Zeitschrift für Kristallographie 157, 147–166 (1981)
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X-Ray and neutron diffraction study of alums

II. The crystal structure of methylammonium aluminium alum

III. The crystal structure of ammonium aluminium alum

A. M. Abdeen, G. Will, W. Schäfer, A. Kirfel, M. O. Bargouth, K. Recker

Mineralogisches Institut der Universität Bonn, Lehrstuhl für Mineralogie und Kristallographie,
Poppelsdorfer Schloß, D-5300 Bonn, Federal Republic of Germany

and A. Weiss

Institut für Physikalische Chemie der Technischen Hochschule Darmstadt,
Petersenstr. 20, D-6100 Darmstadt, Federal Republic of Germany

Received: September 5, 1980

Abstract. The crystal structure of the alums, $(NH_3CH_3)Al(SO_4)_2 \cdot 12\,H_2O$ and $(NH_4)Al(SO_4)_2 \cdot 12\,H_2O$, has been determined and refined from X-ray and neutron diffraction data. The compounds crystallize cubic in space group $Pa3$ ($Z = 4$) with $a_0 = 12.322(3)$ Å and $a_0 = 12.242(1)$ Å respectively. The positional and thermal parameters of all atoms including hydrogens have been refined by full matrix least-squares analysis resulting in R_w values from the X-ray and neutron data of 0.030 and 0.029 respectively for the methylammonium alum and of 0.024 and 0.014 respectively for the ammonium alum.

The atoms of the cation groups $(NH_3CH_3)^+$ and $(NH_4)^+$ are distributed on 8(*c*) and 24(*d*) positions in two orientations of equal probability on and around the [111] direction related to each other by an inversion centre. The disorder in the cation groups is explained by a quantized rotation. Disorder in the sulfate groups has been determined to 4.2% for the methylammonium alum and to about 17% for the ammonium alum. The disordered sulfate tetrahedra are distorted and in a reversed orientation along the threefold axis. The system of the hydrogen bonds is discussed.

Introduction

Alums with the general formula $M^+T^{3+}(SO_4)_2 \cdot 12\,H_2O$ are attractive for investigations because of their interesting ferroelectric properties and their technical use as adiabatic demagnitization materials. At room temperature, alums crystallize cubic in space group $Pa3$ in one of three polymorphous forms called α, β and γ according to Lipson (1935a). The different structures are characterized by the different orientations of the sulfate ions with respect to the trigonal axes of the unit cell. The type of crystallization is primarily determined by the size of the monovalent cation M^+. The most common type is the α-alum.

Of special interest from a crystallographic point of view are alums where the monovalent cation is replaced by NH_4 or a substituted ammonium group. In such crystals the atoms of the monovalent cation group centered in 4(*b*) at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, the centre of symmetry, must be divided over several more general positions like 8(*c*) and 24(*d*). The nature of such an arrangement has been studied in a previous paper on $(NH_3OH)Al(SO_4)_2 \cdot 12\,H_2O$, abbreviated as HASD alum, by neutron diffraction (Abdeen, Will and Weiss, 1980), where we found a disorder of the (NH_3OH) complex. This could be explained by a dynamical model with a quantized rotation of the (NH_3OH) complex around an axis perpendicular to the [111] direction of the N—O bond.

Replacing the hydroxyl group of HASD alum by a methyl group leads to a similar alum compound, *m*ethylammonium *a*luminium *s*ulfate *d*odecahydrate alum $(NH_3CH_3)Al(SO_4)_2 \cdot 12H_2O$, in the following referred to as MASD alum. Replacing the monovalent cation M^+ by an ammonium group leads to *a*mmonium *a*luminium *s*ulfate *d*odecahydrate alum $(NH_4)Al(SO_4)_2 \cdot 12\,H_2O$, referred to as AASD alum. MASD and AASD alum are the subjects of the structure investigations presented here, obtained from X-ray and neutron diffraction measurements.

X-ray diffraction measurements on MASD alum have been reported already by Lipson (1935b) and later by Fletcher and Steeple (1962). In both studies the authors did not succeed in resolving the methylammonium complex into its components. Okaya et al. (1957) suggested a statistical arrangement for the methylammonium complex but again they could not resolve the hydrogen atoms. Clearly neutron diffraction is more suitable for such an investigation.

AASD alum is distinguished from MASD alum and the previously studied HASD alum with respect to the behaviour of the SO_4-groups. One of the aims of the structural investigations of alum crystals was the study of the behaviour of the SO_4-groups, since abnormally high values of oxygen atom temperature factors were found in several structure investigations in the past. These findings and the deduced different interpretations have been discussed in detail by Ledsham, Steeple and Hughes (1970).

A further important aim of our present structure investigations of alum crystals was the localization of the hydrogen atoms of the water molecules in order to understand the hydrogen bonding system in the alums.

Experimental

Single crystals of MASD and AASD alum were grown by slow cooling of a saturated aqueous solution as described by Weiden and Weiss (1974). The cooling rate $\Delta T/\Delta t$ was 0.03 °C/h in the temperature range from $T_{\max} = 45\,^{\circ}\mathrm{C}$ to $T_{\min} = 20\,^{\circ}\mathrm{C}$ for the MASD alum and 0.05 °C/h in the temperature range from 40 to 20 °C for the AASD alum crystals. For the X-ray and neutron diffraction experiments the crystals were ground to spheres.

The X-ray diffraction data were collected on an automatic four-circle diffractometer SYNTEX $P2_1$ using Mo-$K\alpha$ radiation ($\lambda = 0.7107$ Å) and a graphite monochromator ($2\theta_M = 12.2°$). The lattice constants were calculated by least-squares methods from the refined angular settings of 25 independent reflections each to be $a_0 = 12.322(3)$ Å for MASD alum and $a_0 = 12.242(1)$ Å for AASD alum. The intensity measurements were carried out in the $\theta - 2\theta$ scan mode with a 1.0° (α_1, α_2)-dispersion scan range. The scan speed was adjusted between 0.5 and 10.0° per minute, and the total background counting time equaled the time spent for the peak counting. The six equivalent reflections 10.00 were measured as standards after every 28 reflections. In the data reduction procedure the intensities were adjusted to the fluctuation of the sum of the standard reflections. Symmetry related reflections were averaged, resulting in a set of 877 and 905 unique reflections for MASD and AASD alum respectively. With an absorption coefficient

Table 1. Summary of crystallographic and experimental data for X-ray and neutron diffraction

