

### Refinement of the Alum Structures. III. X-ray Study of the $\alpha$ Alums, K, Rb and $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}^*$

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The structures of the  $\alpha$  alums K, Rb and  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  have been refined using single-crystal X-ray diffraction data. The  $\alpha$  alums are disordered, some of the sulfate groups being in a reversed orientation along the threefold axis. The fraction of reversed sulfate groups apparently increases as the monovalent cation decreases in size. The disordered sulfate groups suggest a mechanism for the ferroelectric transitions observed in  $\alpha$  alums at low temperatures. Because of the disorder it was not possible to obtain accurate dimensions for the sulfate group.

#### Introduction

The alums are a large class of double salts having the general formula  $\text{A}^{\text{I}}\text{B}^{\text{III}}(\text{RO}_4)_2 \cdot 12\text{H}_2\text{O}$  and crystallizing in space group  $Pa\bar{3}$ . All alums were thought to be isomorphous until Lipson (1935) showed that there are three different types, which he named  $\alpha$ ,  $\beta$  and  $\gamma$ . In the first paper of this series (Cromer, Kay & Larson, 1966) the refinement by X-ray and neutron diffraction of the structure of  $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , a  $\beta$  alum, was given and the relations among the three types were discussed. In the second paper (Cromer, Kay & Larson, 1967) a similar refinement of  $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , the only known member of the  $\gamma$  alum class, was given.

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In the present paper we give the results of X-ray refinements of the  $\alpha$  alums  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ,  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . In the final paper (Cromer & Kay, 1967) a detailed three-dimensional neutron diffraction analysis of  $\text{ND}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{D}_2\text{O}$  will be described.

#### Experimental

Crystals of K, Rb and  $\text{NH}_4$  alums were grown from water solution and ground into spheres about 0.15 mm diameter\*. Lattice constants were measured with a

\* Rb alum is a good material to use for aligning a single crystal diffractometer. The crystals are stable, easily grown and easily ground into small spheres. With Mo radiation the 200 reflection, quite strong, occurs at  $2\theta = 6.655^\circ$  and can be observed both at  $\chi = 0^\circ$  and  $90^\circ$  if the crystal is mounted along the  $a$  axis.

Table 1. Crystallographic data

Crystal	$a$	Number of independent intensities measured	Number of independent intensities observed*
$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$12.157 \pm 0.003 \text{ \AA}$	540	252
$\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$12.243 \pm 0.003$	547	205
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$12.240 \pm 0.003$	406	239

\*  $F_{\text{obs}} > 0$  if  $(\text{Intensity} - \text{Background}) \geq 3(\text{Intensity} + \text{Background})^{\frac{1}{2}}$ .

Table 2. Least-squares parameters for  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

Standard deviations, in parentheses, apply to the rightmost digit

Atom	$x$	$y$	$z$	$\beta_{11} \times 10^4$ or $B$ ( $\text{\AA}^2$ )	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
K	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	2.6 (9)					
K'	0.485 (4)	$x$	$x$	2.9 (24)					
Al	0	0	0	23 (4)	$\beta_{11}$	$\beta_{11}$	14 (10)	$\beta_{12}$	$\beta_{12}$
S	0.3075 (4)	$x$	$x$	29 (2)	$\beta_{11}$	$\beta_{11}$	3 (6)	$\beta_{12}$	$\beta_{12}$
O(1)	0.2388 (15)	$x$	$x$	96 (17)	$\beta_{11}$	$\beta_{11}$	-28 (32)	$\beta_{12}$	$\beta_{12}$
O(1)'	0.3729 (39)	$x$	$x$	6.3 (27)					
O(2)	0.3105 (13)	0.2648 (14)	0.4228 (14)	71 (15)	57 (20)	31 (12)	36 (29)	-4 (26)	44 (24)
O(2)'	0.2038 (36)	0.3736 (29)	0.2901 (29)	3.2 (1.1)					
W(1)	0.0465 (7)	0.1353 (7)	0.3007 (7)	48 (9)	35 (7)	25 (7)	2 (13)	9 (14)	-5 (15)
W(2)	0.0206 (7)	-0.0190 (7)	0.1544 (6)	22 (8)	40 (9)	17 (7)	4 (15)	4 (12)	-6 (12)

$k = 0.301$  (33)



