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Refinement of the Alum Structures. II. X-Ray and Neutron Diffraction of $NaAl(SO_4)_2.12H_2O$, γ Alum*

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The structure of $NaAl(SO_4)_2.12H_2O$, γ alum, has been refined by use of three-dimensional X-ray and partial three-dimensional neutron diffraction data. The maximum shift in atom positions from those given by Lipson (1935) is about 0·05 Å. The sulfate oxygen atoms have large anisotropic thermal motion which is observed in both the X-ray and the neutron diffraction analyses. An explanation of this motion is given in terms of coupled translational and rotational vibrations.

Introduction

The alums are a large class of double salts having the general formula $A^{I}B^{III}(RO_4)_2.12H_2O$ all crystallizing in space group *Pa*3. The alums were first thought to be isomorphous but Lipson (1935) showed that there are three different types, α, β and γ. In the first paper of this series (Cromer, Kay & Larson, 1966, hereafter CKL) the refinement of the structure of $CsAl(SO_4)_2.12H_2O$, a β alum, was given and the relations among the three types were discussed. In the present paper we give the results of an X-ray and neutron diffraction study of $NaAl(SO_4)_2.12H_2O$, the only known member of the γ alum type.

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Experimental

Crystals for both X-ray and neutron diffraction studies were grown from water solution in the manner described by CKL. Frequent stirring of the solution was necessary because Na alum tends to supersaturate. For X-ray work crystals were ground into spheres and a sphere of about 0·15 mm in diameter was selected. The crystal was coated with Krylon plastic spray to inhibit the slow loss of water in the dry atmosphere of New Mexico. The lattice constant was measured with a carefully aligned single-crystal orienter on a General Electric Co. XRD-5 X-ray diffraction unit and found to be $12·213 \pm 0·003$ Å (Mo $K\alpha_1 = 0·70926$ Å) in good agreement with the value 12·215 Å reported by Haussühl (1961). Mo $K\alpha$ radiation and Zr–Y balanced filters were used in measuring the intensities within the range

Table 1. *Least-squares parameters for* $NaAl(SO_4)_2.12H_2O$ *from X-ray diffraction data*

Standard deviations (in parentheses) apply to the rightmost digit

				$\beta_{11}\times10^5$					
	x	y	z	or B	$\beta_{22}\times10^5$	$\beta_{33}\times10^5$	$\beta_{12}\times10^5$	$\beta_{13}\times10^5$	$\beta_{23}\times10^5$
Na	½	½	½	412 (10)	β_{11}	β_{11}	−30 (20)	β_{12}	β_{12}
Al	0	0	0	284 (7)	β_{11}	β_{11}	50 (14)	β_{12}	β_{12}
S	0·2652 (1)	x	x	397 (5)	β_{11}	β_{11}	44 (9)	β_{12}	β_{12}
$O_s(1)$	0·3343 (2)	x	x	687 (16)	β_{11}	β_{11}	−291 (31)	β_{12}	β_{12}
$O_s(2)$	0·2957 (2)	0·2783 (2)	0·1508 (2)	1417 (32)	724 (22)	535 (19)	−987 (41)	733 (38)	−168 (32)
$O_w(1)$	0·0767 (2)	0·0403 (2)	0·3188 (2)	619 (21)	591 (21)	419 (18)	−367 (39)	48 (33)	110 (32)
$O_w(2)$	0·1371 (2)	0·9596 (2)	0·0573 (2)	338 (16)	438 (17)	498 (17)	77 (28)	−97 (27)	173 (27)
H(1)	0·585 (3)	0·319 (3)	0·378 (3)	3·4 (12)					
H(2)	0·486 (3)	0·308 (3)	0·383 (4)	4·0 (14)					
H(3)	0·555 (3)	0·202 (3)	0·502 (3)	3·2 (10)					
H(4)	0·588 (3)	0·339 (3)	0·113 (3)	2·4 (9)					

$g = 1·65 \pm 0·01 \times 10^{-6}$

$2\theta \leq 50°$. The fixed-crystal, fixed-counter method was used, and of 544 reflections measured 388 were observed according to the criterion $[I - \text{Background}] \geq 3{\cdot}0[I + \text{Background}]^{\frac{1}{2}}$. No absorption correction was necessary.

Table 2. *Observed and calculated X-ray structure factors for* $NaAl(SO_4)_2.12H_2O$

The column headings are k, $10|F_o|/K$ and $10|F_c^*|/K$ (see text). A minus sign preceding F_o means 'less than'.