	MASD		AASD	
	X-ray	Neutron	X-ray	Neutron
a) Crystallographic data				
Formula	$(NH_3CH_3)Al(SO_4)_2 \cdot 12\,H_2O$		$NH_4Al(SO_4)_2 \cdot 12\,H_2O$	
M_r	467.35		453.33	
Space group	$Pa\bar{3}$		$Pa\bar{3}$	
Z	4		4	
Lattice constant (Å)	12.322(3)	12.314	12.242(1)	12.248
V (Å^3)	1870.9	1867.2	1834.7	1837.4
$\varrho_{X,N}$ (g cm^{-3})	1.659(1)	1.662	1.641(1)	1.639
μ (cm^{-1})	4.27	2.06	4.36	2.46
$\mu \cdot R$	0.043	0.330	0.052	0.467
b) Experimental data				
Crystal diameter (mm)	0.20	3.2	0.24	3.8
Wavelength (Å)	0.7107	1.2868	0.7107	1.2868
Maximum 2θ-angle (°)	60	65	90	65
$(\sin\theta/\lambda)_{\max}$ (Å^{-1})	0.700	0.417	0.995	0.417
Number of steps/scan	96	23	96	23
Number of standard reflections	6	1	6	1
Monitor reflection interval	28	9	28	9
Number of total reflections	2196	2288	4813	3360
Number of unique reflections	877	194	905	190
Nummber of unobserved reflections	385	42	419	50

$\mu = 0.427\,\mathrm{mm}^{-1}$ and a MASD alum sphere of 0.2 mm diameter the transmission was 94.19% for $2\theta = 0°$ and 94.20% for $2\theta = 60°$. With an absorption coefficient of $0.436\,\mathrm{mm}^{-1}$ and a radius of 0.12 mm the transmission for the AASD crystal was 92.8% between $2\theta = 0°$ and 60°. Corrections for absorption were consequently neglected.

The neutron diffraction data were collected on the Bonn University computer-controlled four-circle neutron diffractometer NANCY (Zwoll, Müller and Will, 1976), again in the $\theta - 2\theta$ scan mode with $\lambda = 1.2868$ Å and a scan angle of 2.2° per reflection (compare also Abdeen, Will and Weiss, 1980). MASD alum reflections were recorded up to $2\theta_{\mathrm{max}} = 65°$ in the four symmetry equivalent octants hkl, $\bar{h}kl$, $h\bar{k}l$ and $hk\bar{l}$ and AASD alum reflections in the six octants hkl, $\bar{h}\bar{k}\bar{l}$, $hk\bar{l}$, $\bar{h}\bar{k}l$, $h\bar{k}\bar{l}$ and $\bar{h}kl$, monitored after every 9 reflections. Reflections with $I < 2.0 \cdot \sigma(I)$ were considered unobserved. The linear absorption coefficients were determined experimentally to be $\mu = 0.206\,\mathrm{mm}^{-1}$ for the MASD alum crystal and $\mu = 0.246\,\mathrm{mm}^{-1}$ for the AASD alum crystal. Again no corrections for absorption were necessary [$(\mu R)_{\mathrm{MASD}} = 0.33$, transmission = 61.5% for $2\theta = 0°$ and 62.0% for $2\theta = 60°$); $(\mu R)_{\mathrm{AASD}} = 0.47$, transmission = 50.3% for $2\theta = 0°$ and 51.2% for $2\theta = 60°$); i.e. the angle-dependent differences in absorption are less than 1%].

A detailed summary of the crystallographic data and of the experimental data concerning X-ray and neutron diffraction for the MASD and AASD alum crystals is given in Table 1.

Structure refinements

a) X-ray diffraction data

Analogous to the technique adopted for the evaluation of the neutron diffraction data of HASD alum (Abdeen, Will and Weiss, 1980) the atomic positions of the skeleton $\mathrm{Al(SO_4)_2 \cdot 12\,H_2O}$ were taken as starting values for Fourier and difference Fourier calculations. Atomic scattering factors $\mathrm{Al^{3+}}$, $\mathrm{S^{\circ}}$ and $\mathrm{O^{\circ}}$ were taken from the International Tables for X-ray Crystallography (1974). In the three-dimensional difference Fourier maps of the MASD alum measurements three peaks could be observed, one at the centre of symmetry, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and two more on the threefold body diagonal at $\pm\,(xxx)$ with $x = 0.45$. These peaks were attributed to the nitrogen and carbon atoms of the $\mathrm{(NH_3CH_3)^+}$ complex. After analysis of the neutron diffraction data a distinction could be made between N at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and C at $\pm\,(xxx)$ in $8(c)$, yielding a statistical distribution for carbon over two crystallographic sites. The neutron diffraction data also gave accurate positions of the hydrogen atoms, so the refinement of the X-ray data was continued with fixed hydrogen positions and anisotropic temperature factors for all non-hydrogen atoms until an agreement index $R = 0.08$ was reached. The decisive step for further improvement of the MASD alum structure was the removal of the nitrogen atom from the centre of symmetry $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ at $4(b)$ to the more general position $\pm$ (xxx) at $8(c)$ with $x = 0.5 \pm 0.015$. This requires statistical distribution also of the nitrogen atoms over two crystallographic sites.

Difference Fourier calculations between the AASD alum data and the $Al(SO_4)_2 \cdot 12\,H_2O$ skeleton revealed a positive peak at the centre of symmetry $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ which can be attributed to the nitrogen atom of the ammonium group. Including the nitrogen atom into the model, a value of $R = 0.13$ was reached. The refinement was then continued analogous the the MASD alum procedure by allowing the nitrogen atom to move out of $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ along the threefold axis. Consequently, the nitrogen atoms in AASD alum are considered as being distributed over two positions related to each other by a centre of symmetry.

At all stages of the AASD alum refinement, the thermal parameters of the oxygen atoms of the SO_4 tetrahedron were large, while the other thermal parameters behaved normally. Therefore a further difference Fourier map has been calculated which clearly revealed two peaks as shown in Figure 1. One peak $O_S(1)'$ lies on the threefold axis on the opposite side of the sulfur atom and the other one $O_S(2)$ in a general position. These peaks form approximately tetrahedral angles with the sulfur atom, implying that the sulfate group is partially inverted about the sulfur atom, i.e. along the threefold axis. However, the sulfur atom is not an inversion centre. The least-squares refinement was continued therefore by including additional $O_S(1)'$ and $O_S(2)'$ positions (xxx and xyz resp.) and a disorder parameter k in the list of variables. The fraction of the oxygen atoms $O_S(1)'$ and $O_S(2)'$ in the

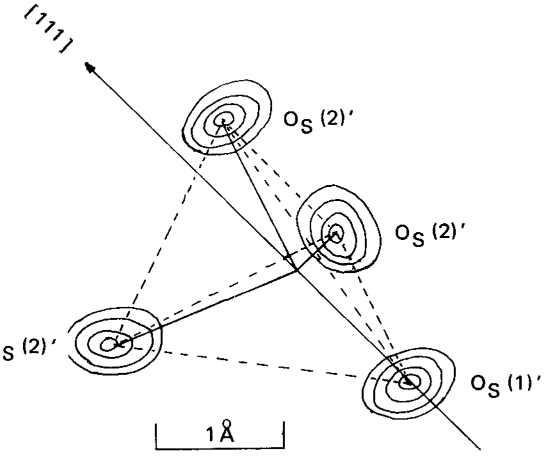

Fig. 1. Projection of difference density showing the "reversed" oxygen atoms $O_3(1)'$ and $O_s(2)'$ in AASD alum

