

## A Structural Study in the System $\text{Al}_2\text{O}_3\text{-WO}_3$

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The crystal structure has been determined of a compound initially reported as having the composition  $2\text{Al}_2\text{O}_3 \cdot 5\text{WO}_3$ . The final structure analysis proved the substance to be  $2\text{Al}_2\text{O}_3 \cdot 6\text{WO}_3$  or  $\text{Al}_2(\text{WO}_4)_3$ , and it is isomorphous with the tungstates and molybdates of the smaller trivalent rare-earth elements.  $\text{Al}_2(\text{WO}_4)_3$  crystallizes in the orthorhombic system, space group *Pbcn*, with lattice constants  $a = 12.588 \pm 0.063$ ,  $b = 9.055 \pm 0.045$ ,  $c = 9.127 \pm 0.046$  Å. The intensities of three-dimensional equi-inclination Weissenberg data were estimated visually and the structure was solved by Patterson and Fourier techniques. Refinement of atomic parameters was carried out by the method of least-squares. The  $\text{Al}_2(\text{WO}_4)_3$  structure consists of  $\text{WO}_4$  tetrahedra and  $\text{AlO}_6$  octahedra which extend into an infinite three-dimensional network by corner sharing. The average tetrahedral W-O distance is 1.783 (23) Å and the average Al-O bond distance is 1.836 (35) Å. The structure contains discontinuous cubic face-centred anion units linked by corner-sharing polyhedra. A high density form of  $\text{Al}_2(\text{WO}_4)_3$  is discussed, based upon a continuous cubic close-packed array of anions.

### Introduction

Phase equilibrium studies in the system  $\text{Al}_2\text{O}_3\text{-WO}_3$  have been carried out by Bayer (1962) and Waring (1965). Bayer observed that sintered equimolar mixtures of  $\text{Al}_2\text{O}_3$  and  $\text{WO}_3$  produce complex X-ray diffraction patterns. Waring studied the system more extensively and concluded that only one compound is formed, melting congruently at 1254°C and with composition  $2\text{Al}_2\text{O}_3 \cdot 5\text{WO}_3$ .

The present study involves an X-ray crystal structure analysis of this compound.

### Experimental

Very small single crystals of  $2\text{Al}_2\text{O}_3 \cdot 5\text{WO}_3$  were supplied by Dr R. S. Roth, National Bureau of Standards, Washington, D.C. They were prepared from an  $\text{Al}_2\text{O}_3\text{:WO}_3$  mixture in the molar ratio 1:3 by heating at 1175°C, just below the melting point, for 13 days and quench cooling.

Unit-cell dimensions were obtained (to ½%) from zero level precession photographs:  $a = 12.588 \pm 0.063$ ,  $b = 9.055 \pm 0.045$ ,  $c = 9.127 \pm 0.046$  Å. Systematic absences in spectra uniquely determine the space group as *Pbcn* (No. 60).

Equi-inclination Weissenberg geometry with Cu *K* $\alpha$  radiation was used for the photographic recording of *hk0-6* data about the *c* axis of the crystal. The intensities were measured visually by comparison with a standard strip. The crystals were approximately spherical in shape, with a diameter of  $5 \times 10^{-3}$  cm and no corrections were made for absorption or extinction. Data processing was effected on an IBM 360/50 computer, using the programs of Craig (1966). Structure amplitudes were internally correlated with intensity data obtained from precession photographs.

### Solution of the structure

A crystal of  $2\text{Al}_2\text{O}_3 \cdot 5\text{WO}_3$  sinks in methylene iodide, an indication that there is more than one formula unit per unit cell. With a unit cell volume of 1040.3 Å<sup>3</sup> one would expect about 45 to 60 oxygen atoms in the unit cell, and so it would seem that there are two or three formula units in each unit cell. However, with only eightfold and fourfold equivalent positions in the space group *Pbcn*; it is not possible to accommodate the resulting number of tungsten and oxygen atoms. For example, with two formula units per unit cell, there would be ten tungsten and forty-two oxygen atoms to position, and these cannot be accommodated with eight- and fourfold equivalent positions. The most reasonable solution seemed to be two formula units of  $2\text{Al}_2\text{O}_3 \cdot 6\text{WO}_3$  per unit cell and this was subsequently proved to be the case from the structure analysis.

A three-dimensional Patterson function was computed with the squares of the observed structure amplitudes listed in Table 1. The tungsten atoms were readily located and a three-dimensional Fourier difference map based upon signs given by the tungsten atoms clearly defined the aluminium atoms. Further cycles of structure factors and Fourier difference syntheses successively revealed the remaining six crystallographically independent oxygen atoms.