A least-squares refinement was then made with a disorder parameter included. The fraction of reversed sulfate oxygen atoms O(1)' and O(2)' was set equal to  $k$ , the fraction of sulfate oxygen and potassium in the normal position to  $(1-k)$ , and the fraction of potassium displaced into  $xxx$  positions was set equal to  $k/2$ . The sulfur atom had not shown anisotropy so it was assumed to be in the same position for both orientations. With all atoms anisotropic except potassium,  $k$  had the value  $0.37 \pm 0.04$  and  $R$  was reduced to 6.8%. However, the thermal parameters for O(1)' did not remain positive definite (although by only about 0.5 s.d.). For the final refinement, the potassium and reversed oxygen atoms were held isotropic and the remaining atoms allowed to be anisotropic. This refinement led to  $R=6.9\%$  with the disorder parameter  $k=0.30 \pm 0.03$ . The final parameters are given in Table 2 and the observed and calculated structure factors in Table 3. (In the Tables and in the discussion we use

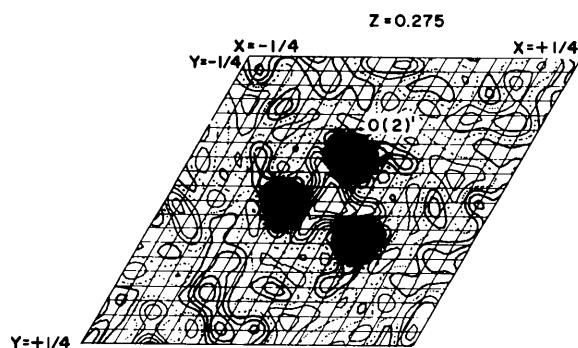


Fig. 1. K alum. Difference Fourier map normal to the threefold axis, after ordered anisotropic refinement. For this Fourier map the cell was transformed to a hexagonal cell by the matrix  $(1, -1, 0; 0, 1, -1; 1, 1, 1)$ . The threefold axis is in the center and the peaks are the reversed O(2)' atoms. The value of  $z$  is the same as  $xxx$  of the cubic cell. The contour interval is  $0.1 \text{ e.}\text{\AA}^{-3}$ . The zero contour is dotted and the positive contours are the heavier lines.

the symbol  $W$  for the water oxygen atoms.) A difference Fourier synthesis showed no significant peaks except at approximately the positions found for hydrogen atoms by Bacon & Gardner (1958) in their neutron diffraction study of  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

Ordered anisotropic refinements of Rb and  $\text{NH}_4$  alums led to  $R=6.4\%$  and  $8.9\%$  respectively. Difference Fourier syntheses revealed disordered oxygen peaks as in K alum, but the peaks were not nearly as pronounced. Fig. 3 shows a section of the Rb alum difference Fourier syntheses. An  $\text{NH}_4$  alum difference Fourier synthesis was of similar appearance.

Attempts were also made to refine these structures with a disorder parameter. The value of  $k$  tended to be in the range 0.1 and 0.15. However, for O(1)' and O(2)' anisotropic thermal parameters did not remain real and isotropic thermal parameters for these frac-

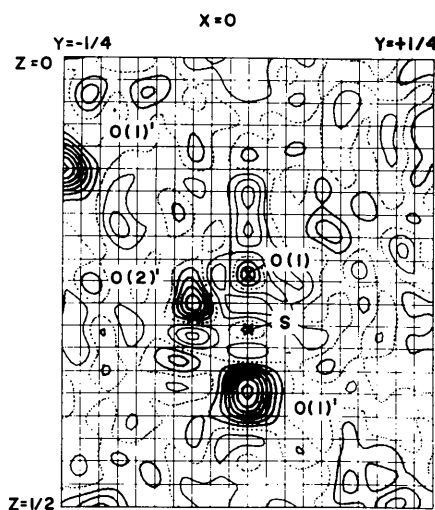


Fig. 2. K alum. Difference Fourier map in a plane containing the threefold axis, after ordered anisotropic refinement. The cell is the same as defined in Fig. 1. The contour interval is  $0.2 \text{ e.}\text{\AA}^{-3}$ .

Table 4. *Least-squares parameters for*  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$   
Standard deviations, in parentheses, apply to the rightmost digit.

