

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 α 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 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, $\text{ND}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{D}_2\text{O}$, 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 $Pa\bar{3}$, 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 α 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 D_2O . 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 \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.

constant for the normal hydrogen compound is $12.240 \pm 0.003 \text{ \AA}$ (Larson & Cromer, 1967) so that there is little if any isotope effect on the cell size.

If the ammonium ion is ordered the symmetry of the cell must be reduced, most likely to space group $P2_13$. In this space group the $hk0$ reflections with k odd are no longer systematically absent as they are in $Pa3$. No such reflections were observed.

Refinement of the structure

Full-matrix least-squares refinement minimized $\sum w(F_o - F_c)^2$ where w is the weight based on counting statistics (Evans, 1961). Anisotropic temperature factors were in the form

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

Scattering lengths were taken from *International Tables for X-ray Crystallography* (1962). Refinement proceeded until $\Delta\xi/\sigma(\xi) < 10^{-2}$ for all parameters ξ . R indices quoted are $\sum ||F_o| - |F_c|| / \sum |F_o|$ with unobserved reflections omitted.

An isotropic refinement was computed starting with the heavy atom X-ray parameters of NH_4 alum (Larson & Cromer, 1967) and with the water hydrogen positions found by Bacon & Gardner (1958) in $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ for the water deuterium atoms. No deuterium on ND_4 was included. A difference Fourier map was computed and peaks were observed which clearly showed that the ammonium ion is disordered in two orientations related by inversion, rather than being disordered by free rotation.

The refinement was continued after adding $\frac{1}{2}\text{D}$ in an xxx position and $\frac{1}{2}\text{D}$ in a general position, the starting parameters of these additional atoms being taken from the difference Fourier map. All atoms were given anisotropic thermal parameters. This refinement led to $R=9.2\%$. As in the case of the X-ray refinement (Larson & Cromer, 1967), the thermal parameters for the sulfate oxygen atoms were quite large and quite

anisotropic. Other thermal parameters behaved normally. The thermal ellipsoids for the sulfate oxygen atoms from this refinement are given in Table 1. These ellipsoids are somewhat smaller than those obtained from the analogous X-ray refinement of ordered NH_4 alum but the directions of the axes are in good agreement for the two cases.

Table 1. *Thermal ellipsoids of sulfate oxygen atoms in $\text{ND}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{D}_2\text{O}$ after refinement with an ordered sulfate group*

These values are to be compared with the X-ray values from NH_4 alum (Larson & Cromer, 1967).

	r.m.s. amplitude	B_i	Direction angles relative to crystal axes		
			α	β	γ
$\text{O}_s(1)$	0.16 (2) \AA	2.0 (6) \AA	54.7°	54.7°	54.7°
	0.28 (1)	6.1 (6)	—	—	—
	0.28 (1)	6.1 (6)	—	—	—
$\text{O}_s(2)$	0.17 (1)	2.2 (3)	31 (7)	100 (6)	119 (9)
	0.33 (1)	8.4 (6)	66 (3)	36 (2)	65 (2)
	0.11 (1)	1.0 (2)	71 (9)	124 (3)	41 (8)

A second difference Fourier map clearly revealed small peaks from disordered sulfate oxygen atoms. A model with a fraction, k , of reversed sulfate oxygen atoms was then refined as in the X-ray refinement of K alum (Larson & Cromer, 1967). However, no attempt was made to displace $k/2$ ND_4 groups along the three-fold axis as was done for the potassium atom in K alum, as this additional disorder would have introduced too many highly correlated parameters. Anisotropic thermal parameters for the reversed oxygen, $\text{O}_s(2)'$, did not remain real so final refinement was made with the reversed oxygen atoms isotropic and all other atoms anisotropic. The final R index was 8.4%. The final parameters are given in Table 2 and the observed and calculated structure factors are in Table 3. The disorder parameter is 0.116 ± 0.022 in good agreement with the value indicated by the X-ray data for NH_4 alum. In

Table 2. *Least-squares parameters for $\text{ND}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{D}_2\text{O}$*
Standard deviations, in parentheses, apply to the rightmost digit.

