Al_5O_{12}$ (RE = Y, Gd, Tb, Ho, Er, Yb and Lu; Euler & Bruce, 1965). These compounds were analyzed on the basis of their RE substructure (Ramos-Gallardo & Vegas, 1997). In the garnet structure, the RE atoms are eightfold coordinated by O atoms; two Al atoms are octahedrally coordinated and three Al atoms are tetrahedrally coordinated, forming isolated $Al(O)_4$ tetrahedra. The compound could then be formally formulated as $(RE)_3^{3+}(Al)_2^{3+}(AlO_4)_3^{5-}$, indicating that aluminium also behaves amphoterically here, with the octahedral Al atoms acting as donors and the tetrahedral Al atoms as Zintl acceptors. The 15 e^- donated by the three RE atoms and the two Al atoms convert the remaining three Al atoms into a pseudo-noble gas with 8 e^- in the valence shell, which are later taken by the four O atoms.

The last compounds in this section are $Eu_4Al_2O_9$ and $Y_4Al_2O_9$. They are isostructural and consist of $(RE)^{3+}$ cations, and O^{2-} and $(Al_2O_7)^{8-}$ anions. Here, the transfer of 4 e^- from the (RE) atoms to the Al atoms converts them into pseudo-halogens, producing the Al_2O_7 group with the same structure as the Cl_2O_7 molecule. The remaining electrons are transferred directly to two O atoms which are bonded uniquely to the (RE) atoms and which are located at the center of the $(RE)_4$ tetrahedra. The question which arises here is why the charge transfer does not progress up to convert the Al atoms into a pseudo-noble gas, producing isolated $(AlO_4)^{5-}$ tetrahedra as in the garnet-type compounds.

2.5. Aluminates of the transition metals

The compounds considered in this section are listed in Table 4. In most of these compounds the Al atoms appear hexacoordinated and inserted into the octahedral holes of close-packed arrays of O^{2-} anions. This is the case of delafossites $AgAlO_2$ and $CuAlO_2$, the β-alumina-like structure of $AgAl_{11}O_{17}$, the spinel $FeAl_2O_4$ and also $TaAlO_4$, where the Ta and Al atoms are statistically distributed at the Ti sites of a rutile-like structure. In $AlWO_4$ the Al atoms behave as cations, giving electrons to the more electronegative W atom (Pauling, 1960), which forms isolated WO_4^{3-} anions. As with most of the aluminium-containing oxides where aluminium behaves as a donor, Al reproduces the Al—Al distance of the pure metal (2.86 Å). In the compounds $Al_2(WO_4)_3$ and $Al_2(MoO_4)_3$ the Al atoms are so diluted that they form isolated $Al(O)_6$ octahedra.

In the remaining compounds the Al atoms appear tetracoordinated by four O atoms. In $Cu_2Al_4O_7$, as in the spinels, the cations are arranged as in the Laves phases (Meyer &

Müller-Buschbaum, 1981). However, this structure differs from spinels. The O atoms are arranged in such a way that they produce tetrahedral coordination around the Al atoms (M^{VI} atoms in spinels) and an octahedral coordination around the Cu^{I} atoms (the tetrahedral *A* cations in spinels). As a consequence the Al atoms form the same array as they do in $MgAl_2O_4$, also maintaining the distance of 2.86 Å, which is characteristic of the Al metal and all the compounds where the Al atoms are octahedrally coordinated. In view of the electronegativity values for Cu and Al (1.90 and 1.61, respectively; Pauling, 1960), electron transfer from Cu to Al may not necessarily occur and maybe the best way of interpreting this structure is to consider the cations as forming a true alloy, as discussed above for the spinel itself. The same can be said of the true spinel AlV_2O_4 (Reuter *et al.*, 1983), in which the Al atoms occupy the tetrahedral interstices.