Atom	$x$	$y$	$z$	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
Rb	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	50 (2)	$\beta_{11}$	$\beta_{11}$	31 (8)	$\beta_{12}$	$\beta_{12}$
Al	0	0	0	25 (5)	$\beta_{11}$	$\beta_{11}$	11 (18)	$\beta_{12}$	$\beta_{12}$
S	0.3127 (4)	$x$	$x$	28 (3)	$\beta_{11}$	$\beta_{11}$	-6 (8)	$\beta_{12}$	$\beta_{12}$
O(1)	0.2471 (17)	$x$	$x$	117 (10)	$\beta_{11}$	$\beta_{11}$	56 (46)	$\beta_{12}$	$\beta_{12}$
O(2)	0.3172 (11)	0.2639 (14)	0.4237 (10)	58 (12)	126 (20)	38 (11)	64 (38)	-16 (24)	72 (27)
$W(1)$	0.0451 (10)	0.1406 (9)	0.2975 (10)	39 (12)	30 (10)	16 (10)	1 (17)	-1 (18)	1 (19)
$W(2)$	0.0173 (10)	-0.0148 (11)	0.1554 (7)	11 (10)	40 (12)	13 (8)	6 (24)	15 (17)	-15 (20)

Table 5. *Least-squares parameters for*  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$   
Standard deviations, in parentheses, apply to the rightmost digit.

Atom	$x$	$y$	$z$	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
N	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	59 (14)	$\beta_{11}$	$\beta_{11}$	20 (39)	$\beta_{12}$	$\beta_{12}$
Al	0	0	0	26 (4)	$\beta_{11}$	$\beta_{11}$	6 (11)	$\beta_{12}$	$\beta_{12}$
S	0.3090 (4)	$x$	$x$	27 (2)	$\beta_{11}$	$\beta_{11}$	11 (7)	$\beta_{12}$	$\beta_{12}$
O(1)	0.2408 (14)	$x$	$x$	155 (14)	$\beta_{11}$	$\beta_{11}$	-41 (35)	$\beta_{12}$	$\beta_{12}$
O(2)	0.3142 (10)	0.2607 (11)	0.4173 (9)	83 (13)	170 (18)	37 (10)	122 (29)	37 (22)	153 (24)
$W(1)$	0.0456 (8)	0.1383 (8)	0.2977 (8)	54 (10)	24 (8)	30 (9)	7 (16)	9 (16)	-6 (16)
$W(2)$	0.0184 (8)	-0.0169 (8)	0.1546 (7)	20 (9)	57 (11)	5 (8)	-10 (17)	-3 (14)	8 (16)

Table 6. Observed and calculated structure factors for  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

Column headings are  $k$ ,  $10F_o$  and  $10F_c$ . A minus sign preceding  $F_o$  means 'less than'.

$h$	$k$	$l$	$10F_o$	$10F_c$
1	200	-333	-1177	219
1	177	145	-217	145
1	235	-266	3	-194
1	-194	-224	4	-170
0	638	617	5	-196
1	901	981	6	-212
2	215	2305	7	-218
2	151	1	8	-272
2	954	850	9	-263
1	546	-530	10	-176
2	926	-877	11	1336
2	1336	1281	12	1336
2	176	25	13	652
2	652	654	14	205
2	205	-238	15	995
2	995	1001	16	492
3	189	-117	17	221
3	278	662	18	136
3	1878	-1785	19	816
3	136	5	20	315
3	315	367	21	205
3	205	-60	22	202
3	202	20	23	286
3	286	412	24	208
3	208	61	25	896
3	896	61	26	288
3	288	61	27	350
3	350	514	28	604
3	604	64	29	274
3	274	37	30	704
3	704	37	31	258
3	258	37	32	263
3	263	37	33	231
3	231	37	34	232
3	232	37	35	671
3	671	37	36	643
3	643	37	37	234
3	234	37	38	235
3	235	37	39	236
3	236	37	40	237
3	237	37	41	238
3	238	37	42	239
3	239	37	43	240
3	240	37	44	241
3	241	37	45	242
3	242	37	46	243
3	243	37	47	244
3	244	37	48	245
3	245	37	49	246
3	246	37	50	247
3	247	37	51	248
3	248	37	52	249
3	249	37	53	250
3	250	37	54	251
3	251	37	55	252
3	252	37	56	253
3	253	37	57	254
3	254	37	58	255
3	255	37	59	256
3	256	37	60	257
3	257	37	61	258
3	258	37	62	259
3	259	37	63	260
3	260	37	64	261
3	261	37	65	262
3	262	37	66	263
3	263	37	67	264
3	264	37	68	265
3	265	37	69	266
3	266	37	70	267
3	267	37	71	268
3	268	37	72	269
3	269	37	73	270
3	270	37	74	271
3	271	37	75	272
3	272	37	76	273
3	273	37	77	274
3	274	37	78	275
3	275	37	79	276
3	276	37	80	277
3	277	37	81	278
3	278	37	82	279
3	279	37	83	280
3	280	37	84	281
3	281	37	85	282
3	282	37	86	283
3	283	37	87	284
3	284	37	88	285
3	285	37	89	286
3	286	37	90	287
3	287	37	91	288
3	288	37	92	289
3	289	37	93	290
3	290	37	94	291
3	291	37	95	292
3	292	37	96	293
3	293	37	97	294
3	294	37	98	295
3	295	37	99	296
3	296	37	100	297