### Refinement of the structure

The positional parameters and isotropic temperature factors of the two independent W atoms, one Al and six O atoms were refined by the method of least squares, using a modification (Craig, 1966) of the Busing, Martin & Levy (1962) *ORFLS* program. Interlayer scale factors were also carried as variates in these refinement

Table 1. A list of calculated and observed structure amplitudes

Unobserved reflexions, denoted by the letter *U*, have been assigned an  $F_0$  value based upon  $F_{min}/2$ .

<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>													
2	0	124	163	3	4	1	113	-32	4	2	2	13	3	3	98	7	4	67	-72	6	4	26	-37	3	10	5	21	19				
4	4	1	27	-17	4	4	1	27	-17	13	1	3	29	25	7	4	64	61	6	4	212	267	1	0	171	318						
5	1	432	436	5	4	1	175	174	6	2	156	-18	7	338	-277	5	4	80	-67	6	10	249	-244	4	0	122	-198					
8	4	8	8	6	1	177	-91	1	2	16	119	1	2	162	176	11	3	42	618	1	10	21	-51	6	0	157	175					
17	1	231	-162	U	7	4	1	14	-74	8	2	222	-224	9	2	126	67	11	4	62	65	2	11	4	0	98	-98					
12	7	135	120	9	4	1	159	-101	7	2	113	-69	7	2	219	181	12	4	155	141	23	4	40	-63	5	0	296	-336				
14	2	246	268	10	5	1	177	-91	11	3	2	159	-101	10	3	206	206	13	4	153	0	4	10	4	0	245	-257					
15	1	27	387	15	4	1	16	-9	11	2	6	45	31	5	2	608	-217	14	4	183	-139	5	10	4	3	50	7	13	-5			
1	1	222	-154	11	4	1	63	92	12	2	115	-174	5	2	108	-115	1	1	4	290	364	1	1	5	81	-53	8	0	188	-183		
9	1	224	266	12	4	1	83	-93	13	2	81	61	U	7	1	18	-75	3	1	110	-89	3	1	5	80	10	0	0	1	-6		
11	1	376	372	13	4	1	95	73	14	2	80	-80	6	2	79	-75	3	1	110	-89	3	1	5	80	10	0	0	1	-6			
13	1	34	-23	14	4	1	162	-151	15	2	36	-34	9	2	135	139	4	1	4	73	-67	4	1	5	101	111	13	0	146	-129		
0	2	249	268	10	5	1	163	-165	1	3	2	171	11	2	243	204	11	2	157	162	5	1	9	-81	-28	12	0	102	-77			
2	2	215	207	4	5	1	132	-71	11	2	74	-6	5	1	4	47	-48	6	1	5	19	13	0	1	5	19	13	0	1	5		
2	2	121	174	3	5	1	134	-67	3	5	2	176	-156	12	2	71	87	7	1	4	396	653	7	1	5	116	-106	1	0	113	-177	
9	2	276	273	U	5	1	13	132	8	2	9	71	13	4	2	129	-124	4	4	6	84	9	1	5	151	151	2	0	203	-254		
8	2	202	152	5	5	1	161	-161	5	5	2	176	-163	14	2	153	-195	4	1	4	91	83	9	1	5	5	3	1	0	206	-240	
14	2	170	170	6	5	1	131	-11	6	3	117	105	1	3	285	216	15	1	4	36	25	10	1	5	76	-86	4	0	139	139		
12	2	203	157	7	5	1	177	-17	7	5	2	132	-169	8	3	101	-169	16	1	4	359	-444	11	1	5	37	33	0	0	182	-190	
1	3	295	212	8	5	1	16	-13	8	3	116	-104	3	3	184	-136	13	1	4	264	298	14	1	5	123	118	6	0	192	186		
1	3	378	362	8	5	1	96	-93	4	3	2	111	-123	6	3	163	138	18	1	4	10	11	13	1	5	120	-168	7	0	63	-60	
