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The Crystal Structure of Aluminite

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The crystal structure of aluminite, $Al_2(OH)_4(SO_4).7H_2O$, has been determined and refined from 1737 single-crystal diffractometer data by means of direct methods and least-squares refinement with anisotropic thermal parameters (isotropic for hydrogen atoms), giving $R = 0{\cdot}035$. Hydrogen atoms were located on a ΔF map. Lattice constants determined on the same diffractometer are $a = 7{\cdot}440$ (1), $b = 15{\cdot}583$ (2), $c = 11{\cdot}700$ (2) Å, $\beta = 110{\cdot}18$ (2)°; space group $P2_1/c$; $Z = 4$. An important structural feature is the presence of the complex ion $[Al_4(OH)_8(H_2O)_6]^{4+}$ consisting of four edge-sharing Al octahedra polymerized in chains. These chains, running in the *a* direction, are connected to the SO_4 tetrahedra by a three-dimensional hydrogen-bonding system. In the asymmetric unit there are seven water molecules, four of which lie among the chains and tetrahedra as free water and three are coordinated, together with the hydroxyls, to the Al atoms as ligand waters. Hence the crystal chemical formula of aluminite is best written $[Al_2(OH)_4(H_2O)_3](SO_4).4H_2O$.

Introduction

Aluminite, $Al_2(OH)_4(SO_4).7H_2O$, is one of four well defined compounds (in addition to the alunites) belonging to the basic aluminium sulphates group. The other three are basaluminite, hydrobasaluminite (Hollingworth & Bannister, 1950) and meta-aluminite (Frondel, 1968). Other less known minerals, close in composition to these compounds, are winebergite, felsöbanyite, lapparentite and paraluminite. These basic aluminium sulphates have probably formed by the reaction of acid sulphate solutions, derived from the oxidation of pyrites, with marl or clay minerals at quite ordinary or moderate temperatures. From the study of the system Al_2O_3–SO_3–H_2O at 25 °C (Basset & Goodwin, 1949) it appears that in the phase diagram the region of existence of most basic aluminium sulphates occupies a small area in the neighbourhood of the water corner. In this area there are also the phases hydrargillite and bayerite, which are built up of layers of $Al(OH)_6$ octahedra: moreover sheets having hydrargillite structure are present in kaolinite. On this basis Bassett & Goodwin (1949) inferred that aluminite and basaluminite, frequently associated in their occurrence, might also show layer-lattice structures. From the present investigation it appears that this inference is not true, at least with regard to the structure of aluminite. The main feature of the crystal structure of aluminite is the presence of edge-sharing Al-octahedra clusters, polymerized into chains running in the *a* direction.

It would be of great interest to extend the crystal-chemical study of the basic aluminium sulphates to other members of this group, because a complete structural analysis would yield important information about the mineral chemistry of these compounds. Unfortunately attempts to synthetize basaluminite and hydrobasaluminite were unsuccessful (Bassett & Goodwin, 1949) and natural specimens are described in the literature as microcrystalline, or consisting of minute plates or fibres, unsuitable for single-crystal studies.

Experimental

Aluminite usually occurs as white chalky nodules composed of minute well-formed prisms. Many crystals examined were found to be too small to give reliable intensity data. Crystals suitable for X-ray study were found only on a sample from Beregszasz, Hungary (No. 9297 of the Mineralogical Museum of Florence University).

The unit-cell dimensions were determined from 25 high-angle reflexions measured on a single-crystal diffractometer; the space group, determined from the absences, is $P2_1/c$. All crystal data are summarized in Table 1.

Intensities were collected with a Philips PW 1100 four-circle computer-controlled diffractometer (Centro di Cristallografia Strutturale del CNR, Pavia, Italy), with Cu $K\alpha$ radiation and ω–2θ scan technique. A total of 1737 reflexions in the range $2° < \theta < 57°$ were measured with a scan speed of 0·013° s^{-1} and a scan range of 1·0°; only 1258 reflexions were judged to be actually measured according to the criterion $I \geq 5\sigma(I)$. Intensities were corrected for Lorentz–polarization effects, while absorption correction was considered negligible because of the small size of the crystal.