tional atoms either oscillated wildly or became quite large. These fractional atoms have the approximate scattering power of a smeared out hydrogen atom; consequently they do not have enough effect on the scattering for the least-squares procedure to 'take hold'. Nevertheless the reversed oxygen atoms were clearly visible in difference Fourier maps for both compounds. Water hydrogen atoms were also visible in the difference Fourier maps, but the peaks were not of really useful quality. The least-squares parameters for the ordered anisotropic refinements of Rb and  $\text{NH}_4$  alums are given in Tables 4 and 5. The corresponding observed and calculated structure factors are in Tables 6 and 7.

Table 7. Observed and calculated structure factors for  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

Column headings are  $k$ ,  $10F_o$  and  $10F_c$ . A minus sign preceding  $F_o$  means 'less than'.

$h$	$k$	$l$	$10F_o$	$10F_c$
1	200	-333	-1177	219
1	177	145	-217	145
1	235	-266	3	-194
1	-194	-224	4	-170
0	638	617	5	-196
1	901	981	6	-212
2	215	2305	7	-218
2	151	1	8	-272
2	954	850	9	-263
1	546	-530	10	-176
2	926	-877	11	1336
2	1336	1281	12	1336
2	176	25	13	652
2	652	654	14	205
2	205	-238	15	995
2	995	1001	16	492
3	189	-117	17	221
3	278	662	18	136
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3	350	514	28	604
3	604	64	29	274
3	274	37	30	704
3	704	37	31	258
3	258	37	32	263
3	263	37	33	231
3	231	37	34	232
3	232	37	35	671
3	671	37	36	643
3	643	37	37	234
3	234	37	38	235
3	235	37	39	236
3	236	37	40	237
3	237	37	41	238
3	238	37	42	239
3	239	37	43	240
3	240	37	44	241
3	241	37	45	242
3	242	37	46	243
3	243	37	47	244
3	244	37	48	245
3	245	37	49	246
3	246	37	50	247
3	247	37	51	248
3	248	37	52	249
3	249	37	53	250
3	250	37	54	251
3	251	37	55	252
3	252	37	56	253
3	253	37	57	254
3	254	37	58	255
3	255	37	59	256
3	256	37	60	257
3	257	37	61	258
3	258	37	62	259
3	259	37	63	260
3	260	37	64	261
3	261	37	65	262
3	262	37	66	263
3	263	37	67	264
3	264	37	68	265
3	265	37	69	266
3	266	37	70	267
3	267	37	71	268
3	268	37	72	269
3	269	37	73	270
3	270	37	74	271
3	271	37	75	272
3	272	37	76	273
3	273	37	77	274
3	274	37	78	275
3	275	37	79	276
3	276	37	80	277
3	277	37	81	278
3	278	37	82	279
3	279	37	83	280
3	280	37	84	281
3	281	37	85	282
3	282	37	86	283
3	283	37	87	284
3	284	37	88	285
3	285	37	89	286
3	286	37	90	287
3	287	37	91	288
3	288	37	92	289
3	289	37	93	290
3	290	37	94	291
3	291	37	95	292
3	292	37	96	293
3	293	37	97	294
3	294	37	98	295
3	295	37	99	296
3	296	37	100	297

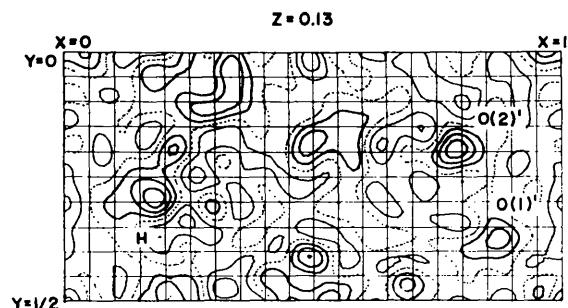


Fig. 3. Rb alum. Difference Fourier map after ordered anisotropic refinement. The cubic unit cell is used here. The contour interval is  $0.1 \text{ e.}\text{\AA}^{-3}$ .