3	3	31	66	10	5	1	63	-60	11	3	2	77	-72	3	3	40	25	3	4	25	3	4	2	5	124	132	8	0	203	-180		
5	3	230	212	11	5	1	9	-83	11	3	2	156	-143	6	3	102	125	1	4	4	67	-62	1	2	235	255	4	0	152	-148		
5	3	354	340	10	5	1	16	-16	12	3	2	156	-143	10	3	288	236	6	2	238	236	12	2	5	134	-134	10	0	186	-185		
3	3	147	114	13	5	1	126	-117	13	4	2	95	-111	4	3	175	-178	3	2	4	75	-53	3	2	159	165	11	0	198	-172		
13	3	238	150	0	6	1	54	52	14	3	2	11	-21	9	3	16	-15	4	2	313	291	6	2	5	228	-236	12	0	203	176		
15	3	145	121	1	6	1	147	128	15	3	2	75	-64	10	3	97	-48	5	2	4	160	60	10	1	5	48	-242	13	0	162	-78	
0	4	261	-255	1	6	1	225	-190	0	4	2	156	-131	11	3	98	-89	6	2	4	132	137	6	2	5	72	2	0	200	-207		
2	4	295	245	3	6	1	117	-47	1	4	2	225	291	12	3	185	162	7	2	4	62	56	7	2	5	76	62	1	0	156	-126	
4	4	161	435	4	6	1	253	-262	4	4	108	-105	3	4	210	158	12	3	4	37	29	7	2	5	48	-242	13	0	156	-126		
6	4	101	77	5	6	1	173	-165	3	4	4	197	178	14	3	39	-34	4	2	4	15	-22	10	2	5	201	217	3	0	10	-13	
8	4	8	8	6	6	1	16	-24	4	4	2	209	-191	0	4	45	18	10	2	4	226	204	10	2	5	111	-202	4	0	137	-131	
10	4	402	378	7	6	1	14	-14	11	5	2	159	-149	11	4	165	159	11	7	1	141	-128	11	7	1	141	-128	5	0	168	-157	
14	4	83	73	8	6	1	71	-62	4	4	2	153	-163	7	4	230	187	12	2	4	104	141	12	2	5	66	-56	6	0	145	-156	
10	4	195	-130	5	6	1	129	116	7	4	2	14	-6	0	4	49	44	13	2	4	12	25	13	2	5	149	-139	7	0	43	-52	
11	4	195	-130	16	6	1	244	-244	8	2	123	-117	13	4	228	217	13	3	228	217	13	3	228	217	13	3	228	217	13	0	175	-168
3	5	295	-264	11	6	1	83	-76	4	4	2	251	264	5	4	4	46	-87	1	3	4	100	111	2	3	5	484	-492	9	0	62	53
5	5	94	71	12	6	1	111	-171	10	4	2	170	-74	6	4	15	-21	2	3	4	83	-50	3	3	5	142	127	10	0	104	-96	
5	5	381	471	13	6	1	118	-191	11	4	2	131	-116	7	4	15	-15	3	3	4	294	302	11	5	154	172	11	0	168	-157		
11	5	195	-144	1	7	1	312	-280	12	4	2	142	-147	8	4	3	42	45	4	4	26	25	5	3	5	13	4	12	2	102	-112	
13	5	282	258	2	7	1	172	-155	13	4	2	168	-172	9	4	195	102	5	3	4	187	173	6	3	5	151	174	13	2	27	-26	
5	6	194	-151	3	7	1	156	-138	14	4	2	156	-138	10	4	196	193	6	3	4	31	23	5	3	5	225	-255	1	0	186	-178	
2	6	100	156	4	7	1	123	127	1	5	2	156	-114	11	4	55	54	7	3	4	14	3	8	3	5	164	-205	2	0	134	-114	
4	6	145	423	5	7	1	160	-95	2	5	2	385	-374	12	4	42	95	8	3	4	0	-52	9	3	5	66	-65	3	0	154	-138	
6	6	190	-142	6	7	1	131	-127	3	5	2	245	-274	13	4	42	95	8	3	4	0	-52	9	3	5	66	-65	3	0	154	-138	
8	6	85	-71	7	7	1	258	-319	4	5	2	193	174	1	5	166	142	10	3	4	15	-13	11	3	5	61	5	0	138	-139		
10	6	253	227	8	7	1	158	-171	5	5	2	163	-192	2	5	54	-46	11	3	6	233	209	12	3	5	208	196	6	0	94	-100	
12	6	157	125	9	7	1	142	-167	6	5	2	160	-112	U	6	5	118	118	13	3	127	-114	13									