Structure determination and refinement

The structure was solved by means of direct methods using the *MULTAN* program (Germain, Main & Woolfson, 1971). The largest 240 normalized structure amplitudes ($E \geq 1·45$) were selected as input for the phase determination (0 or π because of the symmetry centre). The structural model obtained from F_o maps computed with the set of signs with the best figures of merit gave clear indications on all atoms but three oxygens, and of course the hydrogen atoms. The R index was at this stage 0·33. In the next electron density map the missing oxygen atoms were located and two cycles of isotropic full-matrix least-squares refinement led to $R = 0·096$; a weight $1/\sqrt{\sigma}$, with σ deriving from counting statistics, was given to all observed reflexions. Two more least-squares cycles, with the introduction of anisotropic thermal parameters, gave $R = 0·042$. A difference Fourier synthesis at this stage gave indications for the positioning of all the hydrogen atoms. With all positional and thermal parameters (with B fixed at 5·0 Å^2 for hydrogen atoms) being varied at the same time as well

Table 1. *Crystal data*

Formula: $[Al_2(OH)_4(H_2O)_3](SO_4).4H_2O$
FW 344·2
Space group: $P2_1/c$
$a = 7·440\ (1)$ Å
$b = 15·583\ (2)$
$c = 11·700\ (2)$
$\beta = 110·18\ (2)°$
$V = 1273·7$ Å^3
$Z = 4$
$D_m{}^* = 1·66–1·82$ g cm^{-3}
$D_x = 1·794$
μ(Cu $K\alpha$) = 42·9 cm^{-1}
$F(000) = 720$

* From Palache, Berman & Frondel (1951).

Table 2. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

	x	y	z	B_{eq}
S	0·70076 (14)	0·37376 (6)	0·93018 (8)	1·28 Å^2
Al(1)	0·65581 (15)	0·45332 (7)	0·47633 (9)	0·96
Al(2)	1·07306 (15)	0·46600 (7)	0·62873 (9)	0·97
O(1)	0·7166 (4)	0·2878 (2)	0·8897 (3)	2·73
O(2)	0·5012 (4)	0·3905 (2)	0·9217 (2)	2·48
O(3)	0·7539 (4)	0·4342 (2)	0·8525 (2)	2·13
O(4)	0·8284 (4)	0·3836 (2)	1·0584 (2)	2·11
O(5)	0·8713 (3)	0·5403 (1)	0·5230 (2)	0·98
O(6)	0·7393 (3)	0·4539 (1)	0·3423 (2)	1·21
O(7)	0·8684 (3)	0·3947 (1)	0·5778 (2)	1·19
O(8)	0·4451 (3)	0·5226 (2)	0·4023 (2)	1·22
O(9)	0·5257 (4)	0·3487 (2)	0·4235 (2)	1·87
O(10)	1·2421 (4)	0·3758 (2)	0·7019 (2)	1·78
O(11)	1·0346 (4)	0·4930 (2)	0·7774 (2)	1·86
O(12)	0·8517 (4)	0·2530 (2)	0·7101 (2)	2·48
O(13)	1·1782 (4)	0·2181 (2)	0·6079 (3)	2·73
O(14)	1·1737 (4)	0·3019 (2)	0·4012 (2)	2·31
O(15)	0·4317 (4)	0·4095 (2)	0·1035 (2)	2·19
H(1)	0·852 (8)	0·588 (4)	0·554 (5)	
H(2)	0·658 (8)	0·440 (3)	0·283 (5)	
H(3)	0·857 (8)	0·350 (4)	0·608 (5)	
H(4)	0·408 (7)	0·541 (3)	0·342 (5)	
H(5)	0·400 (8)	0·334 (3)	0·410 (5)	
H(6)	0·581 (8)	0·298 (4)	0·409 (5)	
H(7)	1·197 (7)	0·319 (3)	0·680 (4)	
H(8)	1·327 (7)	0·378 (3)	0·780 (5)	
H(9)	0·936 (7)	0·472 (3)	0·802 (4)	
H(10)	1·100 (7)	0·533 (3)	0·831 (4)	
H(11)	0·794 (7)	0·263 (3)	0·775 (4)	
H(12)	0·780 (7)	0·218 (3)	0·661 (5)	
H(13)	1·506 (7)	0·185 (3)	0·594 (4)	
H(14)	1·268 (7)	0·181 (3)	0·621 (4)	
H(15)	1·071 (7)	0·279 (3)	0·331 (5)	
H(16)	1·156 (7)	0·275 (3)	0·467 (4)	
H(17)	0·458 (7)	0·405 (3)	0·061 (4)	
H(18)	0·370 (7)	0·466 (3)	0·130 (4)	