Table 2. Values of w, g and R for X-ray and neutron data refinements

	MASD		AASD	
	X-ray	Neutron	X-ray	Neutron
w (weighting scheme)	0.21 $\|F\| \geq 180$ $0.000005 \cdot F^2$ $+0.0024 \cdot \|F\|$ $+0.001$ $\|F\| < 180$	0.41 $\|F\| \geq 80$ $0.00004 \cdot F^2$ $+0.0019 \cdot \|F\|$ $+0.001$ $\|F\| < 80$	2.5 $\|F\| \geq 50$ $0.0008 \cdot F^2$ $+0.01 \cdot \|F\|$ $+0.002$ $\|F\| < 50$	0.35 $\|F\| \geq 150$ $0.000015 \cdot F^2$ $+0.0001 \cdot \|F\|$ $+0.002$ $\|F\| < 150$
g (secondary extinction coefficient)	$8.0 \cdot 10^{-7}$	$9.8 \cdot 10^{-5}$	$2.6 \cdot 10^{-6}$	$1.2 \cdot 10^{-5}$
R (all reflections)	0.068	0.063	0.053	0.044
R_o (omitting unobserved)	0.043	0.049	0.033	0.025
R_w (all reflections)	0.031	0.029	0.025	0.015
R_{wo} (omitting unobserved)	0.030	0.028	0.024	0.014

"reversed" orientation was labeled k, consequently the fraction of the other oxygen atoms in the "normal" positions is $(1-k)$.

The final least-squares refinements are based on this model. Included are Cruickshanks weighting scheme (1965) with $w = A + B \cdot |F| + C \cdot F^2$ and Zachariasens isotropic extinction correction (1963) according to

$$F_{\text{corr}} = F_c \left[1 + g \left(\frac{1 + \cos^4 2\theta}{1 + \cos^2 2\theta} \right) F_c / \sin 2\theta \right]^{-1/4}.$$

The calculations with the X-ray data resulted in R_w values of 0.030 and 0.024 for MASD and AASD alum respectively (compare Table 2).

b) Neutron diffraction data

Structure factors were first calculated with positional parameters derived from the early X-ray analysis omitting the hydrogen atoms.

For MASD alum the distinguishable neutron scattering lengths of nitrogen ($b_N = 9.94f$) and carbon ($b_C = 6.64f$) were used to differentiate the locations of N and C in the $(NH_3CH_3)^+$ complex. Assuming $b = 6.64f$ for both atoms, the three-dimensional difference Fourier maps revealed a strong positive peak with its centre at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, representing nitrogen due to its higher scattering length. By performing the analogous calculation with $b = 9.94f$ we found two negative peaks on the threefold body diagonal at $\pm$ (xxx) with $x = 0.45$ for the carbon atom. In addition, both difference Fourier maps revealed positions for the hydrogen atoms with negative contours in the nuclear density distribution due to $b_H = -3.72f$ for hydrogen. The following

Table 3. Comparison of the thermal parameters and R values for order ($k = 0$) and partial disorder of the sulfate groups from the neutron diffraction data (k = percentage of $(SO_4)^{2-}$ groups in "reversed" orientation]. The thermal parameters are defined as $B_{ij} = 4a^2\beta_{ij}$ with the temperature factor $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. $B_{equ} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$

	MASD		AASD	
	$k = 0$	$k = 4.3\%$	$k = 0$	$k = 16.9\%$
Thermal parameters for $O_S(1)$ (Å^2)				
B_{11}	4.9	4.3	7.6	5.7
B_{12}	0.3	0.2	0.6	0.1
B_{equ}	4.9	4.3	7.6	5.7
Thermal parameters for $O_S(2)$ (Å^2)				
B_{11}	3.5	3.3	3.4	2.7
B_{22}	7.2	6.7	6.9	5.0
B_{33}	3.0	2.5	4.7	3.2
B_{12}	−2.6	−2.5	2.5	1.8
B_{13}	1.0	0.9	1.8	1.2
B_{23}	−3.0	−2.8	3.6	2.2
B_{equ}	4.6	4.2	5.0	3.6
R values				
R	0.064	0.063	0.064	0.004
R_o	0.051	0.049	0.046	0.025
R_w	0.030	0.029	0.028	0.015
R_{wo}	0.029	0.028	0.026	0.014

refinement was carried out with nitrogen shifted from $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ to $x = 0.5 \pm 0.015$ (taken from the X-ray data).

For the AASD alum the difference Fourier map revealed two orientations of the ammonium group related to each other by the inversion centre in $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Refinement was then started by adding the hydrogen atoms to constitute the water molecules, $\frac{1}{2}$ H on [111] in the position xxx and $\frac{1}{2}$ H in a general position for the hydrogen of the NH_4 group. Isotropic refinement yielded $R = 0.07$.

For the final refinements an isotropic secondary extinction coefficient was included in the list of variables and Cruickshanks (1965) weighting scheme was applied for all observations. With anisotropic vibrational parameters for all atoms including hydrogen we obtained R_w values of 0.029 for MASD alum and 0.026 for AASD alum.

Again, we observed large vibrational parameters for the oxygen atoms of the SO_4 tetrahedron especially for the AASD alum. This means that large thermal parameters are a characteristic feature for the behaviour for the sulfate group in the alums, they are no artefacts. Analogous to the X-ray data

Table 4a. MASD alum: Fractional atomic coordinates (× 10^4) and atomic thermal parameters (× 10^4) with e.s.d.s in parentheses from neutron (upper lines) and X-ray (lower lines) measurements. For hydrogens only neutron results are given