cycles, since the correlation data obtained from precession photographs were not considered extensive enough to enable a reliable internal correlation of structure amplitudes to be made. It was subsequently found that the maximum change obtained in these interlayer scale factors was 8.7%. The weighting scheme used was that suggested by Cruickshank (1965), *i.e.*

$$W = 1/(a + |F_o| + c|F_o|^2)$$

where  $a$  and  $c$  are equal to  $2F_{\min}$  and  $2/F_{\max}$ , respectively.

Atomic form factors for oxygen, aluminum and tungsten were taken from *International Tables for X-ray Crystallography* (1962). The zero oxidation state was taken for each element because of an uncertainty in the relative degree of ionicity and the tungsten curve was corrected for the real component of the anomalous dispersion of Cu  $K\alpha$  radiation with the  $\Delta f'$  values given by Dauben & Templeton (1955).

The final positional coordinates and isotropic temperature factors for the crystallographically independent atoms, together with estimated standard deviations, are given in Table 2. When the unobserved reflexions are given an estimated intensity of  $I_{\min/2}$  the overall reliability index  $R=0.12$ . A list of observed structure amplitudes and structure factors calculated using the atomic parameters listed in Table 2, is given in Table 1.

### Interatomic distances and angles

The unit-cell dimensions and positional coordinates listed in Table 2 were used to derive the interatomic distances listed in Table 3 and the bond angles listed in Table 4. The standard errors in these values were computed from the variance-covariance matrix obtained in the final least-squares refinement and the unit-cell errors using the *ORFFE* program of Busing, Martin & Levy (1964).

Table 3. *Selected interatomic distances (Å) in the compound  $\text{Al}_2(\text{WO}_4)_3$*

The first symbol denotes the atom in accordance with Table 2; the second number denotes the following symmetry transformations of the parameters of Table 2:

0	$x,$	$y,$	$z$
1	$\frac{1}{2}-x,$	$\frac{1}{2}-y,$	$\frac{1}{2}+z$
2	$1-x,$	$y,$	$\frac{1}{2}-z$
3	$\frac{1}{2}+x,$	$\frac{1}{2}+y,$	$\frac{1}{2}-z$
4	$\frac{1}{2}-x,$	$\frac{1}{2}+y,$	$z$
5	$x,$	$\bar{y},$	$\frac{1}{2}+z$
6	$x,$	$y-1,$	$z$

Standard deviations are given in brackets following the bond distance values and refer to the last two places of the preceding number. Bond distances for  $\text{Al}_2(\text{WO}_4)_3$  are given first; the corresponding bond distance in the compound  $\text{Sc}_2(\text{WO}_4)_3$  follows the semicolon.

Table 3 (*cont.*)

W(1) tetrahedron	
W(1)(4)-O(6)(0)	1.764 (33); 1.695 (09)
W(1)(4)-O(4)(3)	1.769 (31); 1.782 (15)
O(6)(0)-O(6)(2)	2.885 (70); 2.731 (18)
O(4)(3)-O(4)(4)	2.925 (63); 3.055 (32)
O(6)(0)-O(4)(4)	2.920 (48); 2.786 (17)
O(6)(0)-O(4)(3)	2.829 (42); 2.830 (17)
W(2) tetrahedron	
W(2)(0)-O(1)(0)	1.825 (31); 1.787 (15)
W(2)(0)-O(3)(0)	1.771 (30); 1.751 (16)
W(2)(0)-O(5)(0)	1.801 (41); 1.829 (16)
W(2)(0)-O(2)(6)	1.804 (42); 1.762 (11)
O(1)(0)-O(5)(0)	3.049 (50); 2.998 (24)
O(1)(0)-O(3)(0)	2.889 (44); 2.885 (23)
O(1)(0)-O(2)(6)	2.834 (52); 2.903 (21)
O(3)(0)-O(5)(0)	2.907 (52); 2.883 (25)
O(3)(0)-O(2)(6)	2.850 (49); 2.902 (20)
O(5)(0)-O(2)(6)	3.075 (64); 2.890 (24)
Al octahedron	
Al-O(6)(0)	1.860 (36); 2.124 (10)
Al-O(5)(0)	1.825 (37); 2.020 (16)
Al-O(3)(2)	1.892 (31); 2.103 (16)
Al-O(4)(1)	1.871 (34); 2.026 (15)
Al-O(1)(1)	1.828 (33); 2.051 (13)
Al-O(2)(1)	1.742 (47); 2.053 (15)
O(5)(0)-O(2)(1)	2.341 (75); 2.865 (24)
O(5)(0)-O(1)(1)	2.611 (46); 2.907 (25)
O(5)(0)-O(3)(2)	2.639 (43); 2.869 (24)
O(5)(0)-O(6)(0)	2.680 (41); 2.951 (16)
O(6)(0)-O(3)(2)	2.663 (42); 2.836 (19)
O(6)(0)-O(1)(1)	2.632 (48); 3.078 (19)
O(6)(0)-O(4)(1)	2.532 (54); 2.777 (20)
O(2)(1)-O(1)(1)	2.576 (51); 2.903 (21)
O(2)(1)-O(3)(2)	2.488 (53); 2.902 (20)
O(2)(1)-O(4)(1)	2.749 (51); 3.026 (17)
O(4)(1)-O(3)(2)	2.581 (46); 2.920 (22)
O(4)(1)-O(1)(1)	2.654 (44); 2.885 (22)
Metal-metal distances	
Al-W(1)(4)	3.504 (16); 3.710 (3)
Al-W(1)(1)	3.635 (17); 3.797 (4)
Al-W(2)(0)	3.442 (20); 3.643 (4)
Al-W(2)(1)	3.543 (17); 3.846 (3)
Al-W(2)(5)	3.514 (18); 3.737 (3)