Atom	x	y	z	$\beta_{11} \times 10^5$ or B (\AA^2)	$\beta_{22} \times 10^5$	$\beta_{33} \times 10^5$	$\beta_{12} \times 10^5$	$\beta_{13} \times 10^5$	$\beta_{23} \times 10^5$	
Al	0	0	0	140 (46)	β_{11}	β_{11}	-130 (100)	β_{12}	β_{12}	
N	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	538 (33)	β_{11}	β_{11}	170 (109)	β_{12}	β_{12}	
$\text{D}(1)'$	0.4479 (21)	x	x	1253 (128)	β_{11}	β_{11}	-253 (390)	β_{12}	β_{12}	
$\text{D}(2)'$	0.4505 (19)	0.5655 (16)	0.5134 (29)	963 (152)	637 (147)	1250 (204)	224 (219)	234 (296)	69 (339)	
S	0.3101 (8)	x	x	249 (42)	β_{11}	β_{11}	161 (108)	β_{12}	β_{12}	
$\text{O}_s(1)$	0.2397 (6)	x	x	651 (53)	β_{11}	β_{11}	-362 (100)	β_{12}	β_{12}	
$\text{O}_s(1)'$	0.3757 (60)	x	x	4.4 (28)						
$\text{O}_s(2)$	0.3139 (6)	0.2649 (8)	0.4194 (7)	467 (49)	673 (76)	285 (48)	506 (100)	87 (85)	561 (103)	
$\text{O}_s(2)'$	0.2177 (38)	0.3775 (38)	0.2942 (36)	1.0 (10)						
$\text{O}_w(1)$	0.0467 (6)	0.1374 (5)	0.2993 (5)	484 (48)	303 (38)	432 (45)	141 (77)	-220 (79)	-144 (73)	
$\text{O}_w(2)$	0.0170 (5)	-0.0171 (5)	0.1505 (4)	351 (38)	289 (36)	156 (31)	-18 (67)	-94 (57)	-4 (58)	
$\text{D}(1)$	0.1163 (6)	0.1681 (6)	0.2926 (6)	518 (48)	699 (59)	762 (59)	-133 (96)	-239 (88)	-346 (87)	
$\text{D}(2)$	-0.0041 (6)	0.1952 (5)	0.2848 (6)	780 (58)	490 (47)	730 (53)	65 (102)	-302 (98)	-331 (78)	
$\text{D}(3)$	0.0273 (5)	0.0441 (5)	0.2027 (4)	527 (43)	542 (43)	307 (33)	65 (79)	-93 (71)	99 (67)	
$\text{D}(4)$	0.0428 (5)	0.9153 (5)	0.1856 (5)	556 (43)	394 (38)	407 (38)	-31 (70)	-168 (69)	120 (68)	
	$k = 0.116$ (22)									

Table 2, and following, the symbols $O_s(1)'$ and $O_s(2)'$ are used for the reversed sulfate oxygen atoms and D' is used for the half deuterium atoms in the disordered ND_4 group.

Discussion

The various interatomic distances and bond angles are given in Table 4; standard deviations have been computed using the entire variance-covariance matrix. The anisotropic thermal parameters were transformed to obtain the thermal ellipsoid parameters, which are given in Table 5. The O-D bond lengths have been corrected assuming that D rides on O (Busing & Levy, 1964). No such corrections were made to S-O and N-D bonds because of uncertainties introduced by the disorder.

Table 4. *Interatomic distances and bond angles in $ND_4Al(SO_4)_2 \cdot 12D_2O$*

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

Distances corrected for thermal motion are in parentheses.