$FeAlO_3$ (Bouree *et al.*, 1996) has an *h.c.p.* (hexagonal close-packed) array of anions. Half of its octahedral holes are occupied by Fe atoms and half by Al atoms. The remaining Al atoms are inserted into 1/12 of the tetrahedral holes. However, this occupancy is not random, but they occupy contiguous tetrahedra forming chains of corner-connected tetrahedra in which the Al atoms also form planar chains with angles of 111 and 116°, similar to those formed by the Si atoms (pseudo-sulfur) in the Zintl-phase BaSi or those formed by selenium in Se_2O_5. This can be interpreted as if the Fe atoms are not electropositive enough to transfer electrons to the Al atoms. Instead, the electrons (3 per atom) are transferred from the Al atoms occupying the octahedral holes, converting them into pseudo-sulfur. It is noteworthy that in this structure the $Al(O)_4$ chains are not isolated, as in other structures described in the above sections, but they are inserted in a close-packed array. Nevertheless, the pseudo-sulfur chains are recognisable.

A similar feature is observed in $Ti_7Al_2O_{15}$ (Remy *et al.*, 1988). Here, the Al atoms also form chains of corner-connected tetrahedra. However, in this compound the Al chains are linear (Al—Al distance of 2.97 Å) and are embedded in a distorted close-packed array of O atoms. The Al array could also be considered as pseudo-sulfur (twofold connectivity), but the fact that they do not form an isolated polyanion indicates that the Ti atoms are not electropositive enough to transform the Al atoms into a pseudo-atom of the main group. This pattern resembles that observed in $Cu_2Al_4O_7$ discussed above.

The last compound to be discussed is $TiAl_2O_5$ (Moroson & Lynch, 1972). In this compound the Ti and Al atoms are statistically distributed in the same octahedral positions as an irregular close-packed array of O atoms. The impression is that neither Ti nor Al is capable of transforming the other into a pseudo-atom. This is in agreement with the electronegativity values of both elements (1.54 and 1.61 for Ti and Al, respec-

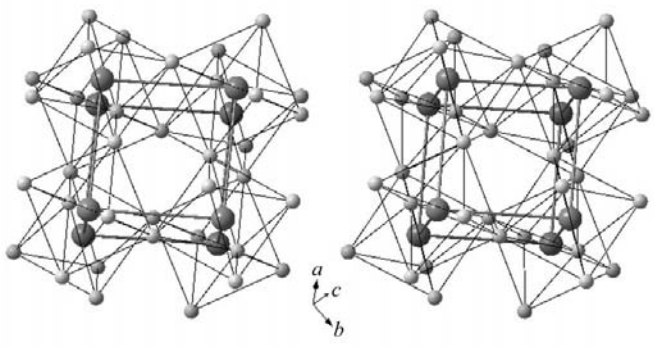

Figure 23
Stereopair of the structure of TeO_3 to show its similarity with the perovskite structure.

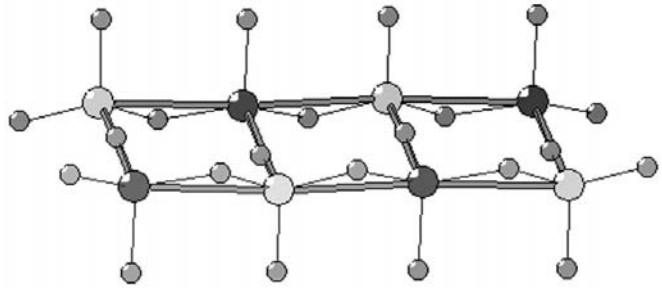

Figure 24
One double chain of three-connected SiO_4 and AlO_4 tetrahedra, which is present in Al_2SiO_5 (sillimanite). Large circles represent Al (dark grey) and Si (light grey). Small circles represent O atoms which lie midway between the Al—Si contacts and on the lone pairs. The structure is similar to that of Sb_2O_3 represented in Fig. 6. In sillimanite, an additional O atom is situated on the free lone pairs.