### Discussion

The most interesting feature in the  $\alpha$  alums is the presence of the disordered sulfate group. This disorder is found in all  $\alpha$  alums that have been studied in sufficient detail. The final difference Fourier map published by Bacon & Gardner (1958), in their neutron diffraction study of  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , clearly shows peaks in the positions we have found for the reversed oxygen atoms. The disorder also accounts for the large thermal parameters of the sulfate oxygen atoms noted by Bacon & Gardner (1958). The  $\alpha$  alums, with the medium size monovalent cations, tend to be like the  $\gamma$  alum, in which the sulfate group is inverted, and the

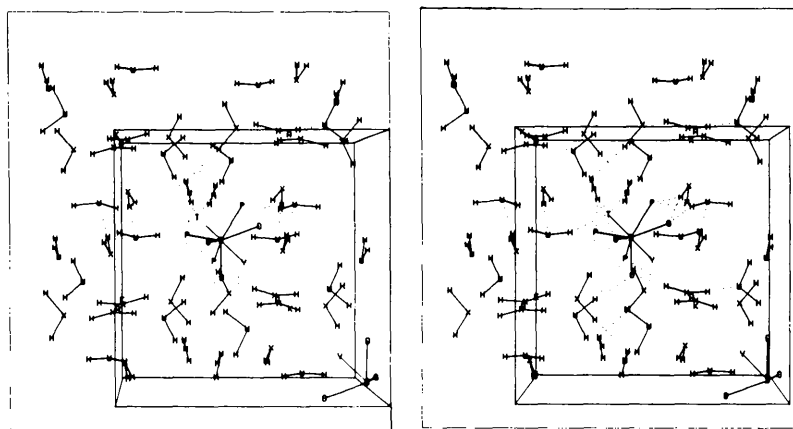


Fig. 4. Stereo plot of the K alum structure as viewed along  $[001]$ . The origin is at the upper left rear, and a right handed coordinate system is used. Only two sulfate groups are plotted, one near the center and part of one near the lower right front. The  $\text{K}'$  atoms have been omitted. Otherwise, all atoms within the range  $xyz$  from  $-\frac{1}{4}$  to  $\frac{1}{4}$  are shown. The box encloses the region  $000$  to  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ . Symbols used are: Potassium, K. Aluminum, A. Sulfur, S. Hydrogen, H. Water(1), W. Water(2), X. Oxygen(1), T. Oxygen(2), O. Oxygen(1)', Y. Oxygen(2)', P. Hydrogen atom positions are taken from the neutron refinement of  $\text{ND}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{D}_2\text{O}$  (Cromer & Kay, 1967).

Table 8. *Interatomic distances and angles in  $\alpha$  alums,  $\text{MAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$*   
Standard deviations, in parentheses, apply to the rightmost digit.

	M = K	M = Rb	M = $\text{NH}_4$		M = K	M = Rb	M = $\text{NH}_4$
Al-6W(2)	1.908 (8) Å	1.923 (9) Å	1.916 (8) Å	< W(2)-Al-W(2)	90.4 (4)°	90.3 (5)°	90.2 (4)°
M-6W(1)	2.983 (9)	3.068 (12)	3.051 (10)	< W(2)-Al-W(2)	89.6 (4)	89.7 (5)	89.8 (4)
M'-O(1)'	2.98 (12)			< W(1)-M-W(1)	105.1 (2)	114.1 (2)	113.8 (2)
M'-3W(1)	2.92 (2)			< W(1)-M-W(1)	74.9 (2)	65.9 (2)	66.2 (2)
M'-3W(1)	3.08 (3)						
<b>Sulfate group</b>							
S-O(1)	1.447 (29)	1.392 (36)	1.447 (29)	< O(1)-S-O(2)	110.8 (8)	108.5 (8)	108.4 (7)
S-O(2)	1.495 (14)	1.485 (12)	1.453 (10)	< O(2)-S-O(2)	118.1 (9)	110.4 (7)	110.5 (7)
S-O(1)'	1.377 (79)			< O(1)'-S-O(2)'	104.8 (16)		
S-O(2)'	1.510 (40)			< O(2)'-S-O(2)'	113.7 (13)		
<b>Hydrogen bonds</b>							
O(1)-3W(1)	2.759 (20)	2.864 (27)	2.787 (20)				
O(2)-W(1)	2.726 (16)	2.730 (15)	2.759 (14)				
O(2)'-W(1)	2.821 (36)						
O(2)-W(2)	2.563 (16)	2.553 (18)	2.565 (16)				
O(2)'-W(2)	2.721 (36)						
W(1)-W(2)	2.604 (13)	2.600 (17)	2.605 (14)				

fraction of reversed sulfate groups evidently tends to increase as the cation becomes smaller.