Distances		Angles	
Al- $6O_w(2)$	1.865 (5) Å	$O_w(2)$ -Al- $O_w(2)$	90.8 (2)°
		$O_w(2)$ -Al- $O_w(2)$	89.2 (2)
N- $6O_w(1)$	3.031 (7)	$O_w(1)$ -N- $O_w(1)$	75.2 (1)
		$O_w(1)$ -N- $O_w(1)$	104.8 (1)
N- $O_s(1)'$	2.64 (13)		
ND_4 group			
N- $2D(1)'$	1.104 (45)	$D(1)'$ -N- $D(2)'$	101.8 (14)
N- $6D(2)'$	1.018 (16)	$D(2)'$ -N- $D(2)'$	115.9 (9)
SO_4 group			
S- $O_s(1)$	1.49 (2)	$O_s(1)$ -S- $O_s(2)$	109.4 (8)
S- $O_s(1)'$	1.39 (13)	$O_s(2)$ -S- $O_s(2)$	109.6 (8)
S- $O_s(2)$	1.448 (9)	$O_s(1)'$ -S- $O_s(2)'$	102 (2)
S- $O_s(2)'$	1.41 (4)	$O_s(2)'$ -S- $O_s(2)'$	116 (2)
Water molecules			
$O_w(1)$ -D(1)	0.934 (9) (0.965)	D(1)- $O_w(1)$ -D(2)	106.1 (9)
$O_w(1)$ -D(2)	0.958 (9) (0.978)		
$O_w(2)$ -D(3)	0.993 (7) (1.008)	D(3)- $O_w(2)$ -D(4)	108.2 (7)
$O_w(2)$ -D(4)	0.984 (7) (1.005)		
Hydrogen bonds			
$O_s(1)$ - $3O_w(1)$	2.772 (11)	$O_s(1)$ -D(1)- $O_w(1)$	163.6 (9)
$O_s(1)$ - $3D(1)$	1.863 (11)		
$O_s(2)$ - $O_w(1)$	2.777 (9)	$O_s(2)$ -D(2)- $O_w(1)$	168.1 (9)
$O_s(2)$ -D(2)	1.832 (10)		
$O_s(2)$ - $O_w(2)$	2.617 (8)	$O_s(2)$ -D(4)- $O_w(2)$	169.7 (7)
$O_s(2)$ -D(4)	1.643 (9)		
$O_s(2)'$ - $O_w(1)$	2.83 (4)	$O_s(2)'$ -D(2)- $O_w(1)$	167 (2)
$O_s(2)'$ -D(2)	1.89 (4)		
$O_s(2)'$ - $O_w(2)$	2.77 (4)	$O_s(2)'$ -D(4)- $O_w(2)$	162 (2)
$O_s(2)'$ -D(4)	1.82 (4)		
$O_w(1)$ - $O_w(2)$	2.652 (9)	$O_w(1)$ -D(3)- $O_w(2)$	174.4 (6)
$O_w(1)$ -D(3)	1.662 (9)		

Agreement of these distances with those from the X-ray study of the α alums (Larson & Cromer, 1967) is reasonable except for three striking exceptions: the $O_s(2)$ - $O_w(2)$ and $O_w(1)$ - $O_w(2)$ hydrogen bond distances are both about 0.05 Å longer than in NH_4 alum, and the Al- $O_w(2)$ distance found here is 1.865 ± 0.005 Å whereas the analogous distance found by X-rays in NH_4 alum is 1.916 ± 0.008 Å. If these differences are real, they must arise from an isotope effect. To settle the question, an X-ray study was made of deuterated ammonium alum and a refinement was made exactly as had been made for NH_4 alum (Larson & Cromer, 1967). There were no significant differences between these X-ray studies of NH_4 and ND_4 alums.

As another check to determine if we had systematic errors in either our X-ray work or neutron work, the neutron data for Na alum (Cromer, Kay & Larson, 1967) were refined while letting all parameters vary. (In the original work heavy atoms had been held in fixed positions for the neutron refinement.) Unfortunately only limited three-dimensional data were available and there were only 144 observations to determine 74 parameters. Nevertheless the refinement converged satisfactorily and the parameters did not change very much. The resulting Al- $O_w(2)$ distance was 1.879 ± 0.014 , in good agreement with the X-ray value. In this case no systematic difference existed in the two techniques.

We believe that the most likely reason for the difference between the present neutron results and the X-ray results is that the model used for refinement does not properly account for the disorder. Thus, the systematic error exists in the least-squares model and not in either of the experimental methods. No provision for positional disorder of the ammonium ion was made in either refinement. In the refinement of K alum potassium disorder was coupled with sulfate group disorder. Neglect of this disorder would have a much greater effect on the neutron results because the deuterium contributes a large amount to the scattering whereas the hydrogen atoms are nearly negligible in X-ray scattering. We therefore reason that the X-ray results are probably correct and the neutron results are in error.