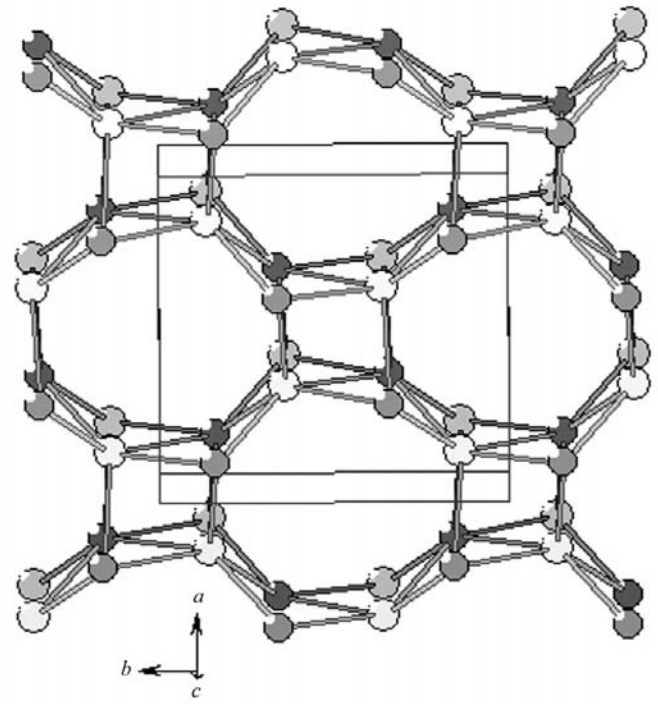

Figure 25
The Bi—Al skeleton in $Bi_2Al_4O_9$ which resembles the β-BeO and metavariscite networks (compare with Fig. 9). Dark circles: Al; light circles: Bi. As seen, all atoms are six-connected as in the Zintl phase $K_{0.4}Cd_2$.

tively). As discussed above, this is the general trend in the transition metal aluminates.

2.6. Miscellaneous compounds

Two thallium aluminates have been reported. One, $Tl_2O(Al_2O_3)_{11}$, is a β-alumina which has already been considered. The other, $TlAlO_2$, is a trigonally distorted stuffed cristobalite in which the more electropositive Tl atom donates one electron to an Al atom, converting it into a pseudo-silicon and adopting the diamond structure.

Three lead aluminates are collected. One is also β-alumina ($PbAl_{12}O_{19}$), with the Al atoms coordinated octahedrally by six O atoms. All the Al atoms in the other two aluminates are in a tetrahedral coordination and their skeleta can be explained by means of the Zintl–Klemm concept. The structure of $PbAl_2O_4$ (Marsh & Bernal, 1995) is a stuffed trydimite in which the Pb atom donates two electrons to the Al atoms, converting them into pseudo-silicon and adopting the structure of hexagonal diamond (also existing in Si). The third compound, $Pb_9Al_8O_{21}$ (Plötz & Müller-Buschbaum, 1981), presents a complicated skeleton in which four-connected and three-connected Al atoms coexist. It can be explained by assuming that the nine Pb atoms donate 18 e^- to the Al atoms. Of these, 12 e^- are transferred towards six Al atoms, transforming them into pseudo-phosphorus, and 2 e^- are given to two Al atoms, becoming pseudo-silicon. The four remaining electrons are transferred directly towards two O atoms which do not bond to the Al atoms, only to Pb atoms. The reason why the electron transfer is distributed in this way is unknown to us, but this concept can account for this complicated skeleton.

The next compounds to be discussed are the four ternary aluminium silicates. They are the minerals pyrophyllite ($Al_2Si_4O_{11}$; Wardle & Brindley, 1972) and the three phases of Al_2SiO_5 (kyanite, sillimanite and andalusite; Burnhan, 1961, 1963*a*,*b*). Pyrophylite, $Al_2(Si_4O_{10})O$, is formed by infinite layers of three-connected SiO_4 tetrahedra which build layers formed by hexagonal rings. The Al atoms are inserted between the layers and are five-coordinated by O atoms belonging to the two contiguous layers, plus an additional oxygen which does not bond to silicon. The Si-containing layers have then the stoichiometry Si_2O_5 and can be compared with one of the phases of P_2O_5 discussed earlier. They differ, however, in that $[Si_2O_5]^{2-}$ is planar, whereas in P_2O_5 the layers are puckered as in As itself. However in both compounds, the Si—Si (P—P) connectivity is threefold. Thus, this Si skeleton can be rationalized by assuming that four electrons are transferred from the more electropositive atom (Al) to the more electronegative atom Si, which is structurally transformed into a pseudo-phosphorus. The two remaining electrons are given directly to the O atom which bonds only to the Al atoms. As discussed in other cases, the O atoms belonging to the $(Si_2O_5)^{2-}$ layers are located close to the midpoint of the Si—Si contacts and near the free-electron pair of each pseudo-phosphorus atom, thus confirming the tetrahedral coordination.

