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Bond Lengths and Valences in Aluminates with the Magnetoplumbite and β-Alumina Structures

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Bond valence sums in a number of compounds with the β-alumina and magnetoplumbite structures show that the tetrahedral Al atom in the center of the "spinel slabs" is consistently underbonded (i.e., the Al–O bonds are longer than normal). Except for bonds to this atom, predicted bond lengths agree well with those observed. Refinements of X-ray data for $CaAl_{12}O_{19}$ and $SrAl_{12}O_{19}$ show that the "anomalous" tetrahedral site is fully occupied and indicates normal temperature factors for the atom at this site. It is proposed that the long Al–O bonds are a result of Al . . . Al nonbonded interactions in accord with previous ideas.

Introduction

In this paper we are concerned with the bond lengths observed in crystals with structures related to those of magnetoplumbite ($PbFe_{12}O_{19}$) and β-alumina ("ideal" formula $NaAl_{11}O_{17}$). These structures are characterized by being built up of slabs of aluminum oxide with the spinel structure ("spinel slabs") separated by mirror planes ("conduction" planes in β-alumina) where the larger cations are found. There are many variations on the basic theme, including compounds where some large atoms are included in the spinel slabs (*1–3*). We consider only those compounds with essentially perfect spinel slabs here.

The basic structures of β-alumina (*4, 5*) and magnetoplumbite (*6*) have long been known. In each structure the spinel slabs consist of a slice of the spinel structure cut normal to the spinel [111] direction, with each slab comprised of four oxygen layers together with the three intermediate cation layers and the layers of tetrahedrally coordinated cations above and below the outer anion layers. The composition of these slabs is $(Al_{11}O_{16})^+$. In both cases the symmetry of the structure is $P6_3/mmc$.

A sketch of a spinel slab is shown in Fig. 1 which serves to illustrate the numbering of the atoms usually adopted. Note that Al(3) is in tetrahedral coordination in the β-alumina structure and in octahedral coordination in magnetoplumbite. The Al(5) position on the mirror plane is only occupied in the magnetoplumbite structure; the aluminum atom in this position is surrounded by a trigonal bipyramid of oxygen atoms.

Observed Bond Lengths and Apparent Valences

The spinel slab is, in a formal sense, a slice of the hypothetical spinel $Al_3O_4^+$ containing only Al^{3+} ions, but it has been noted (*7*) that the bonds from the tetrahedral

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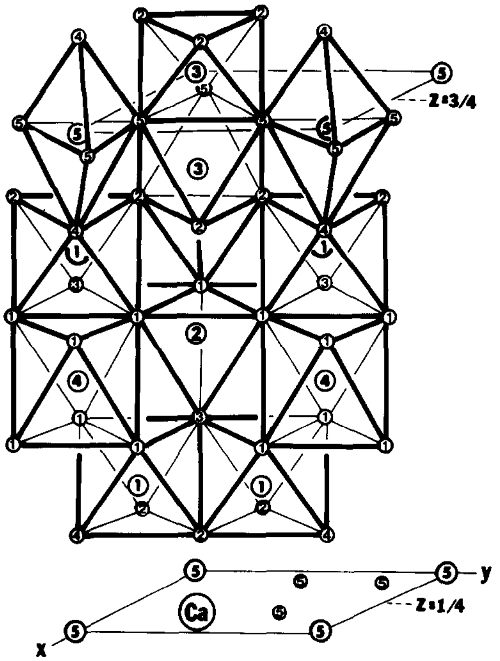

Fig. 1. A sketch of part of the spinel slab in the magnetoplumbite structure of $CaAl_{12}O_{19}$. Ca, large circles; Al, intermediate circles; and O, small circles.

aluminum atom in the middle of the slab [Al(2)] to oxygen are longer than expected for Al^{3+} in tetrahedral coordination. Thus in $CaAl_{12}O_{19}$ (see below) these bonds are 1.804 (3×) and 1.830 Å; contrast the bond lengths of 1.732 (2×) and 1.740 (2×) Å in $AlPO_4$ (*8*).