It is also possible that the neglect of the hydrogen atoms in the X-ray work on NH_4 alum is the source of the discrepancy. However, when these atoms were included in the calculations, their parameters were not well behaved and little change resulted in the other parameters.

Difference Fourier maps revealed no significant features and there is no evidence for water disorder coupled with sulfate group disorder. Further, there is no marked anisotropy in the thermal motion of the deuterium atoms which might suggest positional disorder. As noted in the previous paper of this series, the sulfate oxygen atom can form hydrogen bonds with the same hydrogen atoms whether the oxygen atom is in position $O_s(2)$ or $O_s(2)'$.

Table 5. *Thermal ellipsoids in ND₄Al(SO₄)₂·12D₂O*
 Standard deviations, in parentheses, apply to the rightmost digit

	r.m.s. amplitude	B_i	Direction angles relative to cell axes		
			α	β	γ
N	0.23 (2) Å	4.2 (7) Å ²	54.7°	54.7°	54.7°
	0.18 (1)	2.7 (3)	—	—	—
	0.18 (1)	2.7 (3)	—	—	—
D(1)'	0.28 (5)	6.0 (23)	54.7	54.7	54.7
	0.32 (3)	8.3 (17)	—	—	—
	0.32 (3)	8.3 (17)	—	—	—
D(2)'	0.27 (2)	5.7 (9)	28 (25)	74 (21)	112 (22)
	0.21 (2)	3.6 (8)	107 (19)	17 (20)	90 (17)
	0.31 (2)	7.8 (12)	69 (22)	84 (14)	22 (22)
Al	0.03 (14)	0.1 (6)	54.7	54.7	54.7
	0.12 (2)	1.2 (4)	—	—	—
	0.12 (2)	1.2 (4)	—	—	—
S	0.18 (3)	2.5 (8)	54.7	54.7	54.7
	0.11 (2)	1.0 (4)	—	—	—
	0.11 (2)	1.0 (4)	—	—	—
O _s (1)	0.15 (2)	1.7 (6)	54.7	54.7	54.7
	0.25 (1)	5.0 (5)	—	—	—
	0.25 (1)	5.0 (5)	—	—	—
O _s (2)	0.17 (1)	2.2 (3)	33 (6)	105 (6)	118 (7)
	0.27 (1)	5.7 (6)	63 (4)	36 (3)	68 (4)
	0.09 (2)	0.7 (2)	74 (7)	122 (4)	37 (6)
O _w (1)	0.21 (1)	3.6 (3)	43 (8)	72 (6)	127 (8)
	0.14 (1)	1.6 (2)	98 (18)	20 (12)	72 (20)
	0.16 (1)	2.1 (3)	48 (10)	98 (24)	43 (14)
O _w (2)	0.17 (1)	2.2 (2)	13 (7)	93 (27)	102 (9)
	0.15 (1)	1.8 (2)	89 (27)	10 (14)	100 (13)
	0.10 (1)	0.8 (2)	77 (7)	81 (11)	16 (8)
D(1)	0.18 (1)	2.4 (3)	40 (9)	63 (8)	62 (6)
	0.22 (1)	4.0 (3)	129 (9)	48 (10)	67 (11)
	0.26 (1)	5.5 (4)	98 (8)	127 (9)	38 (8)
D(2)	0.22 (1)	3.9 (4)	43 (9)	114 (9)	57 (9)
	0.17 (1)	2.4 (3)	83 (8)	30 (8)	61 (6)
	0.27 (1)	5.7 (4)	132 (8)	107 (6)	47 (7)
D(3)	0.15 (1)	1.7 (2)	78 (8)	102 (7)	17 (8)
	0.20 (1)	3.1 (3)	38 (40)	123 (42)	107 (8)
	0.21 (1)	3.4 (3)	54 (42)	36 (40)	87 (15)
D(4)	0.16 (1)	2.0 (2)	77 (10)	129 (17)	42 (14)
	0.21 (1)	3.6 (3)	29 (10)	101 (10)	116 (8)
	0.18 (1)	2.6 (2)	65 (12)	42 (17)	59 (16)