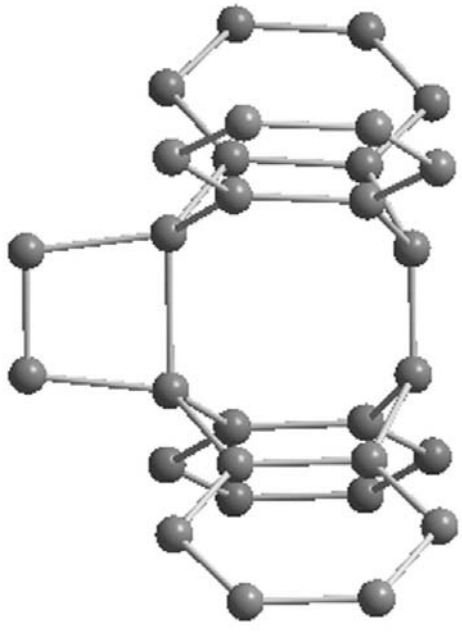

Figure 26
Cycloaddition product of tetradehydroanthracene. This organic molecule contains fragments of the structure of tetragonal carbon as in β-BeO.

The three phases of Al_2SiO_5 possess completely different structures. In kyanite, there are isolated SiO_4^{4-} groups which can be interpreted as if the Si receives four electrons from the two Al atoms. The two remaining electrons are transferred to an O atom which only bonds to the Al atoms.

In sillimanite, however, the Al atoms behave amphoterically and one Al atom (octahedral) transfers its electrons to the other Al atom (2 e^-) and to the Si atom (1 e^-), both becoming pseudo-phosphorus. Consequently, the $(Al_2Si)O_5$ skeleton (represented in Fig. 24) is similar to that of Sb_2O_3 (see Fig. 6). However, in the silicate, additional O atoms are located close to the lone pair region of each (Si, Al) atom.

The structure of andalusite is more complicated. In this compound the Al2 atoms are penta-coordinated by O atoms, whereas the Si atoms are tetrahedrally coordinated. The other Al atom, Al1, is octahedrally coordinated. One O atom is bonded only to this Al atom. All attempts to describe this structure in terms of a framework composed of Si and Al2 atoms were unsuccessful. It seems that penta-coordinated aluminium should be considered as a donor atom and not as an acceptor. For this reason it seems more reasonable to consider andalusite, like kyanite, as an orthosilicate in which both Al atoms donate their electrons to both the Si atom and the O atom not bonded to silicon. This agrees with the fact that the O atoms are not located near the midpoint of the cation–cation contacts, thus making an interpretation similar to that made for other compounds difficult. It should be added that the different structures shown by the three phases of Al_2SiO_5 should be correlated with the differences in directions of the electron transfer from the Al atoms and that these differences must be, in turn, correlated with the synthesis conditions of these minerals. All three are metamorphic minerals, formed under high-pressure and high-temperature conditions, existing in a triple point at 873 K and 6 Kbar,

where all the three phases coexist (Winkler, 1974). An interesting property of these minerals is that, although the three phases are formed under extreme conditions, kyanite and andalusite phases are converted, by heating, into the sillimanite structure (Winkler, 1974). This feature is consistent with the coordination polyhedra shown by the three phases. Thus, an increase in the coordination number (kyanite and andalusite) should correspond to higher pressures in the formation conditions. Consequently, heating would release this pressure and would give rise to the structure which is stable at lower pressures, which, at the same time, shows a lower coordination number for the Al atoms (sillimanite).

In $Al_2Ge_2O_7$ (Agafonov *et al.*, 1986), the Al atoms appear to be penta-coordinated. If we assume that the two Al atoms donate six electrons to the Ge atoms, they would be converted into a pseudo-halogen molecule whose structure is identical to that of Cl_2O_7. One O atom is located close to the $X-X$ bond and the other six close to the six lone pairs of the two X atoms, thus forming two corner-connected tetrahedra.

Al_3O_3N (Yamaguchi & Yanagida, 1959) is an oxide nitride with the spinel structure in which two Al atoms are hexa-coordinated and one tetra-coordinated. As discussed earlier for the other spinels, the structure could be interpreted by electron transfer from the octahedral Al atom towards the tetrahedral Al atom. It is clear that only 5 e^- are needed to convert the Al atom into an AlO_4^{5-} anion, but in this case the structure contains an N atom which is capable of accepting an additional electron.

