Refinement of the Alum Structures. III. X-ray Study of the α Alums, K, Rb and NH₄Al(SO₄)₂. 12H₂O*

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The structures of the α alums K, Rb and NH₄Al(SO₄)₂.12H₂O have been refined using single-crystal X-ray diffraction data. The α 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 α 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 $A^{I}B^{III}(RO_4)_2$. $12H_2O$ and crystallizing in space group *Pa3*. All alums were thought to be isomorphous until Lipson (1935) showed that there are three different types, which he named α , β and γ . In the first paper of this series (Cromer, Kay & Larson, 1966) the refinement by X-ray and neutron diffraction of the structure of CsAl(SO₄)₂. $12H_2O$, a β alum, was given and the relations among the three types were discussed. In the second paper (Cromer, Kay & Larson, 1967) a similar refinement of NaAl(SO₄)₂. $12H_2O$, the only known member of the γ alum class, was given.

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In the present paper we give the results of X-ray refinements of the α alums KAl(SO₄)₂.12H₂O, RbAl(SO₄)₂. 12H₂O and NH₄Al(SO₄)₂.12H₂O. In the final paper (Cromer & Kay, 1967) a detailed three-dimensional neutron diffraction analysis of ND₄Al(SO₄)₂.12D₂O will be described.

Experimental

Crystals of K, Rb and 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° if the crystal is mounted along the *a* axis.

Table	1.	Crystalle	ographic	data
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Crystal	а	Number of independent intensities measured	Number of independent intensities observed*
KAl(SO ₄) ₂ .12H ₂ O	12·157 ± 0·003 Å	540	252
$RbAl(SO_4)_2 \cdot 12H_2O$	$12 \cdot 243 \pm 0 \cdot 003$	547	205
$NH_4Al(SO_4)_2.12H_2O$	$12 \cdot 240 \pm 0 \cdot 003$	406	239

* $F_{obs} > 0$ if (Intensity - Background) ≥ 3 (Intensity + Background)¹.

Table 2.	Least-squ	ares paramete	rs for	KAI(SO ₄) ₂ .12H	[₂ O
Standard	deviations,	in parentheses,	apply	to the rightmost d	igit

Atom	x	,ر	Ζ	$\begin{array}{c} \beta_{11} \times 10^4 \\ \text{or } B \\ (\text{Å}^2) \end{array}$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
K	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	2.6 (9)					
K'	0.485 (4)	x	х	2.9 (24)					
Al	0	0	0	23 (4)	β_{11}	β_{11}	14 (10)	β_{12}	β_{12}
S	0.3075 (4)	x	x	29 (2)	β ₁₁	β_{11}	3 (6)	β_{12}	β_{12}
O(1)	0.2388(15)	x	x	96 (17)	B ₁₁	<i>B</i> ₁₁	-28(32)	B12	B12
O(1)'	0.3729 (39)	x	x	6.3 (27)		,		1.12	1-12
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)	U (1 0)	51 (12)	50 (=>)	. (20)	(=.)
$\hat{W}(1)$	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)

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single-crystal orienter on a General Electric Co. XRD-5 spectrogoniometer using Mo radiation (Mo $K\alpha_1 =$ 0.70926 Å). Intensities were measured by the fixedcrystal, fixed-counter method using Mo $K\alpha$ radiation, within the range $2\theta \le 50^\circ$ for K and Rb alums and $2\theta \le 45^\circ$ for NH₄ alum. Balanced Zr-Y filters were used for the Rb and NH₄ alums and only Zr for the K alum. No absorption corrections were necessary. Pertinent data on the lattice constants and reflections measured are given in Table 1. The lattice constants are in good agreement with those found by Haussühl (1961) and others. Least-squares refinements were by the fullmatrix method which minimized $\sum w(F_o - F_c)^2$, where w is the weight based on counting statistics (Evans, 1961). Form factors were taken from International Tables for X-ray Crystallography (1952) except that the form factor given by Cromer & Waber (1965) was used for Rb. The real part of the anomalous dispersion correction, -0.89 electron, was added to the **Rb** form factor (Cromer, 1965). Refinements generally prcceeded until $\Delta \xi_i / \sigma(\xi_i) < 10^{-3}$ for all parameters ξ . R indices quoted are $\Sigma |\Delta F| / \Sigma |F_o|$ with unobserved reflections omitted. Anisotropic temperature factors are in the form

 $\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\right].$

Refinement of the structures

Starting with the α alum parameters given by Lipson (1935), and omitting hydrogen atoms, several isotropic least-squares cycles reduced R to 12.3% for K alum. Temperature factors were normal except for high values for the sulfate oxygen atoms, $B \simeq 13$ Å² for O(1) and $B \simeq 7 \text{ Å}^2$ for O(2). High B values for these oxygen atoms were also noted by Bacon & Gardner (1958) in a neutron diffraction study of KCr(SO₄)₂.12H₂O. Anisotropic thermal parameters were then given to all atoms, and further refinement reduced R only to 10.4%. At this point the average B for O(1) was 14.5 Å^2 and for O(2), 9.2 Å². O(2) was very anisotropic, the three r.m.s. amplitudes being 0.540, 0.235 and 0.048 Å.

