

Table 6. Relation between the monoclinic and the $P6_322$ hexagonal structures of $BaAl_2O_4$

P1 description of the monoclinic form				Matched P1 description of the $P6_322$ hexagonal form (original coordinates from Table 5)					
				Cell change $a' = c, b' = -a - 2b, c' = -a$					
				Origin shift 0.2405, 0, 0.2507					
				Cell parameters ($\text{\AA}, ^\circ$)					
a	b	c	β	a	b	c	β		
8.438	8.812	5.156	93.14	8.766	9.045	5.222	90.00		
				Atomic coordinates				Deviation parameters of AlO_4^- tetrahedron:	
x	y	z^*		x	y	z		Distance	Turn angle ($^\circ$)
Ba(1)	0.4905	0.0000	0.2507	Ba	0.4905	0.0000	0.2507		
Ba(1')	0.5095	0.5000	0.7493	Ba'	0.4905	0.5000	0.7507		
Ba(2)	1.0292	-0.0071	0.2020	Ba(1)	0.9905	0.0000	0.2507		
Ba(2')	0.9708	0.4929	0.7980	Ba'(1)	0.9905	0.5000	0.7507		
Al(1)	0.1895	0.8314	0.7158	Al(2)	0.1865	0.8333	0.7507	0.03	17.6
Al(1')	0.8105	0.3314	0.2842	Al'(1)	0.7945	0.3333	0.2507	0.04	13.9
Al(2)	0.7997	0.8394	0.7287	Al(1)	0.7945	0.8333	0.7507	0.02	25.3
Al(2')	0.2003	0.3394	0.2713	Al'(2)	0.1865	0.3333	0.2507	0.02	23.0
Al(3)	0.7087	0.6685	0.2236	Al(3)	0.6865	0.6667	0.2507	0.04	20.2
Al(3')	0.2913	0.1685	0.7764	Al'	0.2945	0.1667	0.7507	0.04	16.0
Al(4)	0.6809	0.1707	0.7975	Al'(3)	0.6865	0.1667	0.7507	0.05	21.4
Al(4')	0.3191	0.6707	0.2025	Al	0.2945	0.6667	0.2507	0.06	24.6

* From Schulze & Müller-Buschbaum (1981) for the strontium isomorph.

nizing similarity with the fragment rotations also taken into consideration.

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The Optical Activity and Absolute Optical Chirality of $NaNH_4SO_4 \cdot 2H_2O$

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Abstract

The three independent tensor components of the gyration tensor of a crystal of the orthorhombic

enantiomorphic compound $NaNH_4SO_4 \cdot 2H_2O$, sodium ammonium sulfate dihydrate (SASD), are measured for the first time using the HAUP method. A full structure analysis ($R = 0.03$) has been per-

formed and the *absolute optical chirality* has been determined. The refractive indices and rotatory power have been calculated and an attempt to link the rotatory power to the known structure is made.

Introduction

$\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (SASD) is a well known ferroelectric with a Curie point at 102 K. The structure was first determined by Corazza & Sabelli (1967) to an R -factor of 0.08. SASD crystallizes in the enantiomorphic non-polar space group $P2_12_12_1 (D_2^4)$.

Although other physical properties have been investigated, no attempt has been made hitherto to determine the optical rotation and to link it with the structure. The gyration tensor of the point symmetry group 222 has the form

$$\begin{bmatrix} g_{11} & 0 & 0 \\ 0 & g_{22} & 0 \\ 0 & 0 & g_{33} \end{bmatrix} \quad (\text{Nye, 1979}),$$

and there are no restrictions on the signs of the optical rotation.

Because of the symmetry of the tensor g_{ij} , the maxima of the optical rotation are observed along the crystallographic directions [100], [010] and [001]. Since all of these directions are also linearly birefringent, it is necessary to use a specialized instrument, such as the high-accuracy universal polarimeter (HAUP) (Kobayashi & Uesu, 1983; Moxon & Renshaw, 1990), to determine the rotatory power because the gyration is masked by the much larger birefringence.

A structure analysis ($R = 0.03$) including enantiopole refinement (Flack, 1983) was performed on a fragment of one of the samples used for the optical measurements in order to determine the *absolute optical chirality* (Glazer & Stadnicka, 1989).