$Al(PO_3)_3$ crystallizes in two different phases. The first, $I4\bar{3}d$ (Pauling & Sherman, 1937), contains $[P_4O_{12}]^{4-}$ anions of the tetramer in which the P atoms form puckered four-membered rings. This polyanion can be interpreted as if the Al atom was donating three electrons to three P atoms, converting them into pseudo-sulfur and adopting the structure of S_4, which also exists for Se_4. Although, the S_4 molecules have been experimentally observed with two different conformations (Boumedien *et al.*, 1999; Chen *et al.*, 2001), none of them correspond to the conformation observed in the P_4O_{12} group. However, the possible existence of this puckered four-membered ring has been postulated for both the S_4 and the Se_4 molecules, from theoretical calculations (Chen *et al.*, 2001; Brabson & Andrews, 1992). In the second phase (Van der Meer, 1976), the electron transfer is similar but the PO_3^{3-} groups form infinite chains, as in the structure of asbestos-like SO_3. The P substructures then resemble the structure of fibrous sulfur.

The structures of $AlPO_4$ and $AlAsO_4$ were discussed in §2.1.

$Bi_2Al_4O_9$ (Niizeki & Wachi, 1968) is another structure whose interpretation is not straightforward. In this compound the Bi atoms and half the Al atoms are tetrahedrally coordinated by O atoms, whereas the other half of the Al atoms are located in O_6 octahedra. The cation array of this compound is represented in Fig. 25 and also shows strong similarities with that of β-BeO and metavariscite (see Fig. 9). In $Bi_2Al_4O_9$, the Bi atoms and the tetrahedral Al atoms form $\mathbf{4.8^2}$ layers, whereas the octahedral Al atoms are inserted into the octagonal tunnels formed in the Bi–Al framework. In spite of the similarities with β-BeO, both structures differ in how the $\mathbf{4.8^2}$ layers are connected in the direction perpendicular to the projection plane. Thus, in β-BeO, the connectivity is four, whereas in $Bi_2Al_4O_9$ the $\mathbf{4.8^2}$ layers are stacked in such a way that each Bi (Al) atom is connected to six unlike atoms, forming a network similar to that found in the Zintl phase $K_{0.4}Cd_2$ (Todorov & Sevov, 1998). Another feature is that the tetrahedral Al atoms form dumbbells, separated by a distance of 3.45 Å. Since these two Al atoms are tetrahedrally coordinated, the result is the formation of Al_2O_7 groups composed of two corner-connected tetrahedra. The formation of these groups could be interpreted as if each Al2 atom and the Bi atoms were to donate three electrons. Two of these electrons are accepted by the O atoms which bond to both Al2 and bismuth, and the remaining four are transferred to the Al1 atoms which behave as pseudo-halogens, thus forming an anion with the same structure as Cl_2O_7. In the Al_2O_7 group, the central O atom is located in the centre of the A—Al contact, thus producing a longer distance than in other tetrahedral aluminate groups ($\simeq$3.10–3.20 Å).

The only known ternary aluminium oxide with the group 16 elements is $Al_2(SO_4)_3$ (Dahmen & Gruehn, 1993). Here the Al atoms are octahedrally coordinated and donate their six electrons to the S atoms which become a pseudo-noble gas, thus forming the isolated SO_4^{2-} anions. Its structure is of the corundum type, virtually equal to that of the sulfide Al_2S_3 (Flahaut, 1952). $Al_2(SO_4)_3$ and Al_2O_3 provide a new example of structural identity between the cation array in the oxide and the corresponding alloy, as has been reported for many other oxides and alloys (Vegas & Jansen, 2002).