### Discussion

Some time after the completion of our study it was discovered (Roth, 1966) that the compound  $2\text{Al}_2\text{O}_3 \cdot 6\text{WO}_3$ , or  $\text{Al}_2(\text{WO}_4)_3$ , had previously been shown to be isomorphous with the tungstates of trivalent Gd, Tb, Dy, Ho, Y, Er, Tm, Yb, Lu, In and Sc in addition to the molybdates of trivalent Ho, Y, Er, Tm, Yb, Lu, Sc, In, Fe, Cr and Al (Nassau, Levinstein & Loiacono, 1965). A recent crystal structure analysis of diamagnetic  $\text{Sc}_2(\text{WO}_4)_3$  by Abrahams & Bernstein (1966) leaves no doubt as to the correctness of the formulation for the stable phase  $2\text{Al}_2\text{O}_3 \cdot 6\text{WO}_3$ . It is of interest to compare corresponding bond distances and angles in the isomorphous compounds  $\text{Al}_2(\text{WO}_4)_3$  and  $\text{Sc}_2(\text{WO}_4)_3$ . These comparisons are listed in Tables 3 and 4.

Table 4. Selected bond angles ( $^{\circ}$ )  
in the compound  $\text{Al}_2(\text{WO}_4)_3$

Symmetry operations and standard deviations *etc.* are represented in the same manner as in Table 3.

W(1) Tetrahedron		
O(6)(0)-W(1)(4)-O(4)(4)	111.5 (1.4);	109.0 (0.6)
O(6)(0)-W(1)(4)-O(4)(3)	106.4 (1.6);	106.5 (0.7)
O(6)(0)-W(1)(4)-O(6)(2)	109.7 (1.9);	107.4 (0.5)
W(2) Tetrahedron		
O(1)(0)-W(2)(0)-O(5)(0)	114.4 (1.3);	112.0 (0.8)
O(1)(0)-W(2)(0)-O(3)(0)	106.9 (1.4);	109.3 (0.9)
O(1)(0)-W(2)(0)-O(2)(6)	102.7 (1.8);	110.3 (0.9)
O(2)(6)-W(2)(0)-O(3)(0)	106.0 (1.6);	111.4 (0.8)
O(2)(6)-W(2)(0)-O(5)(0)	117.1 (2.2);	107.2 (0.8)
O(3)(0)-W(2)(0)-O(5)(0)	108.9 (1.5);	106.5 (0.8)
Al Octahedron		
O(5)(0)-Al-O(2)(1)	82.0 (2.2);	89.4 (0.6)
O(5)(0)-Al-O(3)(2)	90.5 (1.4);	88.7 (0.8)
O(5)(0)-Al-O(1)(1)	91.3 (1.4);	91.2 (0.8)
O(5)(0)-Al-O(6)(0)	93.3 (1.7);	90.8 (0.5)
O(4)(1)-Al-O(6)(0)	85.4 (1.5);	84.0 (0.5)
O(4)(1)-Al-O(3)(2)	86.6 (1.4);	90.0 (0.7)
O(4)(1)-Al-O(2)(1)	99.0 (2.3);	95.8 (0.6)
O(4)(1)-Al-O(1)(1)	91.7 (1.4);	90.1 (0.7)
O(2)(1)-Al-O(1)(1)	92.4 (1.7);	90.0 (0.7)
O(2)(1)-Al-O(3)(2)	86.3 (1.6);	90.7 (0.7)
O(6)(0)-Al-O(3)(2)	90.4 (1.4);	84.3 (0.6)
O(6)(0)-Al-O(1)(1)	91.1 (1.4);	95.0 (0.6)

The  $\text{Al}_2(\text{WO}_4)_3$  structure consists of  $\text{WO}_4$  tetrahedra and  $\text{AlO}_6$  octahedra which extend into an infinite three-dimensional network by corner sharing; each  $\text{AlO}_6$  octahedron is connected to six  $\text{WO}_4$  tetrahedra whilst each  $\text{WO}_4$  tetrahedron shares its oxygen atoms with four  $\text{AlO}_6$  octahedra. This is in complete agreement with Pauling's (1960) third rule which implies that edge and face sharing is kept to an absolute minimum in purely ionic compounds. However, it must be kept in mind that the stoichiometry of the compound would result in unshared corners were there to be any sharing of polyhedral faces. This state of affairs can probably be induced with high pressure and further discussion on a possible high pressure form of  $\text{Al}_2(\text{WO}_4)_3$  is to be found later in the paper. The structure, viewed in clinographic projection, is shown in Fig. 1.