A difference Fourier synthesis was then calculated and two highly significant peaks were observed (Figs.1 and 2). These peaks were about 1.4 Å from the sulfur atom, one peak being on the threefold axis on the opposite side of the sulfur atom from O(1) and the other in a general position. These peaks made approximately tetrahedral angles with the sulfur atom. The only reasonable interpretation is that some of the sulfate groups are inverted along the threefold axis. If this interpretation is correct, the inverted O(1) is only about 2.7 Å from the potassium atom at $\frac{1}{2}$. The potassium had an r.m.s. amplitude of 0.25 Å (B= 4.9 Å^2) parallel to the threefold axis and an r.m.s. amplitude of 0.18 Å $(B=2.6 \text{ Å}^2)$ normal to this axis. It seems reasonable that the anisotropy of the potassium, rather than being due to thermal motion, is due to positional disorder caused by the proximity of the reversed O(1).

Table 3. Observed and calculated structure factors for KAl(SO₄)₂.12H₂O

Column headings are k, $10F_0$ and $10F_c$. A minus sign preceding F_0 means 'less than'.

	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$ \begin{array}{c} \mathbf{x}_{-1,0} = -140 & \mathbf{y}_{-1,0} = 151 & \mathbf{z}_{-1,0} = \mathbf{z}_{-1,0} = 151 & \mathbf{z}_{-1,0} = 10 \\ \mathbf{y}_{-1,0} = \mathbf{z}_{-1,0} $	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$ \begin{array}{c} \mathbf{k} -1 + 1 + 0 & 0 & 1 + 1 & 1 & 0 & 1 + 1 & 1 \\ 0 & -1 + 1 & 1 & 0 & 1 \\ 0 & -1 + 1 & 1 & 1 \\ 0 & -1 + 1 & 1 & 1 \\ 0 & -1 + 1 & 1 \\ 0 & -0 + 1 & 1 & 1 \\ 0 & -0 + 0 & 1 \\ 0 & -1 + 1 & 1 \\ 0 & -1 + 0 & 0 \\ 0 & -1 + 0 & 0 & 0 \\ 0 & -1 + 0 & 0 \\ 0 & -1 + 0 & 0 \\ 0 & -1 + 0 & 0 \\ 0 & -1 + 0 & 0 \\ 0 & -1 + 0 & 0 \\ 0 & -1 + 0 & 0 \\ 0 & -1 + 0 & 0 \\ 0 & -1 + 0 & 0 \\ 0 & -1 + 0 & 0 \\ 0 & -1 + 0 & 0 \\ 0 & -1 + 0 & 0 \\ 0 & -1 + 0 \\ 0 & -1 + 0 & 0 \\ 0 & -1 + 0 \\ 0 & -1 $	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
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4 -188 -149 9 -161 51 8 -14 10 -173 -155 9 17 • 0 L 2 11 -168 52 10 -16 12 -175 67 11 -16 • 152 1141 • 155 941 H• 1 L• 8 13 -17	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
	11 -16 -45 H+ 3 2 772 946 12 -176 -A0 4 955 -959 13 -174 -64 3 116 6 958 994 4 2 11 -175 -59 1 -16 -565 H* 1 1 7 59 1 361 -356 H* 1 1 7 59 0 292<-288

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 x x x 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, khad the value 0.37 ± 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 ± 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 e.Å⁻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 KCr(SO₄)₂.12H₂O.

Ordered anisotropic refinements of Rb and NH₄ 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 NH₄ 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-





Table 4.	Least-squares parameters for RbAl(SO ₄) ₂ .12H ₂ O
Standard	deviations, in parentheses, apply to the rightmost digit