H= 1 L= 1			H= 6 L= 3			H= 8 L= 3			H= 9 L= 7			H= 10 L= 9			H= 12 L= 3		
1	454	458	1	618	608	1	73	68	1	-62	-27	1	113	-104	1	92	88
			2	285	-282	2	83	-75	2	-63	41	2	-68	-7	2	157	-166
H= 2 L= 0			3	123	-129	3	115	-119	3	-65	-56	3	128	124	3	84	98
			4	71	-69	4	458	465	4	-61	-53	4	-70	40	4	120	135
0	366	-357	5	238	240	5	203	-208	5	174	178	5	-74	-73	5	-67	-52
1	344	345	6	209	206	6	-58	32	6	-64	11				6	-71	-68
2	1661	1673				7	180	194	7	-68	-37	H= 11 L= 1			7	-68	18
			H= 6 L= 4			8	143	146	8	106	-102						
H= 2 L= 1												1	288	-305	H= 12 L= 4		
			0	131	134	H= 8 L= 4			H= 9 L= 8			2	141	150			
1	248	-250	1	220	229							3	68	-56	0	424	416
2	203	-207	2	986	973	0	728	725	0	-66	-47	4	97	-108	1	155	-150
			3	380	-373	1	476	-478	1	202	216	5	167	167	2	156	156
H= 2 L= 2			4	155	162	2	96	57	2	131	122	6	-65	-23	3	228	220
			5	-51	-16	3	140	134	3	237	-243	7	92	93	4	357	348
2	1149	-1172	6	588	573	4	802	804	4	132	-156	8	-68	-11	5	224	-224
						5	239	-220	5	107	114	9	161	151	6	-68	25
H= 3 L= 1			H= 6 L= 5			6	-61	63	6	-69	58				7	157	146
						7	71	68	7	-67	-14	H= 11 L= 2					
1	339	341	1	304	309	8	360	350	8	127	-135				H= 12 L= 5		
2	135	132	2	416	-422							0	220	-230			
3	69	-69	3	206	-214	H= 8 L= 5			H= 10 L= 0			1	143	133	1	-71	71
			4	-55	65							2	119	126	2	140	-133
H= 3 L= 2			5	-56	-40	1	98	-93	0	408	-397	3	-62	35	3	-70	65
			6	82	-82	2	91	86	1	371	372	4	-63	-35	4	80	-111
0	587	576				3	448	-448	2	592	600	5	97	105	5	-71	67
1	503	-510	H= 6 L= 6			4	-58	14	3	134	-132	6	-69	-67	6	-69	-28
2	549	556				5	183	180	4	141	144	7	-68	19			
3	193	-193	6	-63	54	6	258	255	5	304	295	8	68	6	H= 12 L= 6		
						7	-62	-27	6	276	270	9	-72	-45			
H= 3 L= 3			H= 7 L= 1			8	231	-218	7	-65	-37				0	248	237
									8	258	251	H= 11 L= 3			1	210	201
3	256	-257	1	209	199	H= 8 L= 6			9	367	376				2	274	279
			2	263	-265				10	361	355	1	92	82	3	128	-126
H= 4 L= 0			3	474	487	0	149	-135				2	-62	-52	4	-73	76
			4	160	-166	1	449	459	H= 10 L= 1			3	-64	37	5	234	225
0	1106	1114	5	138	124	2	471	475				4	102	131			
1	1745	-1636	6	190	186	3	190	-177	1	153	146	5	128	126	H= 12 L= 7		
2	501	-521	7	144	-123	4	-62	-36	2	202	-203	6	-68	-78			
3	261	-246				5	109	101	3	-61	7	7	115	117	1	-69	43
4	761	787	H= 7 L= 2			6	533	504	4	264	272	8	-72	71	2	84	-91
						7	-63	31	5	86	-95				3	173	162
H= 4 L= 1			0	-63	-53	8	81	106	6	114	-110	H= 11 L= 4			4	79	-78
			1	-55	-33				7	199	214						
1	-45	34	2	250	255	H= 8 L= 7			8	-69	53	0	143	165	H= 12 L= 8		
2	388	-389	3	-50	-10				9	262	-275	1	128	126			
3	396	-407	4	143	-137	1	-60	-44	10	,87	-102	2	-67	-66	0	213	205
4	96	-85	5	79	81	2	110	-95				3	-66	-14	1	130	-137
			6	82	62	3	196	197	H= 10 L= 2			4	136	135			
H= 4 L= 2			7	-58	8	4	350	355				5	135	-133	H= 13 L= 1		
						5	179	-164	0	478	469	6	-67	-36			
0	68	-68	H= 7 L= 3			6	97	96	1	411	-405	7	-68	-21	1	-71	70
1	183	-178				7	94	88	2	-61	23	8	-68	-47	2	-69	-70
2	796	843	1	64	57	8	-69	65	3	194	177				3	-68	-20
3	576	-580	2	124	-126				4	557	555	H= 11 L= 5			4	127	-118
4	91	82	3	92	-91	H= 8 L= 8			5	257	-271				5	-71	54
			4	415	-401				6	-63	-5	1	-65	-2	6	142	-150
H= 4 L= 3			5	100	113	8	292	273	7	140	134	2	-66	55			
			6	149	-144				8	246	252	3	162	155	H= 13 L= 2		
1	633	623	7	79	75	H= 9 L= 1			9	-72	-47	4	108	-141			
2	138	137							10	180	173	5	-69	66	0	-65	28
3	551	-541	H= 7 L= 4			1	122	124				6	-67	-32	1	-66	-5
4	520	-499				2	314	316	H= 10 L= 3			7	-72	-64	2	-69	-6
			0	115	-116	3	-56	11				8	-71	-42	3	87	105
H= 4 L= 4			1	208	-191	4	204	214	1	160	-163				4	-73	61