Atom	Wyckoff position	Site	Occupancy	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{equ}
Al	4(*a*)	000	1				30(17)			0			1.8
							37(2)			0			2.3
S	8(*c*)	*xxx*	1	3022(15)			31(16)			−15(20)			1.9
				3020(2)			46(4)			12(2)			2.8
$O_S(1)$	8(*c*)	*xxx*	1	2341(10)			80(11)			6(14)			4.9
				2324(5)			108(5)			−8(5)			6.6
$O_S(2)$	24(*d*)	*xyz*	1	6911(3)	7530(5)	914(4)	57(5)	118(5)	48(5)	−14(5)	17(4)	−51(4)	4.5
				6932(2)	7523(2)	917(2)	65(1)	132(2)	75(2)	−42(2)	18(2)	−65(2)	5.5
N	8(*c*)	*xxx*	$\frac{1}{2}$	5156(11)			44(13)			9(16)			2.7
				5137(16)			56(14)			−4(15)			3.4
H_N	24(*d*)	*xyz*	$\frac{1}{2}$	837(11)	5363(17)	275(19)	12(13)	120(23)	175(24)	10(13)	16(14)	17(19)	6.2
C	8(*c*)	*xxx*	$\frac{1}{2}$	4501(42)			162(31)			−15(37)			9.8
				4504(12)			109(8)			−40(10)			6.6
H_C	24(*d*)	*xyz*	$\frac{1}{2}$	3851(52)	5072(56)	4134(53)							13.2
$O_w(1)$	24(*d*)	*xyz*	1	8521(3)	9810(3)	185(4)	22(5)	44(5)	42(5)	−3(4)	11(4)	2(4)	2.2
				8497(1)	9803(1)	197(1)	36(1)	51(1)	43(1)	−2(1)	4(1)	7(1)	2.6
$O_w(2)$	24(*d*)	*xyz*	1	419(4)	1373(4)	2975(3)	53(6)	56(5)	35(4)	−2(5)	−19(3)	−17(4)	2.9
				420(1)	1351(1)	2965(1)	64(2)	57(2)	57(2)	−1(1)	−7(1)	−4(1)	3.6
H(1)	24(*d*)	*xyz*	1	5423(4)	2018(5)	4728(5)	14(7)	44(7)	63(7)	−18(5)	−9(6)	−1(6)	2.5
H(2)	24(*d*)	*xyz*	1	4132(6)	1846(5)	4502(6)	52(7)	41(6)	59(6)	21(6)	−19(6)	−5(6)	3.1
H(3)	24(*d*)	*xyz*	1	2143(5)	4941(6)	1944(6)	66(9)	74(8)	63(9)	−8(7)	29(6)	23(7)	4.1
H(4)	24(*d*)	*xyz*	1	2148(5)	6103(6)	1697(5)	90(9)	45(8)	63(7)	−5(6)	13(6)	1(7)	4.0

Table 4b. AASD alum: Fractional atomic coordinates (× 10^4) and atomic thermal parameters β_{ij} (× 10^4) with e.s.d.'s in parentheses from neutron (upper lines) and X-ray (lower lines) measurements. The $O_S(1)'$ and $O_S(2)'$ parameters are associated with larger e.s.d.'s due to the small scattering contributions from the oxygen in "reversed" orientation

Atom	Wyckoff position	Site	Occupancy	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{equ}
Al	4(*a*)	000	1.0				32(9) 27(1)			0 0			1.92 1.68
S	8(*c*)	*xxx*	1.0	3111(11) 3083(1)			67(12) 34(1)			12(17) 6(1)			4.02 2.04
$O_S(1)$	8(*c*)	*xxx*	0.831	2385(9) 2401(5)			95(18) 78(4)			1(13) −21(5)			5.69 4.68
$O_S(2)$	24(*d*)	*xyz*	0.831	3137(2) 3130(2)	2640(3) 2652(2)	4199(2) 4199(2)	45(3) 55(1)	83(3) 84(2)	52(3) 45(1)	29(4) 30(2)	20(2) 12(2)	36(3) 33(1)	3.59 3.68
$O_S(1)'$	8(*c*)	*xxx*	0.169	3831(39) 3709(33)			161(70) 149(10)			−77(67) −62(8)			9.65 8.93
$O_S(2)'$	24(*d*)	*xyz*	0.169	2105(13) 2098(8)	3556(28) 3701(11)	2823(16) 2889(8)	58(21) 100(9)	367(52) 218(17)	142(27) 103(9)	72(28) 142(10)	−21(17) 53(7)	90(32) 134(10)	11.33 8.41
N	8(*c*)	*xxx*	0.5	5070(8) 5082(11)			27(4) 48(5)			−13(6) 3(7)			1.62 2.88
$H_N(1)$	8(*c*)	*xxx*	0.5	4389(14)			179(64)			95(77)			10.73
$H_N(2)$	24(*d*)	*xyz*	0.5	4375(7)	4969(18)	5314(7)	116(9)	251(16)	37(10)	−10(14)	28(5)	−54(14)	8.07
$O_w(1)$	24(*d*)	*xyz*	1.0	177(2) 171(1)	−171(2) −162(1)	1530(2) 1520(1)	57(3) 47(1)	22(3) 38(1)	40(3) 27(1)	−10(3) 1(1)	5(2) −3(1)	−11(2) 1(1)	2.38 2.24
$O_w(2)$	24(*d*)	*xyz*	1.0	442(2) 454(1)	1367(2) 1377(1)	2990(2) 2979(1)	63(4) 59(1)	34(3) 47(1)	62(3) 55(1)	−5(3) 5(1)	19(2) −11(1)	−7(3) −9(1)	3.18 3.22
H(1)	24(*d*)	*xyz*	1.0	275(3)	432(3)	2059(3)	56(5)	87(6)	42(5)	−1(4)	−1(3)	6(4)	4.86
H(2)	24(*d*)	*xyz*	1.0	429(3)	9171(3)	1874(3)	85(5)	42(4)	37(3)	7(4)	−35(4)	6(3)	3.28
H(3)	24(*d*)	*xyz*	1.0	−42(4)	1965(3)	2834(4)	90(6)	89(6)	64(5)	12(4)	−21(5)	−5(4)	4.86
H(4)	24(*d*)	*xyz*	1.0	1182(4)	1676(3)	2937(4)	92(6)	85(5)	132(6)	4(5)	−59(5)	−40(5)	6.19

refinement a disorder parameter k was included admitting additional oxygen atoms $O_S(1)'$ and $O_S(2)'$ on positions xxx and xyz respectively around the sulfur atom and hence two orientations of the sulfate group. In the final stage we observed an unessential reduction in the R value for the MASD alum refinement to $R_w = 0.028$, but a decisive improvement of the AASD alum refinement to $R_w = 0.014$. A comparison of the thermal parameters and of the values for R without and with a disorder parameter k for the sulfate oxygen atoms is given in Table 3 for the neutron diffraction data of MASD and AASD alum. The final positional and thermal parameters from both neutron and X-ray data refinements are given in Table 4*a* and 4*b* for MASD and AASD alum respectively. Equivalent isotropic temperature factors B_{equ} calculated from $B_{\mathrm{equ}} = \frac{4}{3}a^2 \cdot (\beta_{11} + \beta_{22} + \beta_{33})$ are included in Tables 4a and 4b for the purpose of comparison with literature values.