Atom	x	у	z	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{22} \times 104$
Rb	ł	ł	1	50 (2)	R.,	R.,	31 (8)	<i>P</i> 13.10	0
Al	Ô	ó	ó	25(5)			$\frac{31}{11}$	p_{12}	ρ_{12}
S	0.3127(4)	x	r	$\frac{23}{28}$ (3)		μ_{11}	6(8)	ρ_{12}	p_{12}
O (1)	0.2471(17)	x	r	117(10)	<i>P</i> 11 <i>B</i> 11	β_{11}	-0(8)	p_{12}	ρ_{12}
O(2)	0.3172(11)	0.2639(14)	0.4237(10)	58 (12)	126 (20)	$\frac{p_{11}}{38(11)}$	64 (38)	p_{12}	p_{12}
W(1)	0.0451 (10)	0.1406 (9)	0.2975(10)	39 (12)	30(10)	16 (10)	(17)	-10(24)	12(27)
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 NH₄Al(SO₄)₂.12H₂O

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

Atom	x	у	Z	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{12} \times 104$	$\beta_{22} \times 104$
N	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	59 (14)	β_{11}	B_{11}	20 (39)	B12	B12
Al	0	0	Ō	26 (4)	β_{11}	β_{11}	6 (11)	β_{12}	β_{12}
S	0.3090 (4)	x	x	27 (2)	β_{11}	β_{11}	11 (7)	β_{12}	β_{12}
O(1)	0.2408(14)	<i>x</i>	x	155 (14)	β_{11}	β_{11}	-41 (35)	β_{12}	β_{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)	0.1346 (7)	20 (9)	57 (11)	5 (8)	-10 (17)	-3 (14)	8 (16)