Fig. 4 is a stereo drawing of a portion of the K alum structure. The disorder can be described by reflecting the sulfate group through a mirror normal to the three-fold axis and passing through the sulfur atom, followed by a rotation of  $17.7^\circ$ . The two positions for the oxygen atom O(2) are only  $0.98 \text{ \AA}$  apart and their peaks are not completely resolved in a Fourier synthesis. Fig. 5 shows a section of the observed three-dimensional

Fourier synthesis; the elongated oxygen peak is to be noted. The appearance of this peak is consistent with the final anisotropic thermal parameters. The reversed oxygen atom O(2)' can form hydrogen bonds with the same sets of hydrogen atoms as the normal oxygen O(2). The reversed oxygen atom O(1)' does not form any hydrogen bonds, but it is close to the potassium atom. The O(1)'-K distance would be  $2.68 \text{ \AA}$  if the potassium were not disordered. However, if there are indeed  $k/2$  potassium atoms, K', in an  $xxx$  position

Table 9. *Thermal ellipsoids in KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O*

Standard deviations, in parentheses, apply to the rightmost digit.

	r m s. amplitude	$B_i$	Direction angles relative to crystal axes		
			$\alpha$	$\beta$	$\gamma$
Al	0.17 (2) Å	2.2 (6) Å <sup>2</sup>	54.7°	54.7°	54.7°
	0.11 (2)	1.0 (3)	—	—	—
	0.11 (2)	1.0 (3)	—	—	—
S	0.15 (2)	1.9 (4)	54.7	54.7	54.7
	0.15 (2)	1.7 (2)	—	—	—
	0.15 (1)	1.7 (2)	—	—	—
O(1)	0.23 (6)	4.0 (22)	54.7	54.7	54.7
	0.29 (3)	6.5 (14)	—	—	—
	0.29 (3)	6.5 (14)	—	—	—
O(2)	0.25 (3)	5.1 (13)	43 (24)	50 (19)	77 (16)
	0.21 (3)	3.4 (10)	130 (25)	56 (20)	58 (17)
	0.11 (4)	1.0 (7)	78 (13)	122 (12)	35 (14)
W(1)	0.19 (2)	2.9 (5)	11 (15)	88 (26)	79 (16)
	0.16 (2)	2.1 (5)	90 (28)	13 (34)	103 (34)
	0.13 (2)	1.4 (5)	101 (15)	78 (34)	17 (28)
W(2)	0.13 (2)	1.3 (5)	22 (50)	96 (24)	69 (52)
	0.17 (2)	2.4 (5)	84 (24)	6 (23)	90 (16)
	0.11 (2)	1.0 (4)	111 (52)	88 (16)	21 (52)

Table 10. *Thermal ellipsoids in RbAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O*

Standard deviations, in parentheses, apply to the rightmost digit.

	r.m.s. Amplitude	$B_i$	Direction angles relative to crystal axes		
			$\alpha$	$\beta$	$\gamma$
Rb	0.25 (1) Å	4.9 (5) Å	54.7°	54.7°	54.7°
	0.16 (1)	2.1 (2)	—	—	—
	0.16 (1)	2.1 (2)	—	—	—
Al	0.16 (4)	2.1 (11)	54.7	45.7	54.7
	0.12 (3)	1.2 (6)	—	—	—
	0.12 (3)	1.2 (6)	—	—	—
S	0.13 (3)	1.4 (5)	54.7	54.7	54.7
	0.15 (1)	1.9 (3)	—	—	—
	0.15 (1)	1.9 (3)	—	—	—
O(1)	0.36 (5)	10.4 (30)	54.7	54.7	54.7
	0.26 (3)	5.3 (13)	—	—	—
	0.26 (3)	5.3 (13)	—	—	—
O(2)	0.21 (3)	3.5 (9)	33 (15)	96 (9)	122 (15)
	0.33 (3)	8.8 (14)	73 (10)	24 (6)	74 (7)
	0.11 (4)	0.9 (8)	63 (13)	113 (6)	37 (13)
W(1)	0.17 (2)	2.3 (7)	4 (52)	86 (52)	90 (22)
	0.15 (3)	1.8 (6)	94 (52)	5 (50)	87 (40)
	0.11 (3)	1.0 (6)	89 (21)	93 (39)	3 (40)
W(2)	0.05 (8)	0.2 (6)	44 (25)	101 (17)	132 (24)
	0.18 (3)	2.5 (7)	88 (25)	14 (18)	104 (20)
	0.12 (3)	1.2 (6)	46 (26)	81 (26)	46 (27)