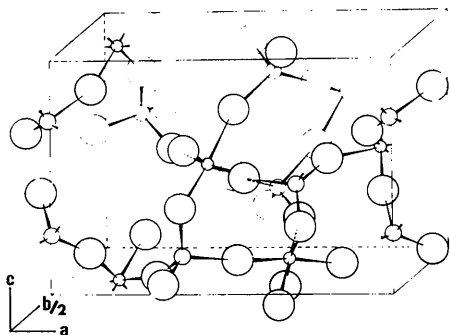


Fig. 1. A clinographic projection of the structure of  $\text{Al}_2(\text{WO}_4)_3$ .

The average tetrahedral W-O distance of 1.783(23) Å compares well with this distance in similar tungstates; 1.785(3) Å in  $\text{CaWO}_3$  (Kay, Frazer & Almodovar, 1964) and 1.79(2) Å in  $\text{Li}_2\text{WO}_4$  (Zachariasen & Plettinger, 1961). This tetrahedral distance is significantly smaller than the octahedral value for W-O which is reported to be 1.92(21) Å in  $\text{NiWO}_4$  (Keeling, 1957) and 1.96(22) Å in  $\text{CdWO}_4$  (Chichagov, Ilukhin & Belov, 1966).

A statistical analysis ( $\chi^2$  test) (Weatherburn, 1947), of the significance of the deviations of the O-O distances from the mean O-O distance for each type of polyhedron yielded the following results. The  $\text{WO}_4$  tetrahedra in  $\text{Al}_2(\text{WO}_4)_3$  are more regular in shape than those in  $\text{Sc}_2(\text{WO}_4)_3$  (see also Tables 3 and 4); the W(1) tetrahedron in  $\text{Al}_2(\text{WO}_4)_3$  is regular and not significantly distorted ( $\chi^2 = 5.02$ , 5 degrees of freedom), whereas the W(2) tetrahedron is significantly distorted from regular at the 1% level. In  $\text{Sc}_2(\text{WO}_4)_3$  these same tetrahedra are significantly distorted at the 0.1% level. Both  $\text{AlO}_6$  and  $\text{ScO}_6$  octahedra are significantly distorted from regular at the 0.1% level, but the distortions are much greater in the case of the  $\text{ScO}_6$  octahedron.

Both octahedra and tetrahedra share corners and distortions in either must result in departures from regularity in the other. The  $\text{AlO}_6$  octahedron is smaller than the  $\text{ScO}_6$  octahedron, and it is likely that in this small unit the oxygen atoms are touching (mean O-O distance, 2.60 Å). Under these conditions of close packing a more regular polyhedron would be expected to form. As the size of the central atom is increased, the radius ratio ( $r_{M^{3+}}/r_{O^{2-}}$ ) is, of course, changed and an increase in coordination number about the central metal atom is to be expected. Thus, the trivalent rare-earth tungstates crystallize in three different types (Nassau, Levinstein & Loiacono, 1965). In the  $\text{Eu}_2(\text{WO}_4)_3$ -type structure, which is characteristic of the larger rare earths, the metal ion is 8-coordinated; in  $\text{Eu}_2(\text{WO}_4)_3$ , the average Eu-O distance is 2.425 Å (Templeton & Zalkin, 1963).

The average Al-O bond distance in  $\text{Al}_2(\text{WO}_4)_3$  is 1.836(35) Å, which compares favourably with similar bond distances in other substances, such as 1.855(3) Å in diaspore (Busing & Levy, 1958). The Al-O(2) distance of 1.742(47) Å is significantly shorter than the average, but is not unreasonable in the light of Al-O distances of 1.60 Å reported (Nithollon, 1955) for  $\text{AlO}_4$  tetrahedra, where metal and non-metal atoms can come into closer contact.

#### The structure as a cubic close-packed array of anions

In the  $\text{Al}_2(\text{WO}_4)_3$  structure there are units consisting of two  $\text{AlO}_6$  octahedra joined by two bridging  $\text{WO}_4$  tetrahedra and the oxygen atoms associated with this unit are located at the corners of a cube and in the centres of four cube faces. Apart from two empty face-centred sites the unit has a cubic close-packed arrange-

ment of oxygen atoms with aluminum and tungsten atoms occupying certain octahedral and tetrahedral interstices.