			2	93	-96	5	130	134	2	65	-42	H= 11 L= 6			5	-72	67
4	773	779	3	271	279	6	115	114	3	170	-159				6	-70	45
			4	217	218	7	-63	-52	4	113	-108	0	213	-194			
H= 5 L= 1			5	318	313	8	74	87	5	193	192	1	138	134	H= 13 L= 3		
			6	117	-117	9	-68	-46	6	132	131	2	-68	51			
1	274	-271	7	360	364				7	129	-152	3	146	-158	1	265	206
2	267	295				H= 9 L= 2			8	189	-186	4	-65	-34	2	-70	55
3	182	191	H= 7 L= 5						9	142	155	5	-67	6	3	130	123
4	171	-165				0	-56	54	10	102	96	6	-68	47	4	100	-116
5	252	248	1	104	91	1	-61	-15				7	118	-115	5	-71	52
			2	322	-320	2	168	-172	H= 10 L= 4								
H= 5 L= 2			3	219	236	3	-57	-21				H= 11 L= 7			H= 13 L= 4		
			4	-56	27	4	-58	19	0	117	114						
0	602	597	5	204	192	5	-60	-16	1	337	327	1	-67	52	0	-70	-43
1	193	-195	6	-57	21	6	241	-237	2	640	645	2	-66	-42	1	124	124
2	842	826	7	237	-235	7	173	184	3	350	-340	3	142	147	2	-70	61
3	367	-286				8	-67	35	4	-64	55	4	80	86	3	148	-153
4	124	120	H= 7 L= 6			9	98	-103	5	-63	14	5	-68	-32	4	83	86
5	99	94							6	372	348	6	-70	-21	5	-71	-64
			0	464	-453	H= 9 L= 3			7	152	-141						
H= 5 L= 3			1	340	348				8	-64	6	H= 11 L= 8			H= 13 L= 5		
			2	-57	-40	1	-56	-4	9	158	177						
1	604	-609	3	317	-329	2	152	161				0	-69	18	1	-68	46
2	818	-827	4	198	-190	3	327	336	H= 10 L= 5			1	142	-176	2	-68	-24
3	66	-65	5	206	196	4	-60	28				2	-73	-73	3	-72	58
4	50	27	6	265	269	5	-60	41	1	371	-368	3	148	163	4	-69	24
5	69	71	7	-60	-5	6	189	205	2	337	-359	4	108	128			
						7	212	-210	3	-61	0	5	-71	47	H= 13 L= 6		
H= 5 L= 4			H= 7 L= 7			8	-65	-49	4	-60	27						
						9	139	137	5	-76	-36	H= 11 L= 9			0	-71	-51
0	220	212	7	309	332				6	192	-202				1	121	-126
1	207	221				H= 9 L= 4			7	175	174	1	191	187	2	-71	34
2	235	244	H= 8 L= 0						8	-67	15	2	-73	14			
3	317	312				0	326	-335	9	-69	23				H= 14 L= 0		
4	277	-283	0	166	180	1	128	106				H= 12 L= 0					
5	86	90	1	670	-653	2	263	259	H= 10 L= 6						0	121	141
			2	76	68	3	251	-246				0	274	257	1	284	271
H= 5 L= 5			3	838	827	4	165	-177	0	535	521	1	153	-156	2	239	223
			4	950	976	5	125	129	1	196	-199	2	88	99	3	244	-238
5	183	188	5	176	189	6	-60	-9	2	-64	47	3	306	310			
			6	115	112	7	-62	26	3	245	235	4	333	326	H= 14 L= 1		
H= 6 L= 0			7	325	306	8	-64	2	4	443	448	5	189	-205			
			8	487	495	9	-65	15	5	143	-128	6	103	119	1	-71	-50
0	461	461							6	96	106	7	-70	51	2	-69	-6
1	565	575	H= 8 L= 1			H= 9 L= 5			7	198	185	8	267	266	3	-71	39
2	800	832							8	251	243						
3	418	-402	1	203	203	1	149	145				H= 12 L= 1			H= 14 L= 2		
4	67	86	2	85	72	2	148	-161	H= 10 L= 7								
5	555	534	3	71	56	3	133	120				1	-68	58	0	140	138
6	601	613	4	209	211	4	-62	71	1	-64	-21	2	76	93	1	183	-177
			5	295	306	5	101	-92	2	92	-100	3	-66	60	2	160	172
H= 6 L= 1			6	382	385	6	267	-265	3	83	-67	4	108	-92	3	171	176
			7	475	-485	7	163	162	4	127	-130	5	-69	66			
1	471	458	8	148	-147	8	-66	13	5	172	169	6	112	-1	H= 14 L= 3		
2	386	382				9	95	-105	6	-68	61	7	193	-194			
3	51	45	H= 8 L= 2						7	-68	-25	8	-71	-38	1	-69	-11
4	77	-75				H= 9 L= 6									2	79	83
5	277	-287	0	142	-144				H= 10 L= 8			H= 12 L= 2					
6	-55	41	1	479	481	0	-60	1									
			2	882	908	1	472	-439	0	191	195	0	-66	-19			
H= 6 L= 2			3	332	-323	2	321	-323	1	189	187	1	309	309			
			4	344	349	3	-62	-40	2	263	266	2	369	364			
0	1109	1116	5	306	296	4	-62	25	3	216	-202	3	138	-154			
1	979	-983	6	601	613	5	109	-108	4	-68	47	4	73	83			
2	632	629	7	241	-235	6	98	-113	5	96	87	5	-67	57			
3	333	331	8	-62	35	7	-67	53	6	350	335	6	160	173			
4	976	985				8	81	93				7	249	-248			
5	59	-47				9	119	-111									
6	140	-135															