A more precise measure of the anomaly in bond lengths is provided by a calculation of the apparent valences of the atoms in the structure using well-established bond length–bond valence correlations. We have used the expression proposed by Brown and Altermatt (*9*),

$$v = \exp[(R_0 - d)/0.37\ \text{Å})], \qquad (1)$$

where v is the bond valence and R_0 is a parameter characteristic of the atom pair forming the bond. The apparent valence of an atom is then the sum of the valences of the bond formed by that atom.

Table 1 lists the apparent valences of the spinel slab aluminum atoms calculated in this way from the structures of a number of magntoplumbites and β-aluminas. It is noteworthy that the numbers differ very little from 3.0 for all the aluminum atoms except the tetrahedral atom [Al(2)] in the center of the slab, for which the apparent valence is consistently close to 2.66. (There are also anomalies, which we discuss later, for the apparent valence of Al(5) in magnetoplumbites.)

Structure Refinement

Many of the compounds listed in Table 1 have incomplete occupancies of some of the sites on the mirror planes, so the structures of the spinel slabs might be considered suspect on that account (although the remarkable constancy of the apparent valence of the aluminum atoms argues against this hypothesis). However, the structures of $CaAl_{12}O_{19}$ (*15*) and $SrAl_{12}O_{19}$ (*16*) appear to be well ordered as far as the occupancy of mirror plane sites is concerned. We had considered the possibility that the anomalous valence sums were due to the Al(2) atom site being incompletely occupied; accordingly we refined the occupancy of that site using the reported structure factors in a full least-squares refinement. For the Ca compound the occupancy refined to 0.99 ± 0.02 and for the Sr compound to 0.95 ± 0.03 so we can confidently reject the hypothesis of partial occupancy. The results of our refinement (R = 3.7%) of

TABLE I

VALENCE SUMS AT ALUMINUM IN β-ALUMINAS AND MAGNETOPLUMBITES

Large atom	Al(1)	Al(2)	Al(3)	Al(4)	Reference
Na	3.00	2.66	3.11	3.10	*10*
Ag	3.00	2.64	3.11	3.12	*11*
K	2.97	2.66	3.02	3.15	*12*
Rb	2.98	2.67	2.94	3.08	*13*
Tl	2.94	2.71	2.98	3.07	*14*
Ca	3.11	2.56	2.97	3.01	*15*
Sr	3.12	2.70	2.92	3.18	*16*
Ba	2.95	2.73	3.09	3.08	*17*
Mean (SD)	3.01(6)	2.66(5)	3.02(7)	3.10(5)	

$CaAl_{12}O_{19}$ did not differ in any very significant way (bond lengths change by typically 0.01 Å) from the originally published (*15*) structure. The results for $SrAl_{12}O_{19}$ were also very similar, although we observed some small change in parameters and a significant decrease in the *R* factor on using atomic scattering factors as opposed to the "ionic" scattering factors used in the original work (*16*).

Although temperature factors must be interpreted with caution, unusually large factors are often a symptom of an incorrect siting of an atom. The temperature factors that we obtained for the Ca and Sr compounds were generally very similar; some selected values are listed in Table 2. The main differences are that the temperature factors for Sr are about half that for Ca. Of some interest is the large value of u_{33} for Al(5), for which exactly the same value (corresponding to an rms amplitude of ~0.25 Å along *c* was found in both compounds. We confirmed Kato and Saalfeld's conclusion that this factor was not due to Al occupying split positions above and below the mirror plane by refining the structure in $P6_3mc$. We return to this point later. Note that the temperature factors for Al(2) are "normal" [indeed they are very similar to those found for Al(1), Al(3), and Al(4)].

TABLE II

TEMPERATURE FACTORS ($10^3 \times$ Å^2) FOR SELECTED CATIONS IN $SrAl_{12}O_{19}$ AND $CaAl_{12}O_{19}$ ($u_{22} = u_{11}$, $u_{13} = u_{23} = 0$)

		u_{11}	u_{12}	u_{33}
$SrAl_{12}O_{19}$	Sr	8	4	7
	Al(2)	7	3	5
	Al(5)	6	3	63
$CaAl_{12}O_{19}$	Ca	17	8	19
	Al(2)	6	3	7
	Al(5)	4	2	63

Predicted Bond Valences and Lengths

Thus we accept the structure of $CaAl_{12}O_{19}$ as correct and enquire into the bond lengths to be expected in the structure. Ionic radii sums are too crude to explain the variations of bond lengths around a given atom. On the other hand, except in the simplest of compounds, the requirement of bond valence sums being equal to the atomic valences is insufficient to uniquely determine the individual bond valences. However, Brown (*18*) has suggested an algorithm that completely determines the bond valences in a crystal structure. In this procedure the vector sum of bond valences around all closed rings in the structure is required to be zero. This procedure was provided with a plausible physical basis, and it was shown that in fact one does not need to know anything more about the structure than nearest neighbor connectivities to implement it (*19*).