with  $x=0.485$ , the  $O(1)'-K'$  distance is  $2.98 \text{ \AA}$ , a value in good agreement with the  $K-W(1)$  distance of  $2.98 \text{ \AA}$ . The minimum  $K'-W(1)$  distance of  $2.92 \text{ \AA}$  does not seem unduly short.

The reversal of some of the sulfate groups does not appear to perturb any atoms in the structure other than the potassium. The thermal parameters of the sulfur atoms or the water oxygen atoms are not sufficiently extreme to suggest positional disorder. Nevertheless a small variation of the sulfur position does not seem unreasonable and therefore it is probably not meaningful to correct bond lengths for thermal motion.

As in the other alums the octahedron of water oxygen atoms about the aluminum is quite regular. The six  $W(1)$  atoms about the potassium are arranged in a trigonal antiprism, compressed along the threefold axis, and when this group is in contact with a reversed sul-

fate group the potassium atom is pushed off center and the antiprism is capped on one end with an  $O(1)'$  atom.

The various interatomic distances are given in Table 8. Corresponding distances are in good agreement with each other and with the other alums. There is considerable variation in the S-O distances but because of the disorder and resulting fractional atoms with large thermal parameters the standard deviations of these distances are relatively large. The hydrogen bonding is the same as in the other alum types. The hydrogen atoms of water(1), which is associated with the monovalent cation, link  $O(1)$  of one sulfate group with  $O(2)$  of another sulfate group. The hydrogen atoms of water(2), associated with the trivalent cation, form hydrogen bonds with water(1) and with an  $O(2)$  atom.

The anisotropic thermal parameters were transformed to obtain the thermal ellipsoid parameters given in Tables 9, 10 and 11. Except for the orientation of the major axis of  $O(1)$  in Rb alum the ellipsoids for the three compounds are in reasonable agreement. The apparent motions of  $O(1)$  and  $O(2)$  are, of course, less in K alum because of the different refinement model.

A number of  $\alpha$  alums have been reported to be ferroelectric at low temperature (Pepinsky, Jona & Shirane, 1956). Ray & Ray (1965) have studied  $KCr(SO_4)_2 \cdot 12H_2O$  by X-ray diffraction and report that at  $192.5^\circ K$  some powder lines appear that are extinct in space group  $Pa3$ . From single-crystal studies they deduce that the cubic cell undergoes a slight distortion and becomes rhombohedral with  $a \approx 12.2 \text{ \AA}$  and  $\alpha = 88^\circ$ . It is quite possible that at this temperature the sulfate groups order so that they all point the same way and the cubic  $[111]$  direction becomes the polar axis.

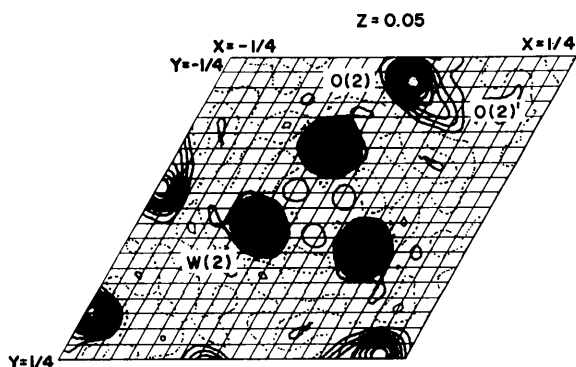


Fig. 5. K alum. Observed Fourier map normal to the threefold axis. The cell is defined as in Fig. 1. Contour interval is  $1 e. \text{ \AA}^{-3}$ .