For neutron diffraction measurements an octahedron 0·5 cm on an edge was selected. The crystal was briefly immersed in liquid nitrogen to decrease its crystallite size and thus reduce the effects of extinction. Intensity measurements were made on the neutron spectrometer at the Puerto Rico Nuclear Center. In the more humid climate of Puerto Rico it was not necessary to coat the crystal. A wavelength of 1·06 Å was used and non-equivalent reflections within the range $2\theta \leq 80°$ were measured for the $hk0$ and hhl zones. General hkl data were collected out to about 40° 2θ and then an accident terminated the experiment. Out of 240 reflections measured, 144 were observed according to the criterion $[I - \text{Background}] \geq 2{\cdot}0[I + \text{Background}]^{\frac{1}{2}}$. Because of the large incoherent neutron scattering of hydrogen, absorption corrections were applied. The linear absorption coefficient for Na alum is 6·77 cm^{-1}, and calculated transmission factors varied from 0·106 to 0·179.

Refinement of the structure with X-ray data

The atomic positions given by Lipson (1935) were used as starting values for a full-matrix, least-squares refinement of the non-hydrogen parameters. Anisotropic thermal parameters were used in the form

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

Scattering factors given in *International Tables for X-ray Crystallography* (1962) were used for all atoms. The quantity minimized was $\Sigma\, w(F_o - F_c^*)^2$ where $w = w_E/(F_o + 0{\cdot}02F_o^2)$, w_E is the weight based on counting statistics (Evans, 1961), and

$$F_c^* = \frac{KF_c}{\left\{1+g\left[\frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2}\right]\mathrm{Lp}F_c^2\right\}^{\frac{1}{2}}}$$

where K is a scale factor, g is an extinction parameter (Zachariasen, 1963), Lp is the Lorentz and polarization factor and F_c is the ordinary calculated structure factor. For unobserved reflections $w = 0$. At the end of the refinements $\Delta\xi_i/\sigma(\xi_i) < 10^{-2}$ for all parameters ξ. R indices quoted for both X-ray and neutron data are $\Sigma\,|\Delta F|/\Sigma\,|F_o|$ with unobserved reflections omitted.

After several cycles of least-squares, R was 0·0588. A difference Fourier synthesis was calculated and the hydrogen atoms were revealed so clearly that it was decided to include them in the least-squares refinement but with isotropic thermal parameters. The hydrogen parameters readily converged and the final R was 0·0343. The final parameters are given in Table 1. The observed structure factors and those calculated with the parameters of Table 1 are given in Table 2. The anisotropic thermal parameters were transformed to obtain the thermal ellipsoid parameters which are given in Table 3.

Refinement of the structure with neutron diffraction data

The heavy atoms were held in fixed positions, as given in Table 1, and a least-squares refinement with anisotropic thermal parameters was computed as before except that no extinction parameter was used. The final R was 0·0691. Observed and calculated structure factors are given in Table 4. The resulting hydrogen parameters are given in Table 5. The anisotropic parameters are not listed as such; instead, for brevity, we give in Table 6 only the resulting thermal ellipsoids. The standard deviations are relatively large because of the rather small number of observations. (There were 144 observations and 63 parameters in this calculation.) The thermal ellipsoids of Table 3 and Table 5 agree within the rather large standard deviations. At first glance some of the standard deviations of the orientations of the ellipsoids in Table 5 are so large as to border on the ridiculous. These large standard deviations arise partly from the relatively large standard deviations of the thermal parameters but are due mostly to the fact that two of the axes are nearly the same and hence the directions become indeterminate. It is of particular interest that the extreme anisotropy of $O_s(2)$ is found from both the X-ray and neutron data.

Discussion

The atom positions found do not differ by more than about 0·05 Å from those reported by Lipson (1935).

Table 3. *Thermal ellipsoids in* $NaAl(SO_4)_2.12H_2O$ *from X-ray data*

Standard deviations (in parentheses) apply to rightmost digit

	r.m.s. amplitude	B_i	Direction angles relative to crystal axes α	β	γ
Na	0·170 (5) Å	2·28 (13) Å^2	54·7°	54·7°	54·7°
	0·180 (6)	2·55 (8)			
	0·180 (3)	2·55 (8)			
Al	0·159 (4)	1·99 (10)	54·7	54·7	54·7
	0·140 (3)	1·54 (6)			
	0·140 (3)	1·54 (6)			
S	0·183 (2)	2·63 (7)	54·7	54·7	54·7
	0·168 (2)	2·24 (4)			
	0·168 (2)	2·24 (4)			
$O_s(1)$	0·173 (7)	2·36 (19)	54·7	54·7	54·7
	0·251 (4)	4·97 (15)			
	0·251 (4)	4·97 (15)			
$O_s(2)$	0·367 (4)	10·62 (21)	31 (1)	115 (1)	74 (1)
	0·202 (4)	3·22 (12)	79 (2)	39 (3)	53 (4)
	0·164 (4)	2·12 (11)	118 (1)	118 (4)	42 (4)
$O_w(1)$	0·245 (4)	4·76 (16)	44 (3)	133 (2)	98 (3)
	0·182 (4)	2·63 (12)	53 (8)	60 (11)	51 (16)
	0·172 (4)	2·34 (12)	111 (11)	122 (10)	40 (16)
$O_w(2)$	0·149 (4)	1·75 (10)	36 (6)	117 (5)	67 (4)
	0·178 (4)	2·50 (11)	54 (6)	46 (6)	114 (6)
	0·206 (3)	3·35 (10)	95 (4)	56 (5)	34 (4)