The overall three-dimensional structure might be imagined as being built up of these cubic blocks, stacked adjacently in a repeating and ordered manner. However, these cubic units are not space filling and some of the units have to be removed from the matrix. The remaining members of the ordered array are linked to each other through corner-sharing tetrahedra and octahedra and constitute an intersecting network of pucker sheets. One of these sheets, running parallel to [010] and [001] is depicted in Fig. 2. This sheet is attached, again by corner sharing polyhedra, to an identical sheet similarly oriented but with an origin displacement of  $(\mathbf{a}/2 + \mathbf{b}/2 + \mathbf{c}/2)$ .

The face-centred cubic anion unit depicted in Fig. 2 contains twelve oxygen atoms. Opposite faces of the

cube are parallel and an analysis of the planarities of the anions is given in Table 5. It can be seen that deviations from planarity range between 0.07 and 0.53 Å for each cube. The distances between opposite sets of faces give the size of the face-centred cube as  $4.14 \times 4.06 \times 3.13$  Å.

The f.c.c. anion units, although discontinuous and separated in the crystal structure, lie in an ordered three-dimensional matrix and, for example, the five oxygen atoms comprising the upper face of one cube, *viz.* O(1), O(3), O(4), O(6), O(4), lie in the same plane as the five oxygen atoms comprising the lower face of an adjacent cube. The equation for this plane as shown in Fig. 2 is

$$0.465x + 0.478y + 0.745z + 6.329 = 0,$$

and deviations of the ten oxygen atoms from this plane average 0.21 Å.