Discussion of the structures

a) Common characteristic features

The structures of all alums have common features. Analogous to HASD alum (Abdeen, Will and Weiss, 1980) MASD and AASD alum form ionic structures with positive Al^{3+} ions, negative $(SO_4)^{2-}$ complexes and monovalent cation complexes $(NH_3CH_3)^+$ and $(NH_4)^+$ respectively. Figure 2 depicts a projection of the atomic arrangement of the alum structure; here for MASD alum, where only one orientation of the $(NH_3CH_3)^+$ complex is shown for simplicity. Table 5 lists interatomic distances and angles of interest calculated from the neutron diffraction data of both MASD and AASD alum.

The 12 water molecules are located on two crystallographically different sites surrounding in octahedral coordinations the aluminium ion and the monovalent cation complex. Likewise to other alums the trivalent Al^{3+} is surrounded by an almost regular octahedron of six water molecules, while the remaining six water molecules surrounding the monovalent cation complexes form a highly distorted octahedron, which will be discussed later for MASD and AASD alum separately.

The structural units of the alums are held together by a system of hydrogen bonds between O_S and O_w and between $O_w(2)$ and $O_w(1)$ as indicated in Fig. 2. The various hydrogen bond distances and angles are given in Table 6 comparatively for MASD and AASD alum. The hydrogen bonding is similar to that in other alum types. The hydrogen atoms of the water molecule $H_2O_w(1)$, which is associated with the trivalent cation, form hydrogen bonds with the water molecule $H_2O_w(2)$ and with an $O_S(2)$ atom. The hydrogen atoms of the water molecule $H_2O_w(2)$, which is associated with the monovalent cation complex, link $O_S(1)$ of one sulfate group with $O_S(2)$ of an adjacent sulfate group. Since $O_S(1)$ lies on a threefold axis, it is bonded

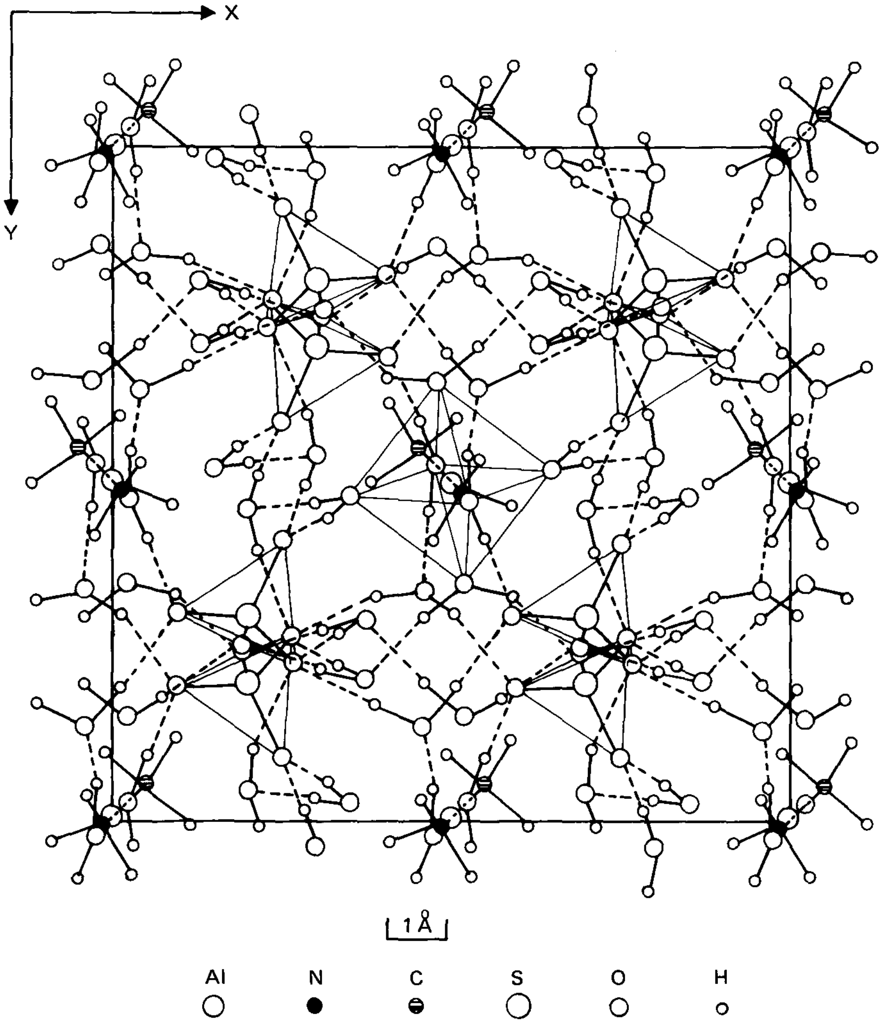

Fig. 2. Projection of the structure of MASD alum. Only one orientation of the monovalent cation complex is shown for simplicity. The hydrogen bonds are indicated by broken lines

simultaneously with three equivalent hydrogen bonds to three different hydrogen atoms H(4). The structural results yield a strong indication that shorter hydrogen bonds tend to be more linear than longer ones.

b) MASD alum

The major part of interest lies in the $(NH_3CH_3)^+$ complex. As has been indicated, we observe a distribution over several sites on and around the

Table 5. Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses from the neutron data refinements using $a_0 = 12.322$ Å for MASD alum and $a_0 = 12.242$ Å for AASD alum

	MASD		AASD	
	Distances	Angles	Distances	Angles
1) Al – $O_w(1)$ octahedron				
Al – $O_w(1)$	1.851(5)		1.897(2)	
$O_w(1) - O_w(1)$	2.634(8)		2.693(1)	
$O_w(1) - O_w(1)$	2.602(7)		2.671(5)	
$\langle O_w(1) - O_w(1) \rangle$	2.618		2.682	
$O_w(1) - Al - O_w(1)$		90.7(1)		90.5(1)
$O_w(1) - Al - O_w(1)$		89.3(1)		89.5(1)
2) Water molecules				
$O_w(1) - H(1)$	1.007(2)		0.989(9)	
$O_w(1) - H(2)$	1.029(12)		0.960(4)	
$H(1) - O_w(1) - H(2)$		106.4(5)		107.4(4)
$H(1) - H(2)$	1.630(5)		1.571(2)	
$O_w(2) - H(3)$	0.929(2)		0.953(2)	
$O_w(2) - H(4)$	0.945(3)		0.984(2)	
$H(3) - O_w(2) - H(4)$		102.8(5)		105.6(5)
$H(3) - H(4)$	1.465(2)		1.543(7)	
$\langle O_w - H \rangle$	0.978		0.972	
$\langle H - O_w - H \rangle$		104.6		106.5
$\langle H - H \rangle$	1.548		1.557	
3) Monovalent cation groups				
$N - O_w(2)$	2.994(1)		2.990(3)	
$O_w(2) - N - O_w(2)$		117.9(1)		115.8(2)
$N - O_w(2)'$	3.159(1)		3.065(5)	
$O_w(2)' - N - O_w(2)'$		108.7(1)		111.5(3)
$C - O_w(2)$	3.481(45)			
$O_w(2) - C - O_w(2)$		95.0(17)		
$C - O_w(2)'$	2.979(7)			
$O_w(2)' - C - O_w(2)'$		119.0(5)		
N – C	1.397(48)			
$N - H_N$	1.026(23)			
$H_N - N - H_N$		110.4(3)		
$C - H_C$	1.159(4)			
$H_C - C - H_C$		112.7(11)		
$C - N - H_N$		108.5(3)		
$N - C - H_C$		106.0(14)		
$N - H_N(1)$			1.15(5)	
$H_N(1) - N - H_N(1)$				115.3(4)
$N - H_N(2)$			0.91(3)	
$H_N(2) - N - H_N(2)$				103.1(4)
$\langle N - H_N \rangle$			1.03	
$\langle H_N - N - H_N \rangle$				109.2