Table 6. Observed and calculated structure factors for RbAl(SO₄)₂.12H₂O

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

H* 1 1* 1	H= 6 L= 3	н. 8 і. 3	H= 9 L= 7	H= 10 L= 9	H. 12 L. 3	visible in di
1 290 -333	1 -177 219 2 -177 145	1 -188 -53 2 -202 179	1 282 - 394 2 - 228 - 63	1 -247 -176 2 -255 -304	1 -235 -63 2 -235 -110	Water hydro
H- 2 L- 0	3 255 -266 4 -179 -55	3 -201 -135 4 -211 -252	3 -232 -98 4 335 277	3 -254 -90 4 -270 196	3 -245 -102 4 -239 183	Fourier ma
0 638 617 1 901 981	5 -146 -65 6 -212 250	5 -210 -72 6 365 374	5 -244 -30P 6 -252 -46	5 295 -290	5 -237 -81 5 -258 85	quality Th
2 2155 2305	H* 6 L* 4	7 - 21 H 90 H - 27 2 L	7 - 246 - 94 B - 259 35	H= 11 (F 1	7 -254 -7	quanty. In
H= 2 L= 1	0 954 850	4* 8 L* 4	9 - 263 - 123	1 -229 -214 2 -214 29	4= 12 L= 4	anisotropic
1 548 -530 2 926 -877	1 -176 25 2 1336 1281	0 1142 1043	H. 9 L. 8	3 -230 -285	1 -246 65	given in Ta
H# 2 L# 2	3 - 184 - 225	2 668 681	1 -234 -80	5 -242 -118	3 - 234 24	and calcula
2 983 978	6 995 1001	4 876 823 5 -213 18	3 - 235 38	a -244 76 a -257 -137	5 -240 -84	und culculu
H= 3 L+ 1	H+ A L+ 5	6 492 509	5 -246 -10	H= 11 L= 2	1 -205 67	T 11 7
1 208 - 206 2 728 662	1 -189 -117 2 -190 -136	8 516 529	7 - 256 - 63 8 - 257 12	0 -223 -209	H. 12 1: >	Table /.
3 1878-1785	3 -190 -83	H= 8 L= 5	н•10 L• 3	1 294 -296 2 310 -384	1 -242 18 2 -246 -24	
H= 3 L= 2	5 -203 -106 6 -210 61	1 315 367 2 -205 -60	0 993 964	3 -231 141 4 -232 -190	3 -251 -107	Column head
1 1259 1183	H= 6 [# 6	4 244 - 288	2 531 643	5 -235 -10	6 -255 -42	
3 745 -692	6 1286 1297	6 -222 11	4 646 646	8 -248 -80	-1• 12 L• 6	н- 1 1- 1 н-
H= 3 L+ 3	H. 7 L. 1	4 -231 -154	6 747 70F 7 -238 -58	44 11 14 3	3 365 364 1 -255 240	1 796 774 5
3 1873-1761	1 240 217 2 -174 -54	H* 8 L* 6	8 -247 133 9 418 493	1 -232 -220	2 513 524 3 -249 59	H• 2 L• 0 H+
H- 4 L- 0	3 -184 -103 4 -183 - 29	0 694 680 1 -208 63	10 352 281	2 -234 172 3 671 -643	4 331 433 5 -208 -57	0 504 -525 0
0 2499 2545 1 1011 -992	5 228 -247 5 479 -489	2 956 898 3 -216 -84	H= 10 L= 1	4 -230 -86 5 -244 113	H= 12 L= 7	1 830 901 1 2 1292 1396 2
2 1793 1780 3 -145 49	7 - 209 109	4 653 692 5 -229 -180	1 -208 -31 2 -220 227	5 -234 75 7 -255 -377	1 -268 -217	H= 2 L= 1 4
4 1055 1006	H= 7 [= 2	7 - 231 79	4 427 -415	9 -276 -267	3 - 253 - 22	1 491 -466 6
H L. I	1 - 175 -1	8 144 142	5 -231 -25	H+ 11 L+ 4	• -263 11B	H= 2 1 = 2
2 179 -152	3 -189 -100	1 - 31 6 - 16	9 -235 94	0 -232 164	- 12 (=	2 127 -113 2
4 N42 588	5 -192 -47	2 -223 -171	10 -251 -84	2 -237 168	1 -274 -292	H= 3 L= 1 4
H= 4 L= 2	7 - 208 0	4 340 374 5 -223 -15	H. 10 L. 2	4 -233 A4 5 294 -309	H# 13 L# 1	1 745 741 B
0 269 330 1 656 560	H= 7 L= 3	6 -239 -110 7 -249 -136	0 415 438 1 328 358	246 -3 7 -265 281	1 -291 94 2 -239 -21	2 761 692 3 940 -817 H*
2 1195 1197 3 428 403	1 813 -820 2 -192 154	9 - 244 - 76	2 6C1 561 3 -211 11	P - 254 87	3 -243 -97 4 -250 44	H• 3 L+ 2 0
4 414 408	3 246 -290	H. 8 L. F	5 266 - 25P		5 -253 -150	0 334 -346 2
1 -153 -170	6 -215 196 7 -217 50	a - 265 - 117	7 307 362	2 -226 72	H+ 13 L+ 2	2 359 306 4 3 698 -666 5
2 227 -180	H= 7 L= 4	1 304 - 395	9 -245 -8	4 -245 102 5 442 -476) -254 153	н. 3 L. 3
4 -161 63	0 -187 -67	2 386 412 3 685 -759	-+= 10 L= 3	5 -254 -5C 7 -258 -20	2 -249 -150 3 -257 -178	3 1057 -920