In the magnetoplumbite structure there are 11 different kinds of atom, and thus there are 10 independent bond valence sums at the atoms (the requirement of electrical neutrality makes one sum redundant). On the other hand there are 13 different nearest neighbor bonds, so that three independent ring sums are required to determine bond valences. Table 3 shows the connectivity matrix for $CaAl_{12}O_{19}$. The Greek letters symbolize bond valences and the numbers are the numbers of atoms or bonds per formula unit.

The bond valence sums (of which only 10 are independent) are

$$\begin{array}{lr}
\text{Al(1)} & 2\alpha + 2\beta + \gamma + \delta = 3 \\
\text{Al(2)} & 3\varepsilon + \zeta = 3 \\
\text{Al(3)} & 3\eta + 3\theta = 3 \\
\text{Al(4)} & 6\iota = 3 \\
\text{Al(5)} & 2\kappa + 3\lambda = 3 \\
\text{Ca} & 6\mu + 6\eta = 2 \\
\text{O(1)} & 2\alpha + \varepsilon + \iota = 2 \\
\text{O(2)} & 2\beta + \eta + \mu = 2 \\
\text{O(3)} & 3\gamma + \zeta = 2 \\
\text{O(4)} & 3\delta + \kappa = 2 \\
\text{O(5)} & 2\theta + \lambda + \nu = 2.
\end{array}$$

TABLE III
CONNECTIVITY MATRIX FOR THE MAGNETOPLUMBITE STRUCTURE

	6O(1)	2O(2)	2O(3)	2O(4)	3O(5)
6Al(1)	12α	12β	6γ	6δ	·
2Al(2)	6ε	·	2ζ	·	·
2Al(3)	·	6η	·	·	6θ
Al(4)	6ι	·	·	·	·
Al(5)	·	·	·	2κ	3λ
Ca	·	6μ	·	·	6ν

$$\begin{tikzcd}
 & \mathrm{O(1)} & \mathrm{O(3)} & \mathrm{O(2)} & \mathrm{O(5)} & \mathrm{O(4)} \\
\mathrm{Al(2)} & \varepsilon \arrow[r, dash] \arrow[d, dash, dashed] & \zeta \arrow[d, dash, dashed] & \cdot & \cdot & \cdot \\
\mathrm{Al(1)} & \alpha \arrow[r, dash] & \gamma & \beta \arrow[rr, dash] \arrow[dd, dash, dashed] & \cdot & \delta \\
\mathrm{Al(5)} & \cdot & \cdot & \cdot & \lambda \arrow[r, dash] \arrow[d, dash, dashed] & \kappa \\
\mathrm{Ca} & \cdot & \cdot & \mu \arrow[r, dash] \arrow[d, dash, dashed] & \nu \arrow[d, dash, dashed] & \cdot \\
\mathrm{Al(3)} & \cdot & \cdot & \eta \arrow[r, dash] & \theta & \cdot \\
\mathrm{Al(4)} & \iota & \cdot & \cdot & \cdot & \cdot
\end{tikzcd}$$

If the connectivity matrix is rearranged as shown in the lower half of Table 3 (in which the numbers are ommitted for clarity) one can identify three closed circuits that provide equations that are identical to those obtained by summing around actual rings in the structure. Summing around each circuit, treating alternate bond valences as positive and negative, yields the necessary three independent equations:

$$\varepsilon - \zeta + \gamma - \alpha = 0$$
$$\mu - \nu + \theta - \eta = 0$$
$$\beta - \delta + \kappa - \lambda + \nu - \mu = 0.$$

The solution of these equations for the bond valences and the calculated and observed bond lengths [from our refinement of the original (*15*) data] in $CaAl_{12}O_{19}$ are listed in Table 4. The bond lengths are calculated using the Brown and Altermatt (*9*) bond length–bond valence parameters. We now discuss the lengths of the bonds to the metal atoms in the order that they occur in Table 4.