Table 5. (Continued)

	MASD		AASD	
	Distances	Angles	Distances	Angles
4) Sulfate tetrahedron "normal" orientation for AASD also "reversed" orientation (lower lines)				
$S-O_S(1)$	1.454(12)		1.539(5) 1.52(6)	
$S-O_S(2)$	1.448(12)		1.452(7) 1.39(4)	
$O_S(1)-S-O_S(2)$		108.3(14)		108.2(7) 155.8(8)
$O_S(2)-S-O_S(2)$		110.6(13)		110.7(7) 102.8(10)
$O_S(1)-O_S(2)$	2.353(21)		2.423(11) 2.47(4)	
$O_S(2)-O_S(2)$	2.380(1)		2.388(8) 2.18(2)	
$O_S(2)-O_S(1)-O_S(2)$		60.7(6)		59.1(2) 52.3(4)
$O_S(2)-O_S(2)-O_S(1)$		59.6(3)		60.5(2) 63.9(1)
$O_S(2)-O_S(2)-O_S(2)$		60.0		60.0 60.0
$\langle S-O_S \rangle$	1.451		1.496 1.46	
$\langle O_S-O_S \rangle$	2.367		2.406 2.33	
$\langle O_S-S-O_S \rangle$		109.5		109.5 109.2
$\langle O_S-O_S-O_S \rangle$		60.1		59.9 58.7

threefold axis including the nitrogen and carbon atoms. The shift from the centre of symmetry is ± 0.333(11) Å for nitrogen and ± 1.605(42) Å for carbon. The hydrogen atoms H_N and H_C are also distributed statistically around the threefold axis over two sites each in the general positions 24(*d*). This means that the $(NH_3CH_3)^+$ complex is found in two orientations related to each other by a centre of symmetry. This is shown in Figure 3.

In this simple picture the crystal exhibits a centre of symmetry due to the distribution over two sites with equal probability (Fig. 3a). One single unit cell would have no centre of symmetry, but the crystal as a whole is centrosymmetric. As we have discussed previously (Abdeen, Will and Weiss, 1980) there is an alternative. A quantized rotation of the $(NH_3CH_3)^+$ complex around an axis perpendicular to the [111] direction leads in an elastic diffraction experiment to a picture where the atoms are seen simultaneously

Table 6. Interatomic distances (Å) and angles (°) for the hydrogen bonding system with e.s.d.'s in parentheses from the neutron data refinements

Hydrogen bridges	MASD				AASD			
	Distances			Angles	Distances			Angles
A – B ... C	A – B	A – C	B ... C	ABC	A – B	A – C	B ... C	ABC
$O_w(1)-H(1)\ldots O_w(2)$	1.007(2)	2.677(6)	1.671(9)	176.3(11)	0.989(9)	2.616(6)	1.628(2)	176.4(1)
$O_w(1)-H(2)\ldots O_S(2)$	1.029(12)	2.654(8)	1.620(3)	174.3(12)	0.960(4)	2.593(2)	1.640(2)	171.1(6)
$O_w(2)-H(3)\ldots O_S(2)$	0.929(2)	2.749(2)	1.824(1)	173.1(11)	0.953(2)	2.758(2)	1.814(2)	170.4(4)
$O_w(2)-H(4)\ldots O_S(1)$	0.945(3)	2.764(7)	1.831(1)	168.9(12)	0.984(2)	2.786(8)	1.836(6)	160.7(1)
Mean values:	0.978	2.711	1.737	173.2	0.972	2.688	1.730	169.7
$O_w(1)-H(2)\ldots O_S(2)'$					0.960(4)	2.99(3)	2.08(3)	156(1)
$O_w(2)-H(3)\ldots O_S(2)'$					0.953(2)	2.92(2)	2.02(2)	157(1)

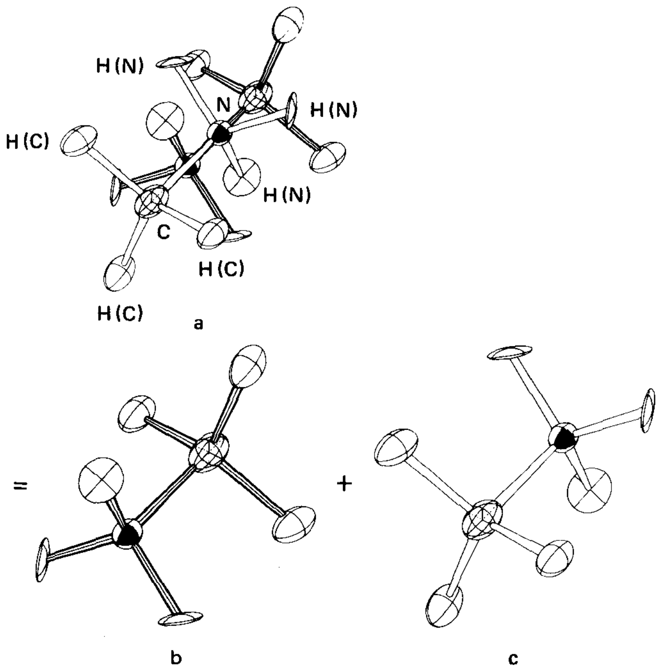

Fig. 3. The $(NH_3CH_3)^+$ complex surrounding the centre of symmetry $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. (*a*) The observed configuration, statistical or dynamical. (*b*) Only one orientation. (*c*) The other orientation generated by inversion of orientation *b*) at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

on two or more crystallographic sites with one half or less occupancy. Statistical and dynamical models are not distinguishable by elastic neutron or X-ray diffraction as has been discussed extensively by Abdeen, Will and Weiss (1980) for HASD alum. Analogous to the argument used for HASD alum we consider also in the case of MASD alum a dynamical model as the most likely one.