H. 4 (. 4	1 522 -475 2 559 545	4 436 -449 5 -220 -224	1 -218 -116	* -251 110	4 -246 5 5 -252 -63	H+ 4 L+ 0 2
4 577 618	3 -201 153	6 -226 207	2 283 -297 3 -221 -5	H= 11 (+ 6	5 - 255 - 52	0 1413 1539 4
1 583 -595	6 361 -374	9 -248 -226	5 -235 -163	1 298 -240	1 - 156 - 231	2 858 838 6 3 105 69
2 -154 126	н. 7 с. 5	H• 9 1• 2	7 -235 -70	3 -238 -61	2 -247 35	4 231 125 Hz
4 -164 22 5 504 -462	1 - 201 52	0 410 -354 1 -202 156	9 - 256 43 10 - 256 11	5 -255 185 6 -251 96	4 -255 -255 5 -271 -294	H= 4 L= 1 0
H. 5 L. 2	2 - 194 35 3 546 - 521	2 517 452 3 -210 -138	H= 10 L= 4	7 -255 -184	40 13 LA 4	2 227 -160 3
0 -153 58	4 357 297 5 -207 -26	4 -218 -220 5 -218 126	0 233 168	H- 11 L- 7	0 -259 193	4 625 571 5
2 -162 -97	7 -218 -48	7 -232 165	2 381 362	2 -247 -16	2 -248 64	H= 4 L= 7
4 428 -493 5 247 313	H# 7 l+ 6	9 - 24 5 - 94	6 -236 230	4 -259 -107 5 -258 -41	4 -265 109 5 -257 121	0 612 -550 1 649 546 1
H# 5 L# 3	0 861 881 1 -202 -61	н. 7 с. 3	6 491 464 7 -244 -19	6 - 250 - 86	44 23 24 5	2 329 316 2 3 356 327 3
1 -160 -4	2 - 209 - 153 3 - 204 69	1 466 -556 2 328 -32A	8 337 376 9 -261 170	N= 11 L= B	1 -254 64	4 293 -241 4
2 -162 -128 3 1366-1356	4 -212 59 5 -218 174	3 272 -323 4 -218 -12	10 L- 5	C -246 -67 1 -253 123	2 -254 -82 3 304 -341	H- 4 (- 3 6
5 -189 -129	7 - 237 117	5 586 -613	1 -225 104	3 -258 -18	· -257 -23	2 268 -212
H= 5 l= 4	H# 7 L# 7	R -243 -372 9 -251 -318	3 -228 -86	5 -255 18	J -265 202	4 -93 14 H.
0 -166 -70 1 232 246	7 -247 -146	H# 9 L4 4	5 -241 95 6 -242 -88	·· 11 L· 9	1 - 263 67 2 - 261 - 54	H+ 4 L> 4
2 239 -262 3 -181 -211	H* 8 L* C	0 371 256	7 -240 -20 8 -253 41	1 -253 -147 2 -259 105	4= 14 (= 0	4 197 -143 2
4 308 354 5 293 -282	0 484 422	1 -206 -62 2 -207 25	9 - 263 21	3 297 -286	0 278 343	H= 5 [-] 4
H# 5 L# 5	2 1427 1381 3 -198 -169 4 918 910	3 -205 19 4 -220 6A 5 -215 -1	0 A11 747	0 554 ATE	1 -253 -77 2 532 578 3 -269 76	2 203 180 7 3 121 105
5 677 -640	5 -206 -93	6 496 521 7 -240 -318	1 -225 99	1 639 635		4 145 135 H= 5 205 223
H= 6 L= 0	7 -216 -177 8 1083 1081	A -251 -194 9 -249 50	3 -231 160	3 -245 -108	1 -253 -102	H= 5 L= 2 1
0 2337 2345 1 1068 1058	×+ 4 L+ 1		5 -251 179 6 553 559	5 -241 30 6 486 570	2 -252 -67 3 -271 -333	0 111 72 3
2 1383 1321 3 -170 -136	1 -176 -256	1 -217 -207	7 -245 55 8 -265 159	7 427 519 8 407 418	H= 14 (- 2	1 583 -578 4 2 263 -210 5
4 1351 1564 5 500 545	2 -197 -171 3 -197 -246	2 401 382 3 671 -749	H= 10 L= 7	12 L+ 1	5 540 529	3 700 641 6 4 486 -541 7 5 250 272
He 6 1e 1	5 -198 -1 6 324 -273	5 -234 -182	1 -232 -130	1 -236 -183	2 -264 285	H# 5 L# 3
1 478 -484	7 276 -726	7 - 229 - 126	3 328 -459	3 -244 151	He IA	1 740 718 2
2 -164 29 3 632 716	H= 8 L= 2	9 -257 -376	5 -247 9R 6 -253 82	5 379 -396 5 -267 86	1 - 267 - 93	2 -93 -45 3 3 639 -616 4
4 399 -339 5 409 -494	0 1547 1570	4* 9 t* 6	7 -250 -173	7 -253 8 8 -266 108	2 - 257 - 4	4 472 441 5 5 530 579 <u>6</u>
6 266 264	1 210 227 2 564 494	C 270 -256 1 -218 -15	H= 10 L= P	H= 12 L= 2		H= 5 (4
H= 6 L= 2	3 - 204 150	2 482 387 3 -236 -240	0 348 414	0 577 591		0 164 -118 1 320 325 0
1 25# 279 2 930 874	5 -213 -323 6 1386 1347 7 -219 32	223 -72 5 -232 -80 5 -237 -37	2 384 622 3 -250 -98 6 -257 259	2 644 691		2 300 -305 1 3 264 -271 2
3 -170 -3	8 -232 156	7 -236 -22	5 -247 -92	4 332 425 5 -241 121		4 311 347 3 5 191 -1#2 4
5 -189 -118 6 846 892		9 - 270 - 350		6 475 510 7 -250 -20		5