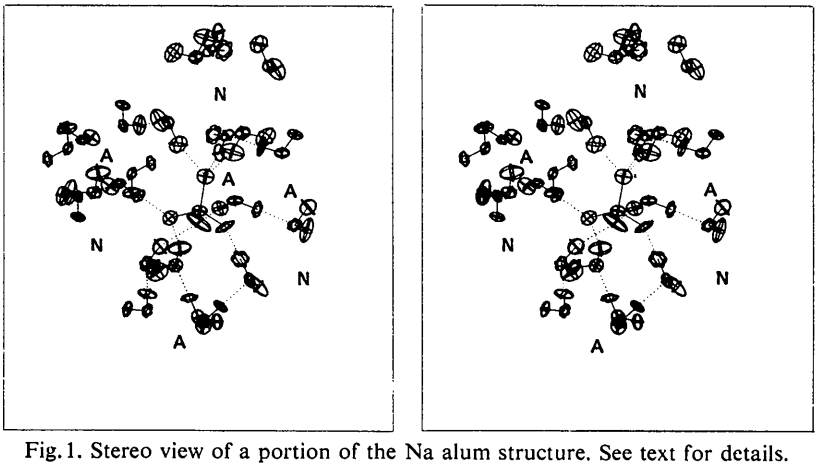

Fig. 1. Stereo view of a portion of the Na alum structure. See text for details.

The interatomic distances and bond angles are given in Table 7. The standard deviations were calculated by use of the entire variance–covariance matrix and include the lattice parameter error. However, the values involving hydrogen atom positional parameters from the neutron data refinement assume no error in heavy atom positions.

The water molecules about the aluminum atom form a perfect octahedron although this is not required by the crystal symmetry. Whereas the principal orthogonal axes of this octahedron coincide almost exactly with the cell axes in β alum, and within a few degrees in α alum, the octahedron at the origin in γ alum is rotated by 39·4° about the threefold axis of the body diagonal of the unit cell. The Al–O distance is the same in both Cs alum and Na alum. The octahedron of water about the sodium atom is somewhat distorted by being stretched out along the threefold axis of the cell.

The angles in the sulfate group depart from those of a regular tetrahedron by a small but apparently significant amount. The differences, for equivalent angles, are in the same direction as those in Cs alum although the departures from tetrahedral symmetry of the sulfate group in Cs alum were not of statistical significance. The rigid body motion, discussed below, might well account for the apparent deviation from tetrahedral symmetry.

The anisotropic thermal parameters of the sulfate group do not seem to be consistent with the rigid body analysis given by Cruickshank (1956). The τ and ω matrices are given in Table 8. The r.m.s. $\Delta U_{ij}=$ 0·0154 Å^2, as compared with 0·0026 Å^2 in Cs alum and 0·0015 Å^2 for the sulfate group in $Li_2SO_4.H_2O$ (Larson, 1965). We might expect a torsional oscillation of the group about the threefold axis. However, the major axis of the $O_s(2)$ thermal ellipsoid, instead of being normal to the threefold axis, is at an angle of 65·5°. We believe that this is a case in which the translational and the rotational motions are coupled. Thus the Cruickshank analysis does not apply. The $O_s(2)$–$O_w(2)$ hydrogen bond is fairly short, 2·62 Å, and the $O_s(2)$–H(4) distance is 1·64 Å. The principal axis of the $O_s(2)$ thermal ellipsoid makes an angle of 84·5° with the S–O bond and an angle of 79·9° with the O---H(4) bond. Thus a motion of 0·367 Å (the r.m.s. amplitude along this axis) changes the O---H(4) distance from 1·64 to 1·61 Å, a small amount. However, if this 0·367 Å motion were to be directed along a line normal to both the S–O bond and the threefold axis, the O---H(4) distance would be reduced to 1·51 Å. This sulfate group lies on a threefold axis so that a simple rotation about this axis will reduce three O---H distances and we reason that the whole group therefore is forced to translate along the threefold axis whenever it rotates about this axis. Thus the total motion cannot be described by independent τ and ω matrices. It should be emphasized that in the above discussion we are *not* making a correction to the observed *bond distances* in the manner of Busing & Levy (1964).

Fig. 1 is a stereo view of a portion of the structure. A sulfate group is at the center of the figure and the direction of view is normal to the threefold axis and in a plane containing the S–$O_s(1)$ and S–$O_s(2)$ bonds. The ellipsoids have been derived from the neutron diffraction data and are scaled so that their axes are three times the r.m.s. amplitude. The aluminum atoms are plotted by the letter A and the sodium atoms by the letter N. The aluminum and its water neighbors is at the left and the sodium atom with its water neighbors is at the top center. A threefold axis passes through

Table 4. *Observed and calculated neutron structure factors for* $NaAl(SO_4)_2.12H_2O$

The column headings are l, $100F_o/K$ and $100F_c/K$. A minus sign preceding F_o means 'less than'.