Nevertheless, in this picture with quantized jumps over 120° around [111] on three positions we calculate unreasonably high temperature factors for the hydrogen atoms, namely $B_{\mathrm{equ}} = 6.2\,\text{Å}^2$ for H_N and $B_{\mathrm{equ}} = 27.5\,\text{Å}^2$ for H_C despite a good R value of 0.029. A reasonable approach to reduce these high B values is to enlarge the number of rotational positions and consequently diminish the rotational angle. We have persued this in a systematic way up to 120 positions for H_C atoms, principally thus simulating a continuous distribution of the hydrogen atoms H_C in the $(NH_3CH_3)^+$ complex over a ring around [111] (Fig. 4a). As is depicted simultaneously in Fig. 4b the temperature coefficient dropped by this procedure gradually from $B_{\mathrm{equ}} = 27.5\,\text{Å}^2$ with just three positions occupied to $B_{\mathrm{equ}} = 13.2\,\text{Å}^2$ (as is listed in Table 4a). The R value was not improved by this procedure, positional parameters were not allowed to vary.

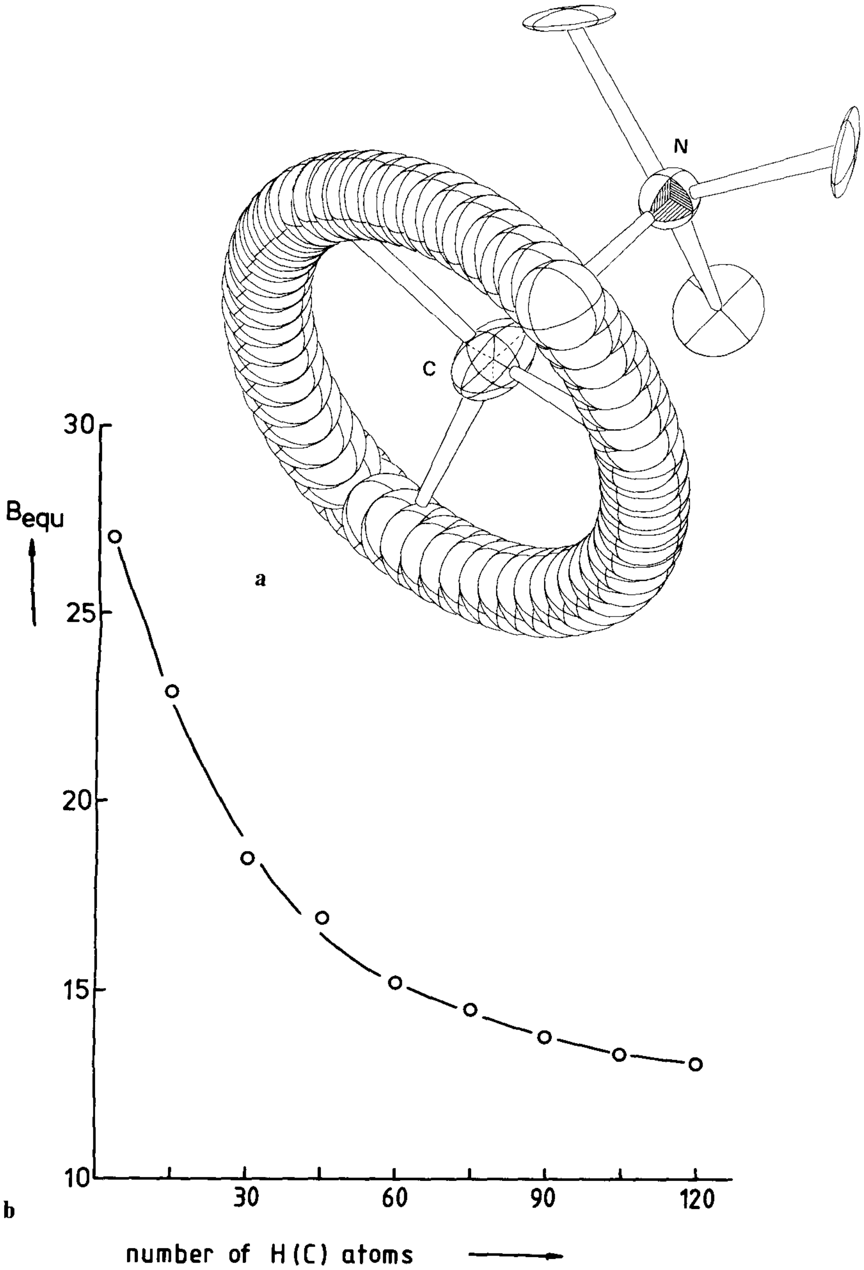

Fig. 4. Distribution of the hydrogen atoms H_C in the $(NH_3CH_3)^+$ complex. (*a*) Simulation of a continuous distribution over a ring around [111]. (*b*) The temperature coefficient B_{equ} ($Å^2$) in dependence of an increased distribution over several sites around [111], thus indicating a continuous smearing or rotation of the H_C atoms

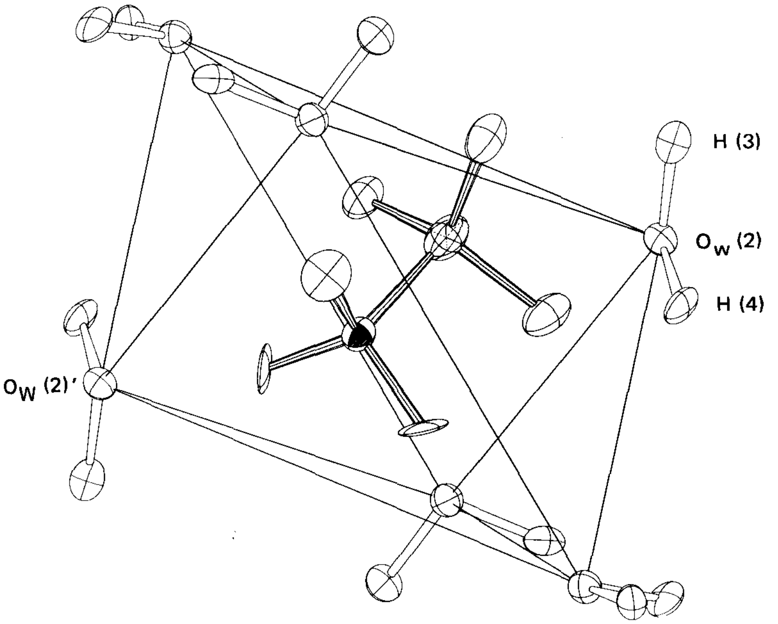

Fig. 5. The distorted octahedron of the six water molecules surrounding the $(NH_3CH_3)^+$ complex. (Only one orientation of the complex is shown)