Crystal preparation and optical measurements

Colourless crystals of SASD were grown by slow evaporation from aqueous solutions at room temperature. The crystal used measured ca 3 cm and contained large areas of optical quality. Laue back-scattering photographs were used to orient the crystal. Three sections perpendicular to the crystallographic axes [100], [010] and [001] were cut from the same crystal with a diamond wire saw and polished by hand. The thicknesses of the three samples were $t_{[100]} = 0.913$, $t_{[010]} = 0.396$ and $t_{[001]} = 0.508$ mm.

For the measurements of the optical rotation we used the HAUP apparatus constructed by Moxon & Renshaw (1990) and based on the instrument designed by Kobayashi & Uesu (1983), which allows measurements of linear retardation Δ , optical

rotatory power ρ , linear dichroism ϵ and circular dichroism σ . The HAUP apparatus consists of a polarizer-sample-analyser arrangement. By measuring the transmitted intensities as a function of two angles θ (sample stage) and Y (polarizer) and fitting of the data to a biquadratic equation containing θ and Y , the normal mode ellipticity k and hence the optical rotatory power ρ can be extracted.

The transmitted intensity I has the form (see Moxon & Renshaw, 1990)

$$I = \text{base term} + (4\sin^2 \Delta/2)\theta^2 + (-4\sin^2 \Delta/2 + 2E)\theta Y - [(2k - \gamma)\sin \Delta]Y + (1 - E)Y^2,$$

where Δ is the overall retardation given by $\Delta = \delta t$ [δ is the retardation per unit length $\delta = 2\pi(n_o - n_e)/\lambda$, t is the sample thickness], $E = 2\epsilon t$, $\gamma = (p - q)$, p and q are the parasitic ellipticities introduced by the imperfections in the polarizer and analyser.

A few different places on the sample had to be measured before it was possible to obtain solvable results. This is probably due to the variable quality of the surface (water absorption) and a certain amount of twinning. Figs. 1(a-c) show $2k\sin \Delta$ and $\sin \Delta$ curves measured along [100], [010] and [001]. The turning points of the $2k\sin \Delta$ curve were used to calculate the rotatory power $\rho = 2k\Delta n 180/\lambda^\circ \text{ mm}^{-1}$ and the tensor components g_{11} , g_{22} and g_{33} of the axial second rank tensor g_{ij} from the components of the pseudo-scalar gyration vector $G = \bar{n}\rho\lambda/\pi$, where \bar{n} is the mean refractive index [using the refractive indices published by Anistratov & Melnikova (1975)] [Figs. 2(a) and (b)]. The relationship between the refractive indices and the coordinate system is ambiguous in the publication of Anistratov & Melnikova (1975). However, from the published refractive indices and the measured birefringence we can relate with reasonable probability n_α to the a axis, n_β to the b axis and n_γ to the c axis. There is then good agreement between the published and measured birefringences (Table 1). Fig. 3 shows the measured dispersion of the birefringences.

Structure refinement

A small almost spherical piece (radius = 0.14 mm) was cut from the [010] section used for the optical measurements and mounted on a glass fibre. The intensity data were collected on a Stoe-Stadi-4 four-circle diffractometer [$\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$]. The experimental details of the structure analysis are given below and the atomic coordinates with isotropic and anisotropic temperature factors are given in Tables 2(a) and 2(b).

Experimental details: Sodium ammonium sulphate dihydrate, $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$, $M_r = 173.124$, orthorhombic, $P2_12_12_1 (D_2^4)$, $a = 6.253 (1)$, $b = 8.228 (1)$,

$c = 12.856(1) \text{ \AA}$, $V = 661.44(14) \text{ \AA}^3$, $Z = 4$, $D_x = 1.745 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$, $\mu = 47.2 \text{ cm}^{-1}$, $F(000) = 360$, $T = 295(2) \text{ K}$, $R = 0.0303$, $wR = 0.0304$ for 1388 merged reflections with $I > 3\sigma(I)$.

There were 1423 reflections in the unique set. The lattice parameters were determined by the Stoe double-scan method applied to 12 reflections. Two unique sets plus their Bijvoet pairs were collected in the range $3 \leq 2\theta \leq 65^\circ$ (index range $-9 \leq h \leq 9$, $-12 \leq k \leq 12$, $-19 \leq l \leq 19$), giving a total of 5692 reflections.