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 NH₄ 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 NH₄Al(SO₄)₂.12H₂O

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

				No. 16 . 10 . 0	
	H. , (, ,				
1 796 774	5 205 -195	7 345 -35P	5 -140 -146	0 638 551	3 -136 102
			6 -144 00	1 422 -479	4 -136 -134
			8 422 469	3 435 410	5 -137 -35
0 504 -525	3 1357 1436	1 657 573		4 318 319	
1 830 901	1 1011 1027	2 - 116 44	H= 8 (* 7	5 -131 146	··· 11 (* 3
2 1242 1346	3 190 -178	5 142 -176	1 -133 96	7 -137 -90	1 -134 136
H= 2 L= 1	4 892 914	5 558 567	2 -136 -15#	# 165 -256	2 215 214
	5 48h 495	5 426 -4PR	3 -128 -12		3 236 -248
1 491 -466	6 1021 101A	7 164 212	4 287 307	4* 10 L* 1	4 169 -107
	H+ 6 L= 1	H= 7 L= 6	6 -140 -176	1 -125 -8	5 -147 198
H= 2 L= 2			7 -140 -27	2 313 286	
	1 437 -479	0 780 846		3 421 -481	H+ 11 L+ 4
2 127 -115	3 626 638	2 239 -229	M• • • • •	5 240 261	3 -132 1
H+ 3 L+ 1	4 354 -290	3 -118 70	1 149 83	6 -144 137	1 328 308
	5 458 -467	4 -127 39	2 455 420	7 151 -176	2 180 161
2 761 692	5 321 275	5 173 187 5 178 517	5 137 -204	6 -138 -14	5 -140 -135
3 940 -817	HN 6 L4 2	7 210 232	5 177 144	H= 10 L= 2	5 226 -240
			5 197 258		n -130 -60
H4 3 L4 2	1 315 322	H. / L. /	A -129 10	1 282 280	HE 11 15 5
0 334 -346	2 251 213	7 335 238	9 -142 62	2 261 271	
1 1120 1103	3 - 100 9			3 -124 -13	1 -137 93
2 359 306	4 513 487	A 4 1 4 0	N. 9 L. 2	4 -130 -143	2 - [3 3 3 8
3 070 -000	A 336 347	0 151 -144	0 489 -434	A -134 -99	4 182 214
H* 3 L* 3		1 435 -430	1 -120 46	7 172 180	5 -150 -145
	HI A 1= 3	2 813 756	2 517 447	b 452 455	
3 1057 - 420	1 206 210	4 288 328	5 -125 -67	HS 10 1 4 1	41.11 (4.9
H. 4 L. 0	2 128 141	5 187 -177	5 -128 96		0 210 250
	3 273 -724	6 -124 56	6 184 -/37	1 -127 -57	1 192 -143
U 1413 1539 1 922 -935	4 -105 -48 5 -114 -4A	7 254 -289	7 - 138 127 8 150 186	2 311 - 354	2 -138 -59
2 858 838	6 148 184		9 -136 -39	4 266 291	4 -139 37
3 105 69		11= A L= 1		5 -134 -88	
4 231 125	H= 6 L= 4	1 116 110	HF 9 L4 3	6 236 -287	4+11 L* 7
H= 4 L= 1	0 175 188	2 190 -142	1 -119 -90	P -135 -29	1 -155 122
	1 -106 -64	3 277 - 311	2 283 - 101		
1 662 -529	2 519 594	4 178 729	3 -128 120	44 10 L+ 4	H= 12 (H)
2 227 -160	5 -113 132	5 145 151 A 386 -331	5 -129 -126	0 -131 -115	0 -160 131
4 625 571	5 367 -331	7 250 -275	5 445 -462	1 -129 -96	1 619 548
	6 508 4P7	H 153 107	7 -131 -65	2 -127 -105	2 260 275
H= 4 (- 2	MA 6 14 6		8 -146 -727	4 -129 21	3 207 -152
0 612 -550			• -157 -57	5 -136 -77	5 -141 39
1 649 546	1 -109 -34	0 931 1000	-1. V [. 4	6 211 177	
2 329 316	2 132 -130	1 276 287		7 -134 -80	HF 12 LF 1
4 293 -241	5 100 189	3 -118 28	0 335 330	0.10.11.5	1 -162 -193
	5 -120 -67	4 -118 ×5	2 -131 -63		2 -137 150
H= 4 L= 3	6 -120 37	5 363 -395	3 -123 34	1 152 189	3 199 198
1 155 -156	HD 5 11 6	7 -127 27	5 -127 -11	2 - 130 - 34	4 -143 61 5 480 -431
2 268 -212		8 -141 -196	5 476 453	4 -142 154	/ ///
3 444 -400	n 756 796		7 187 -217	5 -141 165	4≤ 12 l= 2
4 -93 14	H. 7 1. 1	·· 8 1.4 1	8 245 -263	· -138 -77	
H+ 4 L> 4		1 -110 -21	44. 4. 1.4. 5	11 10 LF N	1 -134 -91
	1 962 854	2 146 200			2 268 329
4 197 -143	2 - 104 - 12	3 - 114 - 7	1 184 203	0 302 324	3 -145 91
H• 5 L• 1	4 125 110	5 -127 -147	3 157 -225	2 -135 106	5 -13* /1
	5 343 320	6 402 407	4 669 -648	3 -131 57	
2 203 180	A 427 -424	7 168 177	5 -135 114	4 151 159	HE 12 LE 3
3 121 105			7 251 223	6 278 255	1 -135 -17
4 145 135	HF 7 LF 2	H+ 8 (+ 4	8 -137 2		2 -135 -77
5 205 223	· · · · · · · · ·			H 10 L 7	3 -141 -140
H= 5 L= 2	1 144 67	1 -114 -103		1 -132 -15	• -134 11/
	2 788 -811	2 208 199	0 336 - 350	2 -137 84	H= 12 (= 4
0 111 72	3 194 -141	3 - 119 72	1 -127 -10	3 224 - 321	
2 263 -210	5 = 117 21	5 - 122 - 41	2 4/3 404	4 176 -151	0 363 394
3 706 641	6 136 190	6 -133 107	4 -136 -132	H4 10 L4 8	2 212 278
4 486 -541	7 -127 58	7 153 -176	5 -128 -47		3 - 134 - 36
\$ 250 272	HR 7 1- 3	4 226 157	6 -135 -100	0 -136 106	
H# 5 L# 3			-110 11	2 336 310	
1 1/0	1 121 -165		HF 9 1+ 7	3 -142 -71	1 -138 29
1 /40 718	2 166 165	1 199 453	1 -130 -16	HN 21 18 1	2 -139 -3
3 639 -616	4 541 -554	3 -122 70	2 -136 -109		13 L= 1
4 472 441	5 133 -146	• 231 -267	3 167 202	1 -138 134	
5 530 579	6 277 263	5 312 389	4 378 40H	2 -132 66	1 337 358
H= 5 [. 4		7 -132 83	5 -147 -87	4 -130 28	H+ 13 L# 2
	344 7 L. 4	8 -139 -121		-135 -1	
0 164 -118	0 -115 -110		H+ 9 L+ A	-146 -37	0 - 136 31
2 300 -305	1 535 -498		0 203 116	/ 164 116	
3 264 -271	2 476 477	0 264 21#	1 -135 -66	H• 11 (• 2	
4 311 347	3 244 242	1 -121 79	2 -139 -121	0 -128 -15"	
5 191 -182	5 -122 113	3 -127 -91	4 - 130 - 17	1 240 -228	
	6 312 -319	4 267 306	5 -140 - 5	391 -420	