Table 6. Al-O and hydrogen bond distances in alums

Bond	Alums						
	K ^(a)	Rb ^(a)	NH ₄ ^(a)	Na ^(b)	Cs ^(c)	NH ₃ CH ₃ ^(d)	ND ₄
O _w (2)-O _s (1)	2.563 (16)	2.553 (18)	2.565 (16)	2.623 (3)	2.648 (7)	2.648	2.617 (8)
O _w (2)-O _w (1)	2.604 (13)	2.600 (17)	2.605 (14)	2.649 (3)	2.615 (7)	2.625	2.652 (9)
Average of above	2.584	2.576	2.585	2.636	2.632	2.636	2.634
Al-O	1.908 (8)	1.923 (9)	1.916 (8)	1.881 (2)	1.882 (5)	1.886	1.865 (5)

^(a) Larson & Cromer (1967).

^(b) Cromer, Kay & Larson (1967)

^(c) Cromer, Kay & Larson (1966)

^(d) Okaya, Ahmed, Pepinsky & Vand (1951)

The two N-D distances in the ND₄ group differ by 0.086 Å but this difference is probably not real. The longer distance has a large standard deviation and further there is the possibility for some positional disorder of the ND₄ group coupled with the sulfate group disorder. Although the thermal ellipsoid of the nitrogen atom suggests this possibility, the ellipsoids of the deuterium do not. The ND₄ group perhaps has to move very little to accommodate the reversed O_s(1) atom because either an O---D-N hydrogen bond can form (the O---N distance is 2.64 Å) or the van der Waals radius of the nitrogen atom is smaller along a symmetry axis of the ND₄ group than in other directions.

The O-D bonds of water(1) are significantly shorter than those of water(2). This difference is related to the strength of the hydrogen bonds, the shorter O-D bonds being associated with longer hydrogen bonds. The shorter hydrogen bonds also tend to be closer to linearity.

A stereo drawing of a portion of the structure is shown in Fig. 1. The ammonium ion at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (in its two orientations) is shown with its six water neighbors in the lower right front. The octahedron about the aluminum at $\frac{1}{2}, 0, \frac{1}{2}$ is shown at the lower left front. The sulfate group (in its normal orientation only) is in the middle. All water molecules hydrogen bonded to the sulfate group are shown.

Except as noted below, all calculations were performed with an IBM 7094 computer using codes written by Larson, Roof & Cromer (1963, 1964, 1965). Bond lengths were corrected for thermal motion using a modification of a code by Trueblood (1962). Fig. 1 was drawn with an SC-4020 microfilm plotter using a code by Larson (1966). We are indebted to F.H. Ellinger for the lattice constant measurement of ND₄ alum.

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The Zinc Sulphide Polytypes 14L (7 7); 18L (4 2)₃; 24L (7 5 5 7) and 36L (6 2 2 2)₃

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The identification of the layer sequences of the polytypes listed above is reported. The birefringence of these structures is also given. Two of the identified structures [14L (7 7) and 24L (7 5 5 7)] have unit-cell dimensions identical with those of structures previously reported [14L (5 4 2 3) and 24L (5 3)₃ respectively] but the layer sequences are different.

Introduction

It has been recently demonstrated (Brafman & Steinberger, 1966) that physical properties, namely the birefringence and the absorption edge, of ZnS polytypes are determined primarily by the layer sequence of the structure and not by the dimensions of the unit cell. Some new ZnS polytypes, found in vapour-phase grown crystals, have been reported in a previous publication (Brafman, Alexander & Steinberger, 1967). It has been noted there that the detailed mechanism

of polytype growth in ZnS differs from that proposed by Krishna & Verma (1965) for SiC. This conclusion was based on the comparison of the morphology of ZnS and SiC crystals as well as on the differences between the types of layer sequence reported for the two compounds. It was, however, stressed that for the construction of a reliable theory on ZnS polytypism the unit-cell dimensions and layer sequences of many more ZnS polytypes have to be known.

The present work deals with the structure of four new ZnS polytypes. The crystals used, as well as the