We will end this section with the description of aluminium borates. Of these, the HP phase $AlBO_3$ (Vegas *et al.*, 1977) presents the calcite-type structure. The Al atoms are hexa coordinated and donate their electrons to the BO_3^{3-} group. $(Al_2O_3)_{10}(B_2O_3)_2$ is mainly aluminium oxide and will not be discussed here. $Al_4B_2O_9$ presents disorder and will not be commented. The last compound to be considered is $Al_5(BO_3)O_6$ (Sokolova *et al.*, 1978). There are four independent Al atoms in the asymetric unit. Al1 occupies a site with multiplicity 8, and Al2, Al3 and Al4 occupy sites with multiplicity 4. Al1 is hexa-coordinated and Al4 is clearly tetrahedrally coordinated. The remaining Al atoms, Al2 and Al3, are also tetra-coordinated up to a distance of 1.85 Å. However, both atoms have a fifth O neighbour at 2.16 and 2.25 Å respectively. On the other hand, the Al—Al contacts show a wide variety of distances. Some of them have values around 2.80 Å. A second set of distances is around 3.14 Å and finally a third set contains distances of 3.46 Å. When contacts are drawn up to 3.14 Å, they appear as a pattern with four-, three- and one-connected Al atoms. However, in this framework the O atoms do not always appear located near the center of the Al—Al contacts and the model applied to the other structures fails. The only way of interpreting the structure is to assume that the Al1, Al2 and Al3 atoms act as electron donors which are accepted by the Al4 atoms (5 e^-), forming isolated $(AlO_4)^{5-}$ anions, the BO_3 groups (3 e^-) and the two O atoms (4 e^-) which only bond to the three donor Al

atoms. In this way this compound should be reformulated as $Al_4(BO_3)(AlO_4)O_2$. As occurs with other structures where the Al atoms act as donors the Al subarray, up to a distance of 2.90 Å, consists of fragments of a f.c.c. net reproducing the distances of the Al metal.

3. Concluding remarks

The structures described and the above discussion clearly indicate that the Zintl–Klemm concept is maintained in the oxides and that the atoms forming the Zintl phases, all cations in the oxides, behave structurally as real Zintl phases in spite of being plunged in an oxygen matrix. All these compounds are new examples of how cations, in oxides, recognize themselves as previously stated for many other compounds (Vegas & Jansen, 2002).

The application of the Zintl–Klemm concept has served to rationalize and understand the structures of 94 aluminates whose skeleta had not been explained as yet and where the Al atoms occupying tetrahedral holes can be considered as 'cations *ex-officio*', following the name proposed by Parthé & Chabot (1990). Now we know that aluminium does not occupy either tetrahedral or octahedral holes as a function of the size of the Al^{3+} cation (the size should always be the same), but as a function of both the nature of the cations accompanying it in the oxide and of the behaviour of the Al itself. Thus, very electropositive atoms convert the Al atoms into a pseudo-main group element, thus adopting a tetrahedral coordination, as they do with the majority of binary main-group oxides. On the other hand, when more electronegative atoms, such as Si or W, coexist with aluminium it donates its valence electrons (behaves as a cation) and adopts an octahedral coordination. Examples of this behaviour are the aluminium silicates and tungstates described above. It should be remembered that this amphoteric character of aluminium was already made clear in the distribution of the Al—Al distances in their oxides (Isea *et al.*, 1998). Thus, a structure cannot be completely understood if only the size of the ions is taken into account, as predicted by the ionic model. We also need to know the nature (electronegativity) of all the cations forming the structure.

Good examples of this influence are the compounds $AgAlO_2$ and $LiAlO_2$. Both are aluminates of monovalent cations (Ag^+ and Li^+). Both have similar ionic radii (0.67 and 0.59 Å, respectively). However, Li^+ forces the Al atoms to be converted into a pseudo-silicon, whereas Ag^+ produces a delafossite structure in which the Ag^+ cations develop their own bonding features, giving rise to $\mathbf{3^6}$ planar nets of both Ag and Al atoms. Another interesting example is provided by the oxides $TiAl_2O_5$ and $Ca_2Al_2O_5$. In the former, the Ti atoms are not electropositive enough to convert the Al atoms into pseudo-phosphorus, both occupying octahedra holes of a closest-packed array of O atoms, whereas in the latter the Al atoms adopt the structure of the Sb atoms in Sb_2O_5.