The equivalent reflections are hkl , $h\bar{k}l$, $\bar{h}kl$, $\bar{h}\bar{k}l$ and $h\bar{k}l$, hkl , $h\bar{k}l$, hkl . The structure factors were

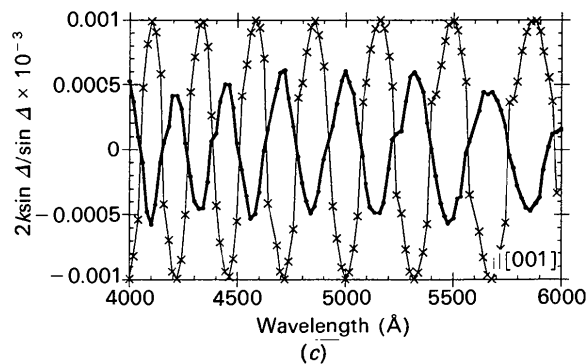
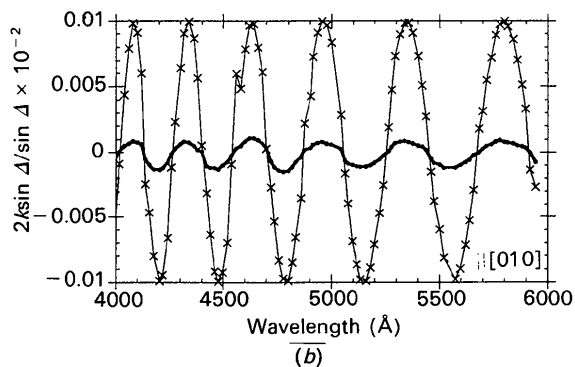
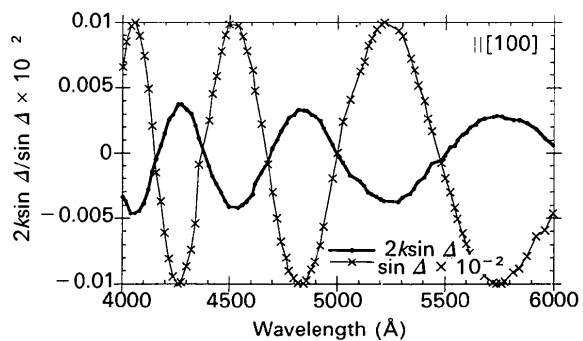


Fig. 1. $2k\sin \Delta$ and $\sin \Delta$ curves along (a) [100], (b) [010] and (c) [001].

Table 1. Comparison of (a) the birefringence and (b) the rotatory power for $\lambda = 5000 \text{ \AA}$, measured and calculated values

(a)						
$\lambda = 5000 \text{ \AA}$	n_α	n_β	n_γ	$n_\alpha - n_\beta$	$n_\alpha - n_\gamma$	$n_\beta - n_\gamma$
Published	1.443	1.458	1.461	0.015	0.018	0.003
Measured				0.016	0.017	0.004
Calculated using OPTACT	1.447	1.470	1.476	0.023	0.029	0.006
(b)						
$\lambda = 5000 \text{ \AA}$	$\rho[100] (\text{^\circ mm}^{-1})$	$\rho[010] (\text{^\circ mm}^{-1})$	$\rho[001] (\text{^\circ mm}^{-1})$			
Measured	-4.0	+6.5	-3.0			
Calculated using OPTACT	-0.3	+2.4	-1.3			

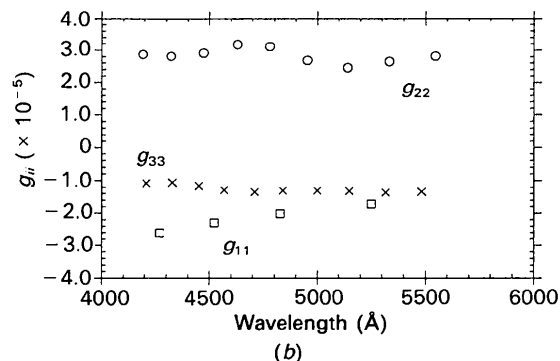
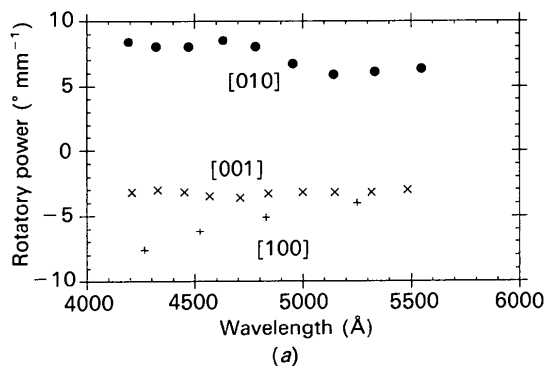


Fig. 2. (a) The optical rotation along [100], [010] and [001] and (b) the three independent gyration tensor components g_{11} , g_{22} and g_{33} of SASD.