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

Discussion

The most interesting feature in the α alums is the presence of the disordered sulfate group. This disorder is found in all α alums that have been studied in sufficient detail. The final difference Fourier map published by Bacon & Gardner (1958), in their neutron diffraction study of KCr(SO₄)₂.12H₂O, 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 α alums, with the medium size monovalent cations, tend to be like the γ 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 K' atoms have been omitted. Otherwise, all atoms within the range xyz from -¼ to ¼ are shown. The box encloses the region 000 to ¼¼¼. 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 ND₄Al(SO₄).12D₂O (Cromer & Kay, 1967).

Table 8.	Interatomic	distances and	l angles in	α alums,	$MAl(SO_4)_2$.	12H ₂ O
S	tandard devia	tions, in parent	heses, apply	y to the rig	ghtmost digit.	

M =	к	M = Rb	$M = NH_4$		M = K	M = Rb	$M = NH_4$
Al-6 $W(2)$	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) - AI - W(2) < W(1) - M - W(1)	$105 \cdot 1 (2)$	114.1(2)	113.8(2)
M'-O(1)' M'-3W(1) M'-3W(1)	2·98 (12) 2·92 (2) 3·08 (3)			< <i>W</i> (1)-M- <i>W</i> (1)	74.9 (2)	63.9 (2)	00.2 (2)
Sulfate group							
S-O(1) S-3O(2) S-O(1)' S-3O(2)'	1·447 (29) 1·495 (14) 1·377 (79) 1·510 (40)	1·392 (36) 1·485 (12)	1·447 (29) 1·453 (10)	< O(1) -S-O(2) < O(2) -S-O(2) < O(1)'-S-O(2)' < O(2)'-S-O(2)'	110.8 (8) 118.1 (9) 104.8 (16) 113.7 (13)	108·5 (8) 110·4 (7)	108·4 (7) 110·5 (7)
Hydrogen bor	nds						
O(1) - 3W(1) O(2) - W(1) O(2)' - W(1)	2·759 (20) 2·726 (16) 2·821 (36)	2·864 (27) 2·730 (15)	2·787 (20) 2·759 (14)				
O(2) - W(2) O(2)' - W(2)	2.563 (16) 2.721 (36)	2.553 (18)	2.565 (16)				
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 threefold axis and passing through the sulfur atom, followed by a rotation of 17.7° . The two positions for the oxygen atom O(2) are only 0.98 Å apart and their peaks are not completely resolved in a Fourier synthesis. Fig. 5 shows a section of the observed three-dimensional

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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 Å if the potassium were not disordered. However, if there are indeed k/2 potassium atoms, K', in an xxx position

Direction angles relative to crystal axes rms. B_i amplitude α β γ 54·7° 54·7° 0·17 (2) Å 2·2 (6) Å² 54·7° Al 1.0(3)0.11(2)_ ____ 0.11(2)1.0(3)-____ ____ 0.15 (2) S 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 6.5 (14) 0.29 (3) ____ 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) 58 (17) 56 (20) 0.11(4)1.0 (7) 78 (13) 35 (14) 122 (12) W(1)0.19 (2) 2.9(5)11 (15) 88 (26) 79 (16) 0.16(2) $2 \cdot 1$ (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) 84 (24) 0.17(2)2.4(5)6 (23) 90 (16) 0.11(2)1.0 (4) 111 (52) 88 (16) 21 (52)

Table 9. Thermal ellipsoids in KAl(SO ₄) ₂ .12H ₂ O	
andard deviations, in parentheses, apply to the rightmost digit.	