Oxygens O(5) to O(8), O(9) to O(11) and O(12) to O(15) belong to hydroxyl groups, ligand water and free molecules respectively.

as the scale factor, the last cycle achieved convergence at $R = 0{\cdot}035$ for the observed reflexions, and $R = 0{\cdot}056$ including 'less-thans'. Five reflexions (002, 011, 020, 031, 102) were considered to be affected by secondary extinction and therefore excluded from least-squares calculations. Scattering-factor curves for neutral non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974) and for hydrogens from Stewart, Davidson & Simpson (1965).

Positional parameters along with their standard deviations and isotropic thermal parameters are given in Table 2.*

Discussion

From the results of the present study, the crystal-chemical formula of aluminite is best written as $[Al_2(OH)_4(H_2O)_3](SO_4).4H_2O$ and the mineral may be considered as a hydrated sulphate of a hydroxy-aluminium complex.

In the structure, the Al ions are octahedrally coordinated to hydroxyls and water molecules and are arranged in condensed groups. These clusters formed by four edge-sharing octahedra are connected to each other to make chains running in the *a* direction (Fig. 1). The repeat unit of these chains is the complex ion $[Al_4(OH)_8(H_2O)_6]^{4+}$. A cluster of four edge-sharing Al octahedra of formula $[Al_4(OH)_{16}]^{4-}$ was found by Dent Glasser & Giovanoli (1970, 1972) in the synthetic compound $Ba_2[Al_4(OH)_{16}]$ and described as a new kind of hydroxoaluminate anion. Like this anion, the basic unit found in the present structure is formed by the octahedra of two independent Al atoms as well as two others related to them by a centre of symmetry. However, in barium aluminate the Al cluster is isolated while the corresponding cluster in aluminite is polymerized edge to edge to form chains. Unlike $Ba_2[Al_4(OH)_{16}]$, in aluminite the oxygen atoms attached to only one Al are not bonded to any other cation, and so they do not belong to hydroxyl groups but exist as water molecules. As Dent Glasser (1971) pointed out it seems quite rare to find water molecules and condensed anions in the same structure; this thesis is actually verified for aluminate compounds where the cation is the alkaline-earth metal. In aluminite, however, it is the hydroxy-aluminium complex which behaves as the cation, the anion of the structure being the SO_4 group: here the water, as well as being rather abundant both as ligands and as free water, plays the important role of providing a close net of hydrogen bonds to which the three-dimensional connexion of the structure is due. The structure of aluminite can, on the whole, be envisioned as consisting of two independent Al octahedra arranged in chains, of one independent SO_4 tetrahedron and of four free water molecules (Fig. 2).

There is a remarkable distortion in the Al octahedra, presumably caused by Al—Al repulsion across the shared edges; this can be easily noted by examining the bond distances and angles given in Tables 3 and 4, together with their estimated standard deviations. The mean O—O distance for shared edges within the cluster is as short as 2·423 Å; the O(8)—O(8) edge between

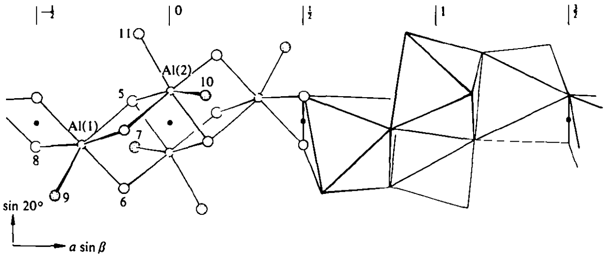

Fig. 1. A section of an Al-octahedra chain. One cluster shows Al—O bonds and the atom numbering (large open circles represent hydroxyls, and stippled ones ligand waters). In the other cluster the four distorted Al octahedra are outlined. Filled circles denote symmetry centres.