Al(1). We predict four different bond lengths with a range of 0.21 Å. The observed bond lengths are correctly ordered with a range of 0.18 Å; the only significant discrepancy is between the calculated and observed Al(1)–O(4) bond length.

Al(2). The calculated valences are very close to the value ($\frac{3}{4}$) for regular tetrahedral coordination, but as already noted the observed bond lengths are longer than bond valence–bond length correlations would predict. We discuss a likely reason for this below.

Al(3). The two distinct Al(3)–O bonds are calculated to have the bond valences expected for regular octahedral coordination ($\frac{1}{2}$). However, we note that the $Al(3)O_6$ octahedra share faces and that the bonds to the oxygen atoms in the shared face [Al(3)–O(5)] are longer (1.96 Å) than the bonds to the other oxygen atoms (1.87 Å). A comparable situation exists in α-alumina (corundum) in which the bond lengths are 1.97 and 1.86 Å. The fact that the bond lengths are perturbed by Al . . . Al interactions across the shared face provides a clue to the interpretation of the increased bond lengths to Al(2).

Al(4). There is by symmetry only one independent Al(4)–O bond length. The observed and calculated values are in fair agreement. We note, in order to give a mea-

TABLE IV
CALCULATED BOND VALENCES AND CALCULATED BOND LENGTHS (OBSERVED VALUES IN PARENTHESES) IN Å FOR $CaAl_{12}O_{19}$

Bond	Symbol	Valence	Bond length
Al(1)–O(1)	α	25/66	2.01 (1.99)
Al(1)–O(2)	β	2/3	1.80 (1.81)
Al(1)–O(3)	γ	27/66	1.98 (1.97)
Al(1)–O(4)	δ	1/2	1.91 (1.85)
Al(2)–O(1)	ε	49/66	1.76 (1.80)
Al(2)–O(3)	ζ	51/66	1.75 (1.83)
Al(3)–O(2)	η	1/2	1.91 (1.87)
Al(3)–O(5)	θ	1/2	1.91 (1.96)
Al(4)–O(1)	ι	1/2	1.91 (1.88)
Al(5)–O(4)	κ	1/2	1.91 (2.21)
Al(5)–O(5)	λ	2/3	1.80 (1.74)
Ca–O(2)	μ	1/6	2.63 (2.70)
Ca–O(5)	ν	1/6	2.63 (2.79)

sure of the precision of bond length determinations, that our refinement of the $CaAl_{12}O_{19}$ X-ray data gave a slightly different z parameter for O(1) to that found by Kato and Saalfeld (*15*) and this affects mainly the length of the Al(4)–O(1) bond length. Kato and Saalfeld's coordinates for O(1) result in a bond length exactly equal to that calculated.

Al(5). If Al(5) is on the mirror plane (as the structure refinement indicates), the coordination figure is a trigonal bipyramid. We expect shorter axial bonds and longer equatorial bonds than are observed; however, the very large thermal amplitude of the aluminum atom in the axial direction suggests that there should be a large correction for thermal motion of just the sense to remove this discrepancy. We note that if this interpretation is correct, one would expect to find a low frequency ($\bar{\nu} \sim$ tens of cm^{-1}) infrared mode in these crystals.

Ca. The Ca coordination is that of a twinned cuboctahedron (so that Ca and its surrounding twelve O atoms are an element of hexagonal close packing). The observed bond lengths are again longer than predicted and it is possible that the Ca atom is "rattling" in its cage, although relatively week bonds such as Ca–O ($v = \frac{1}{6}$) are more easily perturbed; the variation of Ca–O bond lengths in crystals is the topic of a separate paper (*19*).