H= 1 K= 1

1	218	178
2	-149	105
3	-178	183
4	257	-280
5	372	-338
6	534	524
7	352	334
8	646	640
9	-242	7
10	615	611
11	736	-824
12	-261	-77
13	-265	23
14	-268	-135

H= 2 K= 0

0	4C1	-382

H= 2 K= 1

C	221	189

H= 2 K= 2

0	1454	1664
1	-182	-143
2	307	-283
3	206	74
4	-196	-175
5	1414	1437
6	959	891
7	807	756
8	592	950
9	358	-354
10	-259	-245
11	308	241
12	278	279
13	-265	51
14	-268	282

H= 2 K= 3

0	-166	-201
1	-177	112

H= 2 K= 4

C	258	-215
1	283	226

H= 2 K= 5

0	4C3	410
1	237	-207

H= 2 K= 6

C	453	410
1	969	-932

H= 2 K= 7

C	713	697
1	-237	-98

H= 2 K= 8

0	819	830

H= 2 K= 9

0	-259	-227

H= 2 K= 10

C	-276	292

H= 2 K= 11

C	767	-845

H= 2 K= 12

0	334	-138

H= 2 K= 13

C	-298	-75

H= 2 K= 14

0	-300	-145

H= 3 K= 2

1	-176	-3

H= 3 K= 3

1	277	235
2	209	184
3	457	430
4	836	-818
5	-216	-49
6	-224	-12
7	-240	-56
8	917	-924
9	477	426
10	404	-363
11	-254	-237
12	309	302
13	437	472
14	275	298

H= 3 K= 4

1	329	338
2	401	444

H= 3 K= 5

1	666	-618
2	1285	-1351

H= 3 K= 6

1	1213	1264
2	589	-535

H= 3 K= 7

1	-244	68

H= 4 K= 0

0	968	978

H= 4 K= 1

0	677	-708

H= 4 K= 2

0	-179	-135
1	515	-481

H= 4 K= 3

0	254	-257
1	249	-267
2	220	-181

H= 4 K= 4

0	821	-753
1	253	163
2	-194	83
3	1056	-1095
4	416	439
5	-223	-117
6	267	293
7	-251	190
8	684	665
9	530	-540
10	-247	-1
11	562	572
12	333	290
13	-250	176

H= 4 K= 5

0	214	-216
1	278	260
2	-215	-93
3	547	571

H= 4 K= 6

0	-212	56
1	380	376
2	469	395
3	676	-689

H= 4 K= 7

0	560	-570

H= 4 K= 8

0	679	651

H= 4 K= 9

0	403	-446

H= 4 K= 10

0	347	342

H= 4 K= 11

0	446	451

H= 4 K= 12

0	666	652

H= 4 K= 13

0	297	-291

H= 4 K= 14

0	360	271

H= 5 K= 2

1	803	774

H= 5 K= 3

1	738	-652
2	665	-579

H= 5 K= 4

1	495	-504
2	396	370
3	262	-249

H= 5 K= 5

1	291	-224
2	-205	113
3	-206	-5
4	-212	21
5	-222	50
6	-242	329
7	-247	81
8	-235	52
9	-260	175
10	-270	152
11	-268	73
12	-266	-233

H= 6 K= 0

0	314	238

H= 6 K= 1

0	-207	137

H= 6 K= 2

0	385	-355
1	832	866

H= 6 K= 3

0	279	-261
1	308	-281
2	-228	-166

H= 6 K= 4

0	451	418
1	-237	-311
2	869	883
3	405	-366

H= 6 K= 5

0	1120	1116

H= 6 K= 6

0	466	458
1	663	682
2	-218	-168
3	-214	74
4	-220	-87
5	-223	268
6	-232	-86
7	607	635
8	550	552
9	-249	-386
10	-256	395
11	-255	-15
12	270	347

H= 6 K= 7

0	480	-450

H= 6 K= 8

0	571	-596

H= 6 K= 9

0	262	-280

H= 6 K= 10

0	391	460

H= 6 K= 11

0	-278	-258

H= 6 K= 12

0	623	758

H= 6 K= 13

0	385	-322

H= 7 K= 2

1	-226	133

H= 7 K= 3

1	917	909
2	-234	-82

H= 7 K= 4

1	461	-504
2	541	-508

H= 7 K= 5

1	759	702

H= 7 K= 7

1	359	-302
2	406	419
3	238	-215
4	571	569
5	539	-556
6	248	262
7	367	371
8	335	-355
9	-244	-53
10	-247	75

H= 8 K= 0

0	675	-667

H= 8 K= 1

0	1040	-1C20

H= 8 K= 2

0	-235	-391
1	-240	310

H= 8 K= 3

0	1033	1C43
1	263	-232
2	447	-519

H= 8 K= 4

0	712	744
1	932	901
2	650	585

H= 8 K= 5

0	1349	1349
1	249	243

H= 8 K= 6

0	612	548

H= 8 K= 7

0	-254	236

H= 8 K= 8

0	637	657
1	-236	-346
2	-226	132
3	257	-197
4	-225	95
5	339	-302
6	-227	135
7	-233	-280
8	-239	102
9	299	-242