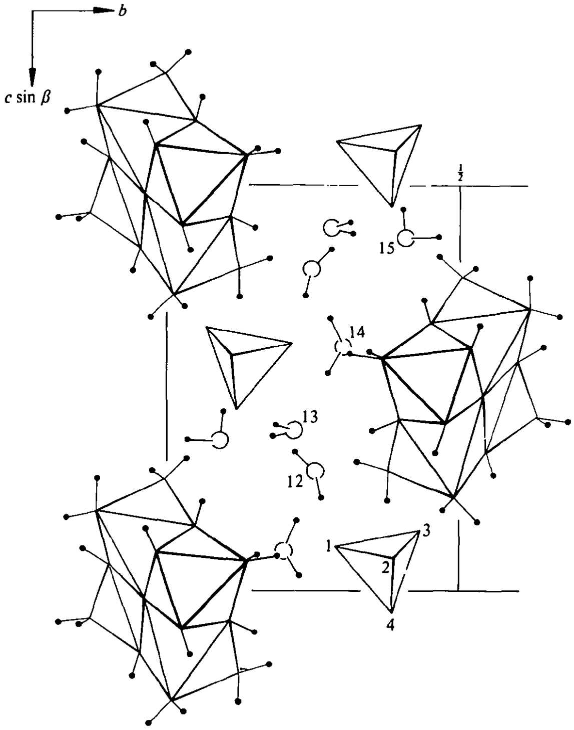

Fig. 2. Projection of the structure along the *a* axis. Three clusters belonging to three different chains (which run perpendicular to the drawing) are represented. Oxygen atoms of a SO_4 group and of free water molecules are labelled.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33500 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

adjacent clusters is even shorter, reaching the limit value of 2·259 Å. The bond angles involved, ranging from 74 to 79°, are smaller than the ideal value of 90°. There is also a lengthening of corresponding Al—O distances, especially those where O(5) is concerned: the three Al—O(5) bond distances 2·025, 1·960 and 1·959 Å are longer than the 1·893 and 1·889 Å mean values for the two octahedra.

No unusual feature is shown by the SO_4 tetrahedron, where the mean S—O bond length is 1·463 Å. This value is quite similar to 1·473 Å, the average S—O distance of well-refined structures of hydrated sulphates (Baur, 1964).

Between the SO_4 groups and the H_2O and OH neighbours of the Al chains there are free water molecules, so that the H-bonding system is of particular relevance to the cohesion of this structure. In all, there are three ligand water molecules, four free water molecules and four hydroxyls which supply the eighteen H-bonds of the asymmetric unit (Table 5). The donor(*D*)—acceptor(*A*) average distance is 2·735 Å, the individual values ranging from 2·638 to 2·929 Å. From Table 5 one can note that the H-bonds involving the ligand water oxygens O(9), O(10) and O(11) are to be considered strong bonds after Brown's (1976) criterion, which fixes 2·73 Å as the limit value between strong and weak H-bonds; as regards hydroxyls and free waters, some bonds are strong and others are weak, the stronger being 2·675 and the weaker 2·929 Å. The angles *A—D—A* range from 99·1 to 135·1°, the average being 111·5°, and 107·6° with the exclusion of the too large value of 135·1°. The hydrogen atoms lie approximately along the vectors

Table 3. *Bond distances,* Al—Al *distances and edges of polyhedra* (Å)