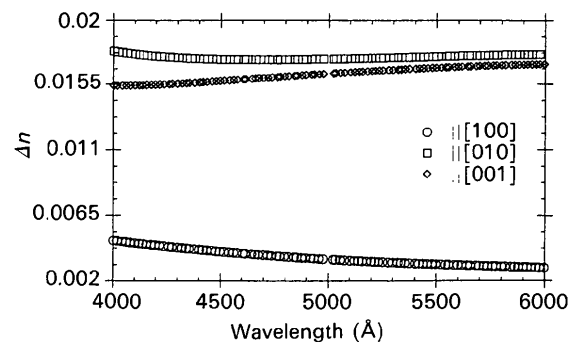


Fig. 3. The dispersion of the birefringence $||[100] (n_\beta - n_\gamma)$, $||[010] (n_\alpha - n_\gamma)$ and $||[001] (n_\alpha - n_\beta)$ of SASD.

Table 2(a). Final fractional coordinates and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s for $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$

$$U_{\text{eq}} = 1/3(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
S	0.3729 (2)	0.0841 (1)	0.1283 (1)	0.0237 (6)
Na	0.9112 (3)	0.2652 (2)	0.4848 (1)	0.028 (1)
O(1)	0.1884 (5)	0.0674 (5)	0.1990 (3)	0.043 (3)
O(2)	0.5732 (6)	0.0652 (5)	0.1882 (3)	0.046 (3)
O(3)	0.3674 (7)	0.2453 (4)	0.0805 (2)	0.049 (3)
O(4)	0.1399 (6)	0.0402 (3)	0.5468 (2)	0.030 (2)
O(5)	0.6896 (5)	0.2118 (5)	0.6352 (3)	0.034 (2)
O(6)	0.6590 (7)	0.0791 (5)	0.4040 (2)	0.035 (2)
N	0.3696 (9)	0.1729 (6)	0.8553 (4)	0.038 (3)
H(1)	0.789 (9)	0.889 (7)	0.160 (3)	0.045 (6)
H(2)	0.85 (1)	0.729 (7)	0.172 (4)	0.045 (6)
H(3)	0.392 (9)	0.600 (8)	0.142 (3)	0.045 (6)
H(4)	0.38 (1)	0.486 (6)	0.080 (4)	0.045 (6)
H(5)	0.85 (1)	0.38 (1)	0.189 (6)	0.10 (1)
H(6)	0.78 (1)	0.329 (9)	0.101 (6)	0.10 (1)
H(7)	0.94 (1)	0.24 (1)	0.136 (5)	0.10 (1)
H(8)	0.75 (1)	0.26 (1)	0.171 (5)	0.10 (1)

Table 2(b). Anisotropic thermal parameters (\AA^2) for $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	0.0297 (6)	0.0199 (4)	0.0215 (5)	-0.0031 (6)	0.0007 (6)	0.0008 (6)
Na	0.0229 (9)	0.031 (1)	0.0290 (9)	-0.0003 (8)	0.0020 (8)	0.0025 (9)
O(1)	0.042 (2)	0.050 (3)	0.037 (2)	-0.005 (2)	0.014 (2)	-0.005 (2)
O(2)	0.041 (2)	0.051 (2)	0.038 (2)	-0.018 (2)	-0.016 (2)	0.006 (2)
O(3)	0.081 (3)	0.021 (2)	0.042 (2)	0.001 (2)	0.000 (2)	0.000 (3)
O(4)	0.035 (2)	0.026 (2)	0.031 (2)	0.012 (1)	0.009 (2)	-0.001 (2)
O(5)	0.038 (2)	0.035 (2)	0.028 (2)	-0.004 (2)	-0.003 (2)	0.003 (2)
O(6)	0.055 (3)	0.024 (2)	0.031 (2)	0.001 (2)	-0.010 (2)	-0.002 (2)
N	0.040 (3)	0.044 (2)	0.031 (3)	-0.003 (2)	-0.002 (3)	0.002 (3)

averaged from two symmetry-equivalent reflections ($hkl + \bar{h}\bar{k}\bar{l}$ and $\bar{h}\bar{k}\bar{l} + hkl$). The intensities of three standard reflections (0 $\bar{1}$ 5, $\bar{1}$ 34, 006) were measured every 60 min. An absorption correction based on a Ψ -scan with nine reflections was carried out.