H= 8 K= 9

0	-262	95

H= 8 K= 10

0	542	551

H= 8 K= 11

0	-279	-37

H= 8 K= 12

0	-284	5

H= 9 K= 2

1	-248	160

H= 9 K= 3

2	338	273

H= 9 K= 9

1	-233	-178
2	-233	-434
3	-238	43
4	-227	44
5	-234	-232
6	-235	-6
7	281	245

H= 10 K= 0

0	1548	-1599

H= 10 K= 1

0	-253	217

H= 10 K= 2

0	-252	102

H= 10 K= 3

0	512	462

H= 10 K= 4

0	-252	197

H= 10 K= 5

0	-247	92

H= 10 K= 6

0	424	-493

H= 10 K= 7

0	-248	-79

H= 10 K= 8

0	364	401

H= 10 K= 9

0	695	722

H= 10 K= 10

0	604	604
1	-231	-28
2	366	410
3	-240	229
4	-240	67

H= 12 K= 0

0	-263	118

H= 12 K= 1

0	-251	99

H= 12 K= 2

0	272	236

H= 12 K= 3

0	-250	36

H= 12 K= 4

0	583	588

H= 12 K= 5

0	-255	-12

H= 12 K= 6

0	-261	373

H= 12 K= 7

0	-255	-5

H= 12 K= 8

0	278	320

H= 14 K= 0

0	-271	419

H= 14 K= 1

0	315	168

H= 14 K= 2

0	-261	-21

H= 14 K= 3

0	-260	-185

H= 14 K= 4

0	265	166

Table 5. *Hydrogen parameters in* $NaAl(SO_4)_2.12H_2O$ *from least-squares refinement of neutron diffraction data*

	x	y	z
H(1)	0·5958 (21)	0·3172 (20)	0·3663 (21)
H(2)	0·4709 (22)	0·3123 (21)	0·3808 (20)
H(3)	0·5504 (18)	0·2031 (15)	0·4958 (17)
H(4)	0·5926 (17)	0·3422 (16)	0·1104 (18)

this sodium atom and the sulfate group in the center. The motion of $O_s(2)$, so as to avoid the hydrogen neighbors, can be clearly seen. This figure was produced by the SC-4020 microfilm plotter using a code recently developed by Larson (1966).

The fact that the thermal motion of $O_s(2)$ was found to be essentially the same from both the X-ray and neutron diffraction measurements is strong evidence that the apparent motion is not an artifact resulting from systematic error in the data. If the motion is so large that the ellipsoid approximation is inadequate, there is then a systematic error in the model which might account for the failure of the independent τ and ω description of the motion. However, there is a logical structural explanation for the peculiar motion which makes it unnecessary to rationalize the results on the basis of a systematic error in the ellipsoid model.

Corrections to the S–O bond lengths were computed according to the in phase or 'riding motion' assumption of Busing & Levy (1964). The S–O bond lengths appear to be about 0·015 Å shorter than those found in Cs alum (CKL) but because of the uncertainty in the thermal motion correction the difference is probably not significant.

The O–H distances, except for $O_w(2)$–H(4), show the usual feature that X-ray determined bonds are shorter than those determined by neutron diffraction. The O–H bonds in this structure are all nearly the same and do not show any particular correlation of long O–H bonds and short O–O hydrogen bonds. As in β alum, water (1), which is associated with the monovalent cation, forms hydrogen bonds that link $O_s(1)$ of one sulfate group with $O_s(2)$ of another. Again, as in β alum, water (2) forms hydrogen bonds with $O_s(2)$ and water (1). In the present case there is a strong indication that shorter hydrogen bonds tend to be more nearly linear.

The α alums which will be discussed in a forthcoming paper show disorder of the sulfate groups. In view of the extreme anisotropy of the sulfate group found in γ alum a difference Fourier map of the X-ray data was carefully inspected. However no significant features were observed and there is no evidence for disorder in γ alum.

All calculations were done with an IBM 7094 computer. The calculation of the τ and ω matrices used a modification of a code by Trueblood (1962). All other calculation used codes by Larson, Roof & Cromer (1963, 1964, 1965).

Table 6. *Thermal ellipsoids in* $NaAl(SO_4)_2.12H_2O$ *from neutron diffraction data*

Standard deviations (in parentheses) apply to the rightmost digit.

	r.m.s. amplitude	B_i	Direction angles relative to crystal axes α	β	γ
Na	0·06 (27) Å	0·3 (25) Å^2	54·7°	54·7°	54·7°
	0·20 (6)	3·3 (20)			
	0·20 (6)	3·3 (20)			
Al	0·17 (10)	2·3 (28)	54·7	54·7	54·7
	0·08 (10)	0·5 (13)			
	0·08 (10)	0·5 (13)			
S	0·14 (9)	1·5 (19)	54·7	54·7	54·7
	0·20 (4)	3·3 (12)			
	0·20 (4)	3·3 (12)			
$O_s(1)$	0·20 (5)	3·2 (16)	54·7	54·7	54·7
	0·24 (3)	4·5 (11)			
	0·24 (3)	4·5 (11)			
$O_s(2)$	0·38 (2)	11·6 (13)	27 (4)	113 (4)	76 (3)
	0·19 (3)	2·8 (9)	64 (5)	30 (10)	104 (14)
	0·10 (4)	0·8 (6)	97 (7)	71 (13)	20 (10)
$O_w(1)$	0·20 (2)	3·0 (8)	24 (167)	114 (174)	86 (39)
	0·20 (2)	3·3 (8)	67 (174)	25 (167)	80 (21)
	0·14 (3)	1·6 (6)	97 (23)	98 (17)	11 (19)
$O_w(2)$	0·12 (3)	1·2 (6)	36 (14)	121 (14)	106 (24)
	0·21 (2)	3·4 (7)	56 (15)	34 (18)	85 (35)
	0·18 (2)	2·4 (6)	79 (25)	103 (36)	17 (27)
H(1)	0·32 (4)	8·3 (20)	23 (20)	91 (16)	67 (20)
	0·22 (4)	3·8 (13)	90 (134)	2 (310)	88 (315)
	0·23 (4)	4·0 (15)	113 (20)	92 (342)	23 (36)
H(2)	0·35 (4)	9·4 (22)	44 (15)	110 (13)	127 (11)
	0·24 (4)	4·5 (15)	53 (16)	43 (17)	72 (18)
	0·14 (5)	1·6 (12)	71 (14)	126 (17)	42 (11)
H(3)	0·21 (3)	3·3 (11)	28 (22)	112 (20)	107 (19)
	0·10 (6)	0·7 (9)	83 (18)	38 (11)	127 (10)
	0·27 (3)	5·8 (14)	63 (21)	60 (13)	42 (12)
H(4)	0·21 (3)	3·5 (11)	37 (88)	53 (85)	89 (87)
	0·22 (3)	3·9 (10)	115 (109)	57 (85)	44 (18)
	0·12 (4)	1·1 (9)	65 (19)	19 (17)	46 (17)