Al(1)—O(5)	2·025 (5)	Al(2)—O(5)	1·960 (9)
O(6)	1·875 (6)	O(7)	1·812 (6)
O(7)	1·858 (9)	O(10)	1·882 (6)
O(8)	1·854 (8)	O(11)	1·905 (4)
O(9)	1·888 (4)	O(5^{v})	1·959 (5)
O(8^{vi})	1·859 (7)	O(6^{v})	1·816 (4)
Mean	1·893	Mean	1·889
O(5)—O(6)	2·411 (9)	O(5)—O(7)	2·360 (3)
O(7)	2·360 (3)	O(11)	2·896 (9)
O(8)	3·006 (9)	O(5^{v})	2·499 (6)
O(8^{vi})	2·947 (8)	O(6^{v})	2·782 (9)
O(6)—O(7)	2·746 (9)	O(7)—O(10)	2·672 (9)
O(8)	2·737 (7)	O(11)	2·708 (9)
O(9)	2·674 (7)	O(5^{v})	2·783 (9)
O(7)—O(9)	2·664 (9)	O(10)—O(11)	2·726 (6)
O(8^{vi})	2·744 (9)	O(5^{v})	2·795 (9)
O(8)—O(9)	2·768 (3)	O(6^{v})	2·717 (4)
O(8^{vi})	2·259 (9)	O(11)—O(6^{v})	2·667 (9)
O(9)—O(8^{vi})	2·814 (4)	O(5^{v})—O(6^{v})	2·411 (9)
S—O(1)	1·440 (3)	O(1)—O(2)	2·385 (5)
O(2)	1·477 (3)	O(3)	2·357 (4)
O(3)	1·455 (4)	O(4)	2·384 (8)
O(4)	1·481 (9)	O(2)—O(3)	2·388 (9)
Mean	1·463	O(4)	2·411 (9)
		O(3)—O(4)	2·410 (7)
Al(1)—Al(2)	3·006 (9)		
Al(1)—Al(2^{v})	2·979 (9)		
Al(1)—Al(1^{vi})	2·947 (5)		
Al(2)—Al(2^{v})	3·020 (9)		

Symmetry code

None	x,	y,	z	(v)	$2-x$,	$1-y$,	$1-z$
(i)	$1+x$,	y,	z	(vi)	$1-x$,	$1-y$,	$1-z$
(ii)	x,	y,	$-1+z$	(vii)	$1+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
(iii)	$-1+x$,	y,	z	(viii)	x,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$
(iv)	$2-x$,	$1-y$,	$2-z$				

Table 4. *Bond angles* (°)

The standard deviations for O—Al—O are 0·1° and for O—S—O, 0·2°.

O(5)—Al(1)—O(6)	76·3	O(5)—Al(2)—O(7)	77·3
O(7)	74·7	O(10)	166·8
O(8)	101·5	O(11)	97·0
O(9)	159·2	O(5^{v})	79·2
O(8^{vi})	98·6	O(6^{v})	94·8
O(6)—Al(1)—O(7)	94·7	O(7)—Al(2)—O(10)	92·6
O(8)	94·4	O(11)	93·5
O(9)	90·6	O(5^{v})	95·0
O(8^{vi})	167·2	O(6^{v})	171·1
O(7)—Al(1)—O(8)	168·9	O(10)—Al(2)—O(11)	92·1
O(9)	90·7	O(5^{v})	93·3
O(8^{vi})	95·2	O(6^{v})	94·5
O(8)—Al(1)—O(9)	95·4	O(11)—Al(2)—O(5^{v})	169·6
O(8^{vi})	74·9	O(6^{v})	91·5
O(9)—Al(1)—O(8^{vi})	97·3	O(5^{v})—Al(2)—O(6^{v})	79·3