Table 11. Thermal ellipsoids in  $NH_4Al(SO_4)_2 \cdot 12H_2O$

Standard deviations, in parentheses, apply to rightmost digit.

	r.m.s. Amplitude	$B_i$	Direction angles relative to crystal axes		
			$\alpha$	$\beta$	$\gamma$
N	0.24 (7) $\text{ \AA}$ 0.19 (4) 0.19 (4)	4.7 (26) $\text{ \AA}$ 2.9 (14) 2.9 (14)	54.7° — —	54.7° — —	54.7° — —
Al	0.16 (3) 0.13 (2) 0.13 (2)	1.9 (7) 1.4 (4) 1.4 (4)	54.7 — —	54.7 — —	54.7 — —
S	0.17 (2) 0.13 (1) 0.13 (1)	2.3 (5) 1.3 (2) 1.3 (2)	54.7 — —	54.7 — —	54.7 — —
O(1)	0.29 (5) 0.36 (2) 0.36 (2)	6.8 (21) 10.5 (15) 10.5 (15)	54.7 — —	54.7 — —	54.7 — —
O(2)	0.21 (2) 0.42 (2) 0.03 (12)	3.4 (8) 13.9 (14) 0.1 (6)	25 (6) 67 (4) 82 (9)	107 (5) 33 (3) 117 (4)	107 (9) 68 (3) 28 (6)
W(1)	0.20 (2) 0.13 (3) 0.15 (2)	3.3 (6) 1.3 (6) 1.9 (6)	12 (16) 99 (14) 97 (21)	84 (15) 26 (47) 115 (48)	80 (19) 66 (47) 26 (45)
W(2)	0.12 (3) 0.21 (2) 0.06 (5)	1.1 (5) 3.5 (6) 0.3 (5)	9 (17) 98 (12) 86 (27)	82 (12) 9 (12) 94 (9)	94 (27) 86 (8) 6 (19)

All calculations were performed on an IBM 7094 using codes written by Larson, Roof & Cromer (1963, 1964, 1965). The figures were drawn by an SC-4020 microfilm plotter. Fig. 4 was produced by a code recently developed by Larson (1966).

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## Refinement of the Alum Structures

### IV. Neutron Diffraction Study of Deuterated Ammonium Alum, $\text{ND}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{D}_2\text{O}$ , an $\alpha$ Alum\*

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The structure of deuterated ammonium alum,  $\text{ND}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{D}_2\text{O}$ , an  $\alpha$  alum, has been refined with the use of three-dimensional neutron diffraction data. The presence of sulfate group disorder, as found from the X-ray study of  $\alpha$  alums, is confirmed. There is no evidence for water molecule disorder. The ammonium ion attains average centric symmetry by randomly choosing either of two orientations.

#### Introduction

Deuterated ammonium alum,  $\text{ND}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{D}_2\text{O}$ , was selected as an  $\alpha$  alum to study by neutron diffraction for several reasons. The hydrogen atoms in the water molecules of an  $\alpha$  alum could thus be located accurately and the nature of the disorder of the ammonium ion, which must exist if the space group is  $Pa\bar{3}$ , could also be determined. The ammonium ion can attain the necessary average centric symmetry by freely rotating or by randomly assuming either of two orientations. It was also of interest to verify, by a different technique, the sulfate group disorder found in the X-ray study of the  $\alpha$  alums (Larson & Cromer, 1967) and to determine whether any water molecule disorder is coupled with the sulfate group disorder.

#### Experimental

$(\text{ND}_4)_2\text{SO}_4$  and anhydrous  $\text{Al}_2(\text{SO}_4)_3$ , in equimolar amounts, were dissolved in  $\text{D}_2\text{O}$ . Crystals suspended on fine wires were grown by evaporation of the solvent in a closed desiccator. An octahedron, about 6 mm on an edge and with small  $\{100\}$  and  $\{110\}$  forms developed, was selected, and was briefly immersed in liquid nitrogen in order to reduce the effects of extinction. Intensities of 759 independent reflections with  $2\theta \leq 90^\circ$  were measured by step scanning using a neutron wavelength of  $1.063 \text{ \AA}$ . There were 490 reflections observed according to the criterion  $(I - \text{Background}) \geq 2.5 (I + \text{Background})^\dagger$ . No corrections for absorption or extinction were made. Subsequent comparison of observed and calculated structure factors showed that extinction effects were not serious. The lattice constant was found to be  $12.243 \pm 0.001 \text{ \AA}$  from an X-ray powder photograph ( $\lambda \text{ Cr } K\alpha_1 = 2.28962 \text{ \AA}$ ). The lattice

\* Work performed under the auspices of the U.S. Atomic Energy Commission.