Table 7. *Interatomic distances and angles in* $NaAl(SO_4)_2.12H_2O$

Standard deviations (in parentheses) apply to the rightmost digit.
Distances corrected for thermal motion are in parentheses.
Distances and angles from neutron data are in italics.

Al–6O_w(2)	1·881 (2)Å	< O_w(2)–Al–O_w(2)	90·0 (1)°
		< O_w(2)–Al–O_w(2)	90·0 (1)
Na–6O_w(1)	2·453 (2)	< O_w(1)–Na–O_w(1)	85·0 (1)
		< O_w(1)–Na–O_w(1)	95·0 (1)
The sulfate group			
S–O_s(1)	1·461 (4)	< O_s(1)–S–O_s(2)	110·1 (1)
	(1·476)	< O_s(2)–S–O_s(2)	108·9 (1)
S–3O_s(2)	1·454 (2)	< O_s(2)–O_s(2)–O_s(2)	60·0
	(1·478)	< O_s(2)–O_s(2)–O_s(1)	60·3 (1)
O_s(1)–3O_s(2)	2·389 (4)	< O_s(2)–O_s(1)–O_s(2)	59·4 (1)
O_s(2)–2O_s(2)	2·366 (4)		
Water molecules			
O_w(1)–H(1)	0·78 (4)	< H(1)–O_w(1)–H(2)	*103 (2)*
	0·973 (24)		
	(1·017)		
O_w(1)–H(2)	0·83 (4)		
	0·997 (24)		
	(1·054)		
O_w(2)–H(3)	0·92 (4)	< H(3)–O_w(2)–H(4)	*108 (2)*
	0·976 (17)		
	(1·009)		
O_w(2)–H(4)	1·01 (3)		
	0·991 (20)		
	1·006		
Hydrogen bonds			
O_s(1)–3O_w(1)	2·747 (4)	< O_s(1)–H(2)–O_w(1)	*162 (3)*
O_s(1)–3H(2)	*1·783 (25)*		
O_s(2)–O_w(1)	2·822 (3)	< O_s(2)–H(1)–O_w(1)	*156 (3)*
O_s(2)–H(1)	*1·907 (23)*		
O_s(2)–O_w(2)	2·623 (3)	< O_s(2)–H(4)–O_w(2)	*174 (2)*
O_s(2)–H(4)	*1·635 (20)*		
O_w(1)–O_w(2)	2·649 (3)	< O_w(1)–H(3)–O_w(2)	*178 (2)*
O_w(1)–H(3)	*1·673 (17)*		

Table 8. *Translation and torsional vibration matrices for the sulfate group relative to the unit-cell axes*

$$\tau = \begin{pmatrix} 0{\cdot}0324 & 0{\cdot}0004 & 0{\cdot}0004 \\ & 0{\cdot}0324 & 0{\cdot}0004 \\ & & 0{\cdot}0324 \end{pmatrix} \text{Å}^2 \qquad \omega = \begin{pmatrix} 71{\cdot}3 & 31{\cdot}6 & 31{\cdot}6 \\ & 71{\cdot}3 & 31{\cdot}6 \\ & & 71{\cdot}3 \end{pmatrix} \text{deg}^2$$

$$\sigma\tau = \begin{pmatrix} 0{\cdot}0112 & 0{\cdot}0098 & 0{\cdot}0098 \\ & 0{\cdot}0112 & 0{\cdot}0098 \\ & & 0{\cdot}0112 \end{pmatrix} \text{Å}^2 \qquad \sigma\omega = \begin{pmatrix} 26{\cdot}6 & 24{\cdot}1 & 24{\cdot}1 \\ & 26{\cdot}6 & 24{\cdot}1 \\ & & 26{\cdot}6 \end{pmatrix} \text{deg}^2$$

r.m.s. $\Delta U_{ij} = 0{\cdot}0154$ Å^2.

Added note: – The sulfate group motion in Cs alum (CKL) was re-examined in the light of the present results. The amplitude of the major axis of the general position oxygen thermal ellipsoid is 0·214 Å in Cs alum. This axis makes angles of 85·5° with the S–O bond and 81·5° with the O---H hydrogen bond. The O---H distance is 1·69 Å and a motion of 0·214 Å of the oxygen atom in the observed direction of the major axis reduces this distance to 1·67 Å. On the other hand a motion of 0·214 Å in a direction normal to both the S–O bond and the threefold axis would reduce the O---H distance to 1·54 Å. There is probably coupled rotational and translational motion in Cs alum also, but because of the smaller amplitude the Cruickshank analysis appeared to be satisfactory in terms of the r.m.s. ΔU_{ij}.

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