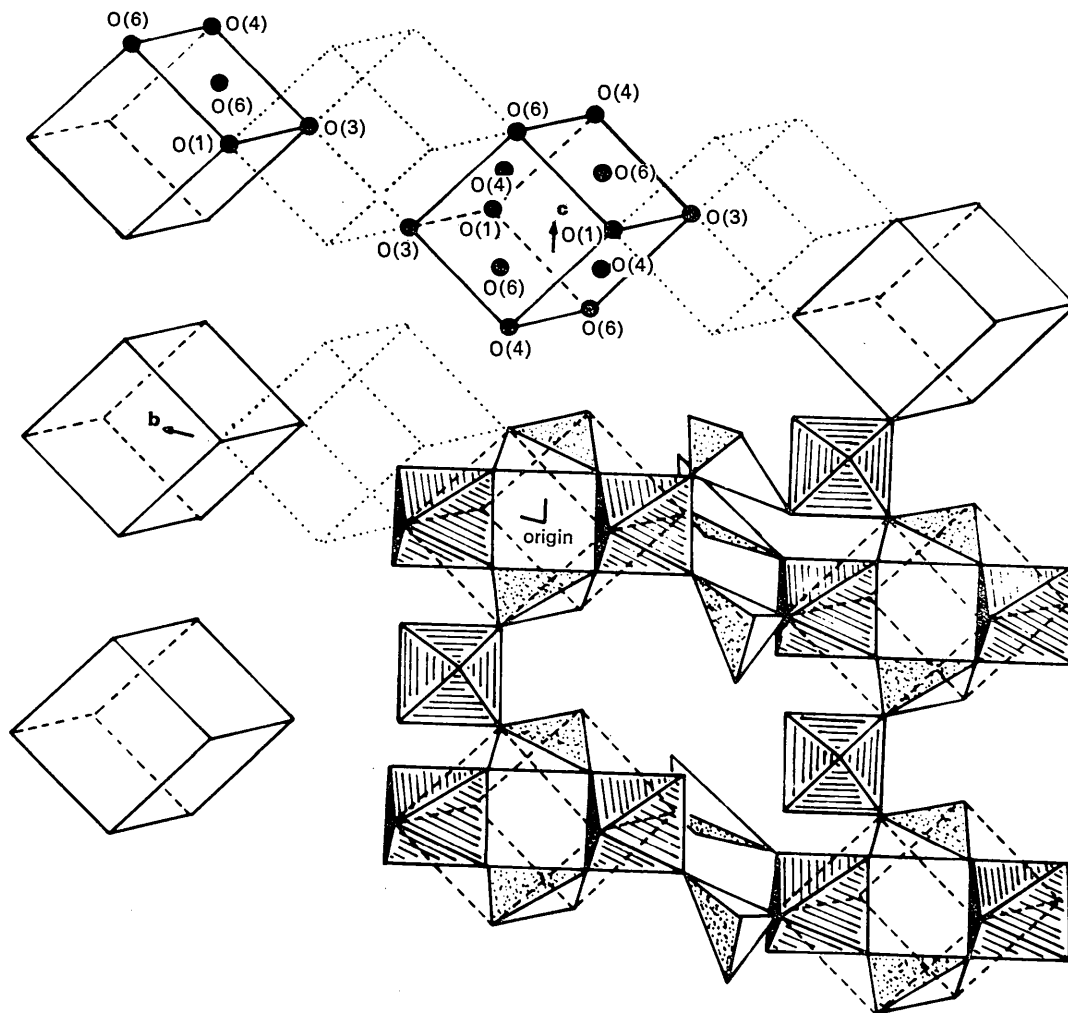


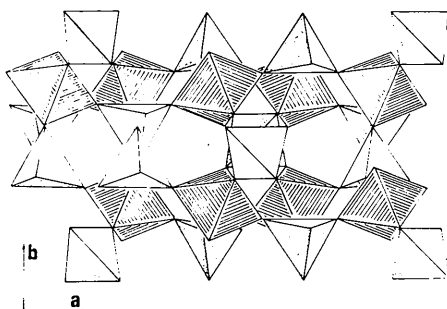
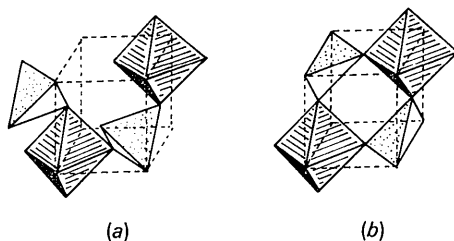
Fig. 2. A pucker sheet of corner-sharing polyhedra running parallel to [001] and [010]. The discontinuous array of face-centred cubic anion units, each consisting of twelve close packed oxygen atoms, is shown. These units are linked by  $\text{WO}_4$  tetrahedra and  $\text{AlO}_6$  octahedra to form the crystal structure.

Table 5. Analysis of the planarity of the f.c.c. anion unit

Deviations,  $\Delta$ , from least-squares planes  $Ax + By + Cz + D = 0$  referred to crystallographic axes.

Best plane through	O(1), O(3), O(4)	O(1), O(3), O(6)	O(1), O(3)
$A$	0.3892	0.4054	0.8307
$B$	0.7369	0.5839	-0.5565
$C$	-0.5527	0.7034	0.0180
$D$	1.2328	6.3310	4.3533
Atom	$\Delta \times 10^2$	$\Delta \times 10^2$	$\Delta \times 10^2$
O(1)	-39	-15	14
O(3)	30	10	25
O(4)	-53, 20	7	-17
O(6)	43	-19, 18	-23

Were the oxygen atoms to form a continuous, face-centred cubic structure, the nature of the anion unit depicted in Fig. 2 would have to change so as to endow it with space filling properties; also, the corner-sharing polyhedra at present connecting these cube units would have to rearrange. At present, the connecting polyhedra have rather an open structure and the presence of tunnels running parallel to [001] is readily detected in a (001) projection of the unit cell contents (Fig. 3). The density of  $\text{Al}_2(\text{WO}_4)_3$  is lower than that to be expected if the structure were a continuous f.c.c. packing of anions, and this is in agreement with the large volume expansion (>25%) observed during the formation from the calcined end members (Waring, 1965).

Fig. 3. A (001) projection of the structure of  $\text{Al}_2(\text{WO}_4)_3$ .Fig. 4. Face-centred cubic units of oxygen atoms for (a)  $\text{Cr}_5\text{O}_{12}$  and (b)  $\text{Al}_2(\text{WO}_4)_3$ . The associated polyhedra are indicated.

The structure of  $\text{Cr}_5\text{O}_{12}$ , synthesized at high pressure, has recently been reported by Wilhelmi (1965). It consists of corner-sharing  $\text{CrO}_6$  octahedra and  $\text{CrO}_4$  tetrahedra, which form a three-dimensional framework in which there is a continuous, slightly distorted cubic close-packed array of oxygen atoms. The average length of cubic anion unit is  $4.06 \text{ \AA}$ , and this space filling unit is depicted in Fig. 4.

It seems not unlikely that a high pressure form of  $\text{Al}_2(\text{WO}_4)_3$  would be isomorphous with  $\text{Cr}_5\text{O}_{12}$  [*i.e.*  $\text{Cr}_2(\text{CrO}_4)_3$ ]. We are at present attempting to synthesize this high pressure polymorph and to determine its structure.

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