Table 10. *Thermal ellipsoids in* $RbAl(SO_4)_2$. $12H_2O$ Standard deviations, in parentheses, apply to the rightmost digit.

	r.m.s.	_	Direction angles relative to crystal axes		
	Amplitude	B_i	α	β	γ
Rb	0·25 (1) Å	4·9 (5) Å	54·7°	54·7°	54·7°
	0.16(1)	$2 \cdot 1 (2)$	_	_	_
	0.16 (1)	$2 \cdot 1$ (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 Å, a value in good agreement with the K-W(1) distance of 2.98 Å. The minimum K'-W(1) distance of 2.92 Å 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-



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

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 α alums have been reported to be ferroelectric at low temperature (Pepinsky, Jona & Shirane, 1956). Ray & Ray (1965) have studied KCr(SO₄)₂. 12H₂O by X-ray diffraction and report that at 192.5°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 $\alpha \simeq 12.2$ Å 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.

Table 11. Thermal ellipsoids in $NH_4Al(SO_4)_2$. $12H_2O$ Standard deviations, in parentheses, apply to rightmost digit.

	r.m.s.	_	Direction angles relative to crystal axes		
	Amplitude	B_i	α	β	γ
N	0·24 (7) Å	4·7 (26) Å	54·7°	54·7°	54·7 °
	0.19 (4)	2.9 (14)			<u> </u>
	0.19 (4)	2.9 (14)	—		_
Al	0.16 (3)	1.9 (7)	54.7	54.7	54.7
	0.13(2)	1.4 (4)	_	_	_
	0.13 (2)	1.4 (4)	—	_	
S	0.17 (2)	2.3 (5)	54.7	54.7	54.7
	0·13 (1)	1.3 (2)	_	_	
	0.13 (1)	1.3 (2)	—		
O (1)	0.29 (5)	6.8 (21)	54.7	54.7	54.7
. ,	0.36 (2)	10.5 (15)			_
	0.36 (2)	10.5 (15)			—
O(2)	0.21 (2)	3.4 (8)	25 (6)	107 (5)	107 (9)
	0.42 (2)	13.9 (14)	67 (4)	33 (3)	68 (3)
	0.03 (12)	0.1 (6)	82 (9)	117 (4)	28 (6)
W(1)	0.20 (2)	3.3 (6)	12 (16)	84 (15)	80 (19)
	0.13(3)	1.3 (6)	99 (14)	26 (47)	66 (47)
	0.15 (2)	1.9 (6)	97 (21)	115 (48)	26 (45)
W(2)	0.12 (3)	1.1 (5)	9 (17)	82 (12)	94 (27)
	0.21(2)	3.5 (6)	98 (12)	9 (12)	86 (8)
	0.06 (5)	0.3 (5)	86 (27)	94 (9)	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, ND₄Al(SO₄)₂.12D₂O, an α Alum*

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The structure of deuterated ammonium alum, $ND_4Al(SO_4)_2.12D_2O$, an α 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 α 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, ND₄Al(SO₄)₂.12D₂O, was selected as an α alum to study by neutron diffraction for several reasons. The hydrogen atoms in the water molecules of an α alum could thus be located accurately and the nature of the disorder of the ammonium ion, which must exist if the space group is *Pa3*, 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 α alums (Larson & Cromer, 1967) and to determine whether any water molecule disorder is coupled with the sulfate group disorder.

Experimental

 $(ND_4)_2SO_4$ and anhydrous $Al_2(SO_4)_3$, in equimolar amounts, were dissolved in D₂O. 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 $2\theta \le 90^{\circ}$ were measured by step scanning using a neutron wavelength of 1.063 Å. There were 490 reflections observed according to the criterion $(I - \text{Background}) \ge 2.5 (I +$ Background)[±]. 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 ± 0.001 Å from an X-ray powder photograph (λ Cr $K\alpha_1 = 2.28962$ Å). The lattice

^{*} Work performed under the auspices of the U.S. Atomic Energy Commission.