Among the structures discussed we have found many similarities with that of β-BeO. We have seen that this structure does not exist among the elements of Group 14. It has only been found in a II–VI compound and in the Zintl compound CrB_4. Here the question arises as to whether this skeleton might be plausible for either carbon or silicon. In a theoretical study, Burdett & Canadell (1988) have concluded that this skeleton, also called tetragonal carbon, would be stable only for a *v.e.c.* (valence electron concentration) either greater or less than four. However, we wish to remember that this network has been obtained in the form of, to date, small molecules such as the cycloaddition products of tetradehydrodianthracene (Battersby *et al.*, 1995; Kammermeier *et al.*, 1997), which are represented in Fig. 26.

Another interesting aspect to be discussed is the positions of the O atoms in these oxides. As seen along the discussion, all the main-group elements and consequently all the pseudo-skeleta formed by the Al atoms in the oxides produce structures which can be interpreted by the formation of two-center, two-electron bonds, obeying the $8 - N$ rule. We have also seen that all the O atoms are located close to either the bonding pairs or the lone pairs. In this way, in the case of the binary oxides of the main-group elements, the oxides reproduce in most cases, the structure of their respective elements. Since one O atom is always inserted into a bonding pair, all the elemental structures appear expanded, in the oxides, with respect to the geometries shown by the elements. We can mention the pairs Si—SiO_2, P_4—P_4O_x, S—SO_3, Te—TeO_3 *etc*. All these oxides are new examples of how the structure of elements (or alloys) are maintained in their oxides and should be added to the more than one hundred examples reported by Vegas & Jansen (2002).

The location of the O atoms is related to a very old question concerning the distribution of the valence electrons in metals and alloys. It is commonly accepted that in these structures the valence electrons are delocalized. However, Nesper (1991), referring to an idea of von Schnering, has suggested considering metals and hence alloys as electrides, with free electrons located in the holes of the three-dimensional array of cations. Consequently, the possibility that anions would be located where the free electrons of the metal (alloy) were has been speculated over and the analysis of the positions of the anions could be used to infer the sites of the free electrons in the intermetallic compounds. It is clear that experimental evidence of this hypothesis is difficult to obtain in the case of alloys. However, the compounds we are dealing with here are in agreement with this hypothesis. The tetrahedral coordination shown by most of these structures should not be considered as a size effect, but rather as a consequence of the number of bond and lone pairs which is always four. In connection with this, it should be added that the structures of both Te and TeO_3 admit a similar interpretation. If we consider that the six valence electrons of Te are distributed octahedrally, then each Te atom is able to form two-center, two-electron bonds with its six like neighbours. The O atoms in TeO_3 would be located close to these bonding pairs, thus producing an octahedral coordination. An interesting question related to this problem is why O atoms see in the same way both the more delocalized bonding pairs and the more localized lone pairs. A nice answer to this question would be that the bonding pairs are also forming non-nuclear maxima

(NNM) between the two cations (bonded atoms). Regarding the possible existence of these NNM the reader is referred to the article of Martín-Pendás *et al.* (1999). However, what can be concluded is that an O^{2-} anion seems to play the same role as a bonding electron pair.

The fact that the O atoms are normally situated close to (but not exactly at) the middle point of a $X-X$ contact produces the same effect as the rotation of the tetrahedra. This rotation was postulated by O'Keeffe & Hyde (1981) to derive the real structure of β-cristobalite ($I4$-2d) from the non-existing ideal C9 structure. It can be concluded that the tetrahedra are physically not tilted, only the O atoms are located 0.5–0.6 Å off the center of the elongated $X-X$ bonds, thus producing Si—O—Si angles of around 140°. In fact, the Si array is the same and with same dimensions in both the tetragonal and the ideal C9 structures. When the structure is seen as derived from Si itself, it is unnecessary to postulate the existence of repulsive forces as responsible for the opening of the Si—O—Si angles, as concluded by O'Keeffe & Hyde (1981).

We have seen that some structures, such as $CaAl_4O_7$ and $Sr_4Al_{14}O_{25}$, are difficult to interpret with this model. These difficulties seem to be correlated with the low number of donor cations, thus avoiding the structural transformation of aluminium in pseudo-atoms of higher atomic number. However, it is true that most of the compounds considered here are better understood in the light of these old concepts.

We will finish by saying that this model can also be applied to other families of compounds such as gallates, borates, silicates and phosphates. Similar studies are being carried out for these compounds and will be the object of forthcoming papers.

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