O(1)—S—O(2)	109·7
O(3)	109·0
O(4)	109·4
O(2)—S—O(3)	109·1
O(4)	109·2
O(3)—S—O(4)	110·4

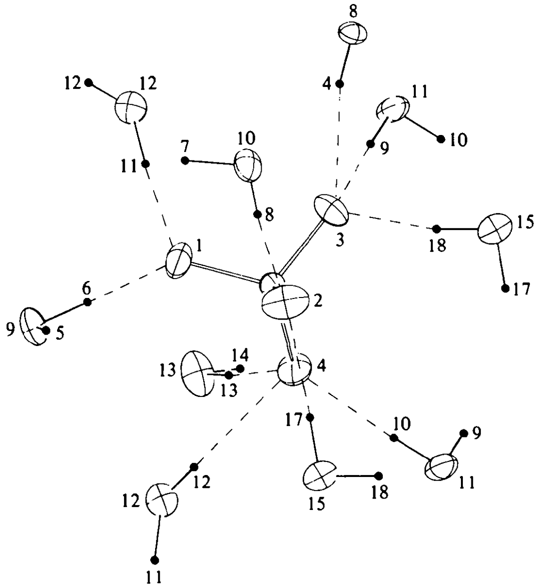

Fig. 3. Environment of a SO_4 group. Dashed lines indicate hydrogen bonds. Thermal ellipsoids are scaled at the 50% probability level.

Table 5. *Distances* (Å) *and angles* (°) *involving hydrogen atoms*

Donor atom (*D*)	H	Acceptor atom (*A*)	*D*···*A*	*D*—H	H···*A*	*D*—H···*A*	H—*D*—H	*A*···*D*···*A*
O(5)	H(1)	O(14^{v})	2·675 (4)	0·86	1·86	170		
O(6)	H(2)	O(15)	2·804 (9)	0·78	2·03	176		
O(7)	H(3)	O(12)	2·723 (4)	0·80	1·93	169		
O(8)	H(4)	O(3^{vi})	2·913 (9)	0·82	2·11	167		
O(9)	H(5)	O(14^{iii})	2·644 (5)	0·93	1·72	174	104	109·0 (1)
	H(6)	O(1^{viii})	2·662 (5)	0·94	1·73	171		
O(10)	H(7)	O(13)	2·668 (4)	0·95	1·76	157	111	116·6 (1)
	H(8)	O(2^{i})	2·638 (9)	0·91	1·73	174		
O(11)	H(9)	O(3)	2·691 (8)	0·94	1·76	178	108	99·1 (1)
	H(10)	O(4^{iv})	2·661 (8)	0·90	1·80	166		
O(12)	H(11)	O(1)	2·680 (9)	1·00	1·68	174	106	135·1 (1)
	H(12)	O(4^{viii})	2·788 (9)	0·84	2·09	134		
O(13)	H(13)	O(4^{viii})	2·929 (7)	1·01	1·92	175	107	99·4 (1)
	H(14)	O(15^{vii})	2·687 (5)	0·86	1·83	171		
O(14)	H(15)	O(12^{viii})	2·788 (9)	0·97	1·82	170	104	107·9 (1)
	H(16)	O(13)	2·739 (4)	0·92	1·94	167		
O(15)	H(17)	O(2^{ii})	2·706 (6)	0·92	1·78	177	107	113·6 (1)
	H(18)	O(3^{vi})	2·835 (4)	0·99	1·86	171		

connecting *D* and *A* atoms, except for the O(12)—H(12)···O(4) bond for which an angle of 134° was calculated. H(12) excluded, the scatter of H—*D*—H angles around the mean value does not show any unexpected trends, though the hydrogen positions are those obtained from the refinement and some inconsistencies in the shifts of their coordinates could have occurred. On the other hand the location of H(12) is only apparently unsatisfactory. In fact, the *A*—*D*—*A* angle of 135·1 is larger than the water angle, but the shift of H(12) from the *D*—*A* alignment leads to an angle of 106° for H(11)—O(12)—H(12), close to the usual water angle values. This result is achieved by bending the O(12)—H(12)···O(11) bond, so that the corresponding angle is altered from 180 to 134° and the H···*A* distance reaches a value of 2·09 Å, otherwise foreseeable on the basis of the hydrogen-bonding-geometry approach of Brown (1976).