Within one $(NH_3CH_3)^+$ complex we calculate 1.397(84) Å for the $C-N$ bond with bonding angles H_N-N-H_N = 110.4(3)° and H_C-C-H_C = 112.7(11)°. Six water molecules are surrounding the $(NH_3CH_3)^+$ complex in the form of a distorted octahedron as shown in Figure 5. These six water molecules can be separated into two groups $H_2O_w(2)$ and $H_2O_w(2)'$ being close to the nitrogen or carbon atoms. The distances between nitrogen and oxygen are $N-O_w(2) = 2.994(1)$ Å ($N-O_w(2)' = 3.159(1)$ Å to the second group). The carbon-oxygen distances are $C-O_w(2)' = 2.979(7)$ Å [and $C-O_w(2) = 3.481(45)$ Å]. The distances of H_N and H_C atoms to their nearest oxygen atoms are $H_N-O_w(2) = 1.995(25)$ Å [$H_C-O_w(2)' = 2.329(31)$ Å]. In this group of water molecules we calculate distances of $O_w(2)-H(3) = 0.929(2)$ Å and $O_w(2)-H(4) = 0.945(3)$ Å, which are clearly shorter than similar distances in the water molecules surrounding the aluminium ion. The angle is $H(3)-O_w(2)-H(4) = 102.8(5)$°.

Again, as in HASD alum (Abdeen, Will and Weiss, 1980) and also in other alums studied by other authors (Bacon and Gardner, 1958; Larson and Cromer, 1967; Ledsham and Steeple, 1968a, b, 1969) we observe large thermal parameters for the O_S atoms, namely $B_{equ} = 4.9$ Å^2 for $O_S(1)$ and $B_{equ} = 4.5$ Å^2 for $O_S(2)$ from the neutron data, and 6.6 and 5.5 Å^2 respectively from the X-ray data. An attempt was made to trace these large thermal parameters back to disorder in the structure. This was studied in detail by including a disorder parameter k in the list of variables. The neutron least-squares calculations led to a disorder parameter of only 4.2% with a moderate reduction of the R values and of the thermal parameters.

c) AASD alum

As discussed above, the $(NH_4)^+$ group is found in two orientations related to each other by a centre of symmetry. Both orientations are of equal probability analogous to our findings for $(NH_3CH_3)^+$ in MASD alum and previously for the monovalent cation group $(NH_3OH)^+$ in HASD alum (Abdeen, Will and Weiss, 1980). Within the $(NH_4)^+$ group we find a mean distance of $\langle N-H \rangle = 1.03$ Å and a mean angle $\langle H-N-H \rangle = 109.2°$. It seems to be justified to extend the interpretation of finding $(NH_4)^+$ in two orientations in terms of a quantized flipping between the two orientations (Fig. 6a and 6b).

Likewise to the MASD alum the six water molecules surrounding the $(NH_4)^+$ group form a highly distorted octahedron with distances of $N-O_w(2) = 2.990(3)$ Å $[N-O_w(2)' = 3.056(5)$ Å$]$, while the Al^{3+} ion is surrounded by an almost regular octahedron of six water molecules with mean oxygen distances $\langle O_w(1)-O_w(2) \rangle = 2.682$ Å and $Al-O_w(1)$ distances of 1.897(2) Å.

An essential result of the combined X-ray and neutron diffraction analysis of the AASD alum is the behaviour of the sulfate group. Contrary to the findings for the HASD and MASD alums we can here establish a pronounced disorder of about 17% in the orientation of the $(SO_4)^{2-}$ groups. About 17% of the sulfate tetrahedra are in the "reversed" orientation with respect to the threefold axis. This becomes clear from Figure 7, where both the "normal" and the "reversed" orientation are shown. The corresponding

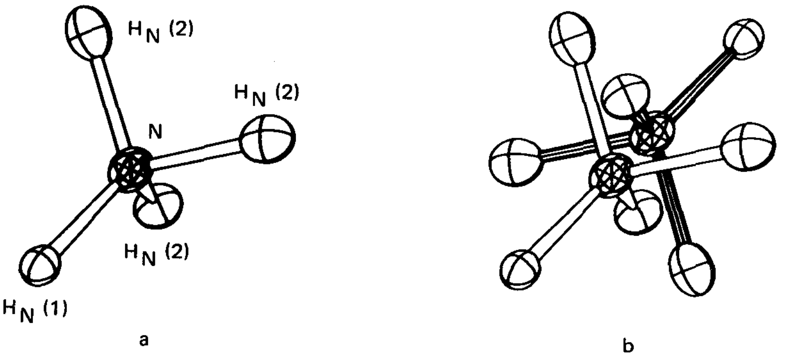

Fig. 6. The $(NH_4)^+$ group. (*a*) Only one orientation. (*b*) The two orientations, which are related to each other by the centre of symmetry at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

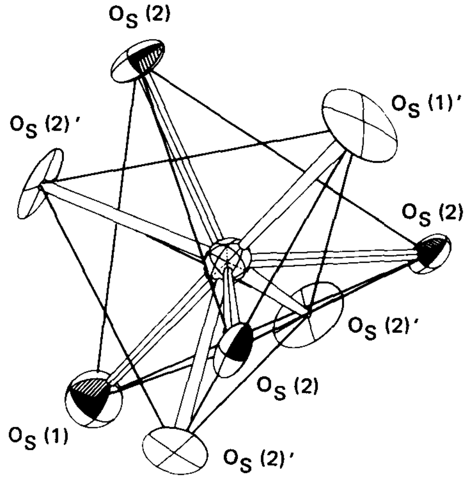

Fig. 7
The sulfate tetrahedron of AASD alum in "normal" (83%) and "reversed" (17%) orientation

degrees of disorder in HASD and MASD alum are only 3.0 and 4.3% respectively. The oxygen atoms $O_S(1)$ and $O_S(2)$ form an almost regular tetrahedron with sulfur in the centre and distances of $O_S(1)-O_S(2) = 2.423(11)$ Å and $O_S(2)-O_S(2) = 2.388(8)$ Å. The "reversed" oxygen atoms $O_S(1)'$ and $O_S(2)'$ form a distorted tetrahedron with distances $O_S(1)'-O_S(2)' = 2.47(4)$ Å and $O_S(2)'-O_S(2)' = 2.18(2)$ Å. Caused by these "reversed" sulfate oxygen atoms occupying a general position there are in AASD alum additional hydrogen bonds between H(2) of $O_w(1)$, H(3) of $O_w(2)$ and $O_S(2)'$ (compare Table 6).

Acknowledgements. We would like to thank Dr. Weiden (Phys. Chem. Inst., TH Darmstadt) for preparation of the MASD alum crystals and E. Jansen (Mineralog. Inst., Univ. Bonn) for assistance in performing the ORTEP plots. This work has been supported by the Bundesministerium für Forschung und Technologie, Bonn, which is gratefully acknowledged. One of the authors (A. M. Abdeen) would like to thank Tanta University, Egypt, for the award of a student fellowship.

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