We feel that the solution to the problem of the long Al(2)–O bonds is to be found in considering Al . . . Al interactions between edge-sharing octahedra. Elsewhere (*20, 21*) it has been argued that oxide spinels AB_2O_4 (e.g., $SiMg_2O_4$) with "small" tetrahedral atoms (A) are destabilized by B . . . B interactions. The hypothetical spinel Al_3O_4 with Al^{3+} in tetrahedral coordination and normal bond lengths has a = 7.79 Å and $d(^{vi}Al \ldots {}^{vi}Al)$ = 2.75 Å. In contrast in $MgAl_2O_4$, $d(Al \ldots Al)$ = 2.86 Å. In $CaAl_{12}O_{19}$ the corresponding distance is across edges shared between $Al(1)O_6$ and $Al(4)O_6$ octahedra; this is 2.89 Å. The Al . . . Al vectors between octahedral shared edges outline a truncated tetrahedron with Al(2) at the center [compare (*20, 21*)]. If this truncated tetrahedron is expanded due to Al . . . Al repulsions, the bonds from the tetrahedral atom are necessarily elongated as observed.

Conclusion

In this paper we have analyzed the bond valences in the magnetoplumbite structure and used these to predict expected bond lengths. We find several discrepancies of which the most interesting is that the bonds from the tetrahedral aluminum atom in the center of the spinel slabs are longer than expected. This phenomenon, which appears to occur for all compounds with aluminum oxide spinel slabs is considered symptomatic of Al . . . Al interactions within the slabs. The importance of such interactions was earlier suggested in a different context (*20*) and the present observations strengthen the case for this approach.

It would be of considerable interest to study the distribution of atoms substituted for Al in $CaAl_{12}O_{19}$. If the ideas presented above are correct, we expect larger atoms to go into the tetrahedral Al(2) sites (or possibly the trigonal bipyramid Al(5) sites). Smaller atoms in contrast should go into octahedral sites, or alternatively "off-center" in the trigonal bipyramid sites (lowering the symmetry of the crystal). In this connection it is interesting (*22*) that it has been reported that Ni(II) enters tetrahedral sites (despite the strong preference of this ion for octahedral coordination) in substituted β-aluminas.

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References

1. N. Iyi, Z. Inoue, S. Takekawa, and S. Kimura, *J. Solid State Chem.* **60,** 41 (1985).
2. N. Iyi, Y. Bando, S. Takekawa, Y. Kitami, and S. Kimura, *J. Solid State Chem.* **64,** 220 (1986).
3. T. R. Wagner and M. O'Keeffe, *J. Solid State Chem.* **72.**
4. W. L. Bragg, C. Gottfried, and J. West, *Z. Kristallogr.* **77,** 255 (1931).
5. C. A. Beevers and M. A. S. Ross, *Z. Kristallogr.* **97,** 59 (1937).
6. V. Adelsköld, *Ark. Kemi Mineral. Geol.* **12,** 9 (1938).
7. A. R. West, *Mater. Res. Bull.* **14,** 441 (1979).
8. N. Thong and D. Schwarzenbach, *Acta Crystallogr. Sect. A* **35,** 658 (1979).
9. I. D. Brown and D. Altermatt, *Acta Crystallogr. Sect. B* **41,** 244 (1985).
10. C. R. Peters, M. Bettman, J. W. Moore, and M. D. Glick, *Acta Crystallogr. Sect. B* **27,** 1826 (1971).
11. W. L. Roth, *J. Solid State Chem.* **4,** 60 (1972).
12. P. D. Dernier and J. P. Remeika, *J. Solid State Chem.* **17,** 245 (1976).
13. T. Kodama and G. Muto, *J. Solid State Chem.* **19,** 35 (1976).
14. T. Kodama and G. Muto, *J. Solid State Chem.* **17,** 61 (1976).
15. K. Kato and H. Saalfeld, *Neues Jahrb. Mineral. Abh.* **109,** 192 (1968).
16. A. J. Lindop, C. Matthews, and S. W. Goodwin, *Acta Crystallogr. Sect. B* **31,** 2940 (1975).
17. F. P. F. VanBerkel, H. W. Zandbergen, G. C. Verschoor, and D. W. J. Ijdo, *Acta Crystallogr. Sect. C* **40,** 1124 (1984).
18. I. D. Brown, *Acta Crystallogr. Sect. B* **33,** 1035 (1977).
19. M. O'Keeffe, to be published.
20. M. O'Keeffe and B. G. Hyde, *Nature (London)* **293,** 727 (1981).
21. M. O'Keeffe and B. G. Hyde, *Struct. Bonding* **61,** 79 (1985).
22. D. R. White, S. Chen., H. R. Harrison, and H. Sato, *Solid State Ionics* **9, 10,** 255 (1983).