As mentioned above, the three-dimensional connexion in the aluminite structure is built up by the H-bonding system just described. This feature is similar to that already observed in the structures of alunogen (Menchetti & Sabelli, 1974), the most hydrated aluminium sulphate, and of apjohnite (Menchetti & Sabelli, 1976), a member of the halotrichite series, which is also a highly hydrated sulphate. As Fig. 3 illustrates, the SO_4 group of aluminite appears 'entrapped' in a close net of H-bonds; there are ten in all and they involve both ligand water oxygens, *i.e.* O(9), O(10) and two O(11), and free water oxygens, *i.e.* O(13), two O(12) and two O(15). Among the hydroxyls, only O(8) forms an H-bond with the SO_4 group, the other three making up hydrogen bridges with as many free water oxygen atoms. The sulphate oxygens O(1) and O(2) show a threefold coordination, while O(3) and O(4) present a tetrahedral environment. Each of these four oxygens accepts one strong H-bond from a ligand water oxygen. The other H-bonds, donated by the free water oxygens and the hydroxyl O(8), are strong for O(1) and O(2) and weak for O(3) and O(4).

Table 6. *Electrostatic balance*

	S	Al(1)	Al(2)	Hydroxyls	Ligand water	Free water	Sums
O(1)	1·60				0·23	0·22	2·05
O(2)	1·44				0·23	0·22	1·89
O(3)	1·53			0·16	0·22	0·18	2·09
O(4)	1·43				0·23	0·18 0·16	2·00
O(5)		0·35	0·41 0·41	0·77			1·94
O(6)		0·52	0·60	0·82			1·94
O(7)		0·54	0·61	0·79			1·94
O(8)		0·55 0·54		0·84			1·93
O(9)		0·50			1·54		2·04
O(10)			0·50		1·55		2·05
O(11)			0·47		1·55		2·02
O(12)				0·21		1·60 0·19	2·00
O(13)					0·22	1·62 0·20	2·04
O(14)				0·23	0·23	1·61	2·07
O(15)				0·18		1·60 0·22	2·00

An electrostatic valence balance (Table 6) was computed according to the method of Brown & Shannon (1973); for the H-bonds the curve by the same authors quoted in Donnay & Donnay (1973) was employed. From this table it can be seen that on the whole the balance is satisfactory; for only O(2) and

O(3) are the bond strength sums not very close to 2 v.u. The oxygen atoms O(5) to O(15) exhibit a slight deviation below the theoretical value for the hydroxyls and above that for the water molecules.

The study of the thermal dehydration of aluminite (Basset & Goodwin, 1949) shows that when the mineral is heated to constant weight at 100–115 °C, the weight loss is about 21%. This corresponds closely to the loss of all the free water molecules simultaneously. Therefore the behaviour of all the free water molecules is the same in spite of the fact that O(14) is not directly H-bonded to any polyhedron, unlike O(12), O(13) and O(15).

As already mentioned in the *Introduction*, aluminite was probably crystallized from weakly acidic solutions. The formation of condensed cations is known to occur in aluminium solution as neutrality is approached from the acid side. The presence of the hydroxy-aluminium cation in the aluminite structure confirms the hypothesis concerning the crystallization environment of this mineral and suggests also that the structures of the other members of the basic aluminium sulphate group are characterized by similar polynuclear cations.

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High-Temperature Intergrowth Structures in the Fe_2O_3–TiO_2 System – Metal Atom Ordering in the Intergrowth Boundaries

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In the Fe_2O_3–TiO_2 system, at temperatures below about 1450 °C, the composition range 8–16 wt% Fe_2O_3 is spanned by a continuous series of $(121)_r$–$(132)_r$ rutile crystallographic shear (CS) structures. Above 1450°C they undergo a reversible transformation to intergrowth structures in which rutile slabs are periodically displaced by $\frac{1}{2}[0\bar{1}1]_r$ across $(0kl)_r$ boundaries. With different Fe_2O_3 contents, the orientation of these boundaries varies between $(020)_r$ and $(031)_r$. Here is reported an analysis of the metal atom ordering within the $(0kl)_r$ boundaries using electron diffraction/microscopy and single-crystal X-ray diffraction techniques. It is found that the boundaries are actually slabs, with widths ranging from about 4·5 to 9 Å, within which elements of rutile and corundum structures form coherent intergrowths, parallel to $(101)_r$. The structures are metastable at low temperatures and decompose under electron-beam heating to give the component oxides, haematite and rutile. Structural relations with the ferric titanate mineral pseudorutile are discussed and a mechanism for the low–high-temperature structure transformation is suggested.