The data reduction was performed by REDU4 (Stoe & Cie, 1988) to a merging R -factor of 0.023. The refinement was initiated using the model based on that given by Corazza & Sabelli (1967) (we re-ordered the axes according to their magnitudes without changing the hand of the structure). This converged using CRYSTALS (Watkin, Carruthers & Batteridge, 1985) to the R -factor 0.0303. The atomic coordinates, anisotropic temperature factors of the Na, N, O and S atoms, isotropic temperature factors of the H atoms and the enantiopole parameter were refined by least-squares. The Flack enantiopole parameter x is defined by

$$|F(h)|^2 = (1 - x)|F(h)|^2 + x|F(-h)|^2,$$

where x is an indicator which gives the contribution of the two enantiomers to the structure (Flack, 1983). x is not highly affected by other errors in the data collection. A refined enantiopole parameter of zero indicates that the chirality of our input model is the right one. Another method of distinguishing

between the two enantiomers is to compare the signs of the Bijvoet pair percentage intensity differences

$$\Delta\% = \{[F^2(hkl) - F^2(\bar{h}\bar{k}\bar{l})]/\frac{1}{2}[F^2(hkl) + F^2(\bar{h}\bar{k}\bar{l})]\} \times 100\%$$

for those with calculated structure-factor differences larger than the R -value. We compared 34 pairs with a calculated structure-factor difference greater than 3%. 30 pairs (88.2%) show the same sign of Bijvoet differences although they differed in magnitude (Table 3), possibly as a result of twinning. One of the reflection pairs (4,10,1) with opposite signs was indicated as not being in good agreement with the calculated structure factors, and the remaining three were relatively weak reflections. The difference in magnitude was also observed by Stadnicka, Glazer & Moxon (1985) and Thomas (1987) in α -LiIO₃ and α -TeO₂, although we did not observe that the observed structure-factor differences tend to be in general slightly higher than those calculated.*

Discussion

From our optical measurements we find a positive (*dextro*) rotation for light transmitted along [010] and negative (*laevo*) rotations along [100] and [001] in the particular crystal used here. Although a 2₁-screw axis itself is not a chiral axis, the space group $P2_12_12_1$ can show two enantiomorphic forms – left-handed and right-handed – which cause a different sense of rotation. Figs. 4(a–c) show a projection of the crystal structure along the [100] axis, together with the refined thermal ellipsoids.

To calculate the refractive indices and the rotatory power we used the program OPTACT (Devarajan & Glazer, 1986), which calculates the rotatory power and refractive indices from atomic parameters and assigned isotropic electronic polarizability volumes. This program works out the electric field interactions between all the atoms in the structure and constructs anisotropic polarizabilities based on these interactions. It has been successfully applied to many uniaxial crystal structures [for example, see Ortega, Etxebarria & Brezowski (1993); Stadnicka, Madej, Tebbutt & Glazer (1992)] and so forms a useful basis for calculating the optical properties of a biaxial crystal such as SASD. As a starting point we chose values of isotropic polarizability volumes from Tessman, Kahn & Shockley (1953) for the O, NH₄⁺ ion and the Na atoms: O²⁻ = 2.0 \AA^3 , Na⁺ = 0.3 and NH₄⁺ = 2.05 \AA^3 , together with the atomic parameters

* List of structure factors has been deposited with the IUCr (Reference: AL0574). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bijvoet pair percentage intensity differences of Bijvoet pairs with a calculated structure-factor difference of $> 3\%$

$hkl/\bar{h}\bar{k}\bar{l}$	$ F_o ^2$	ΔF_o^2 (%)	ΔF_c^2 (%)	$hkl/\bar{h}\bar{k}\bar{l}$	$ F_o ^2$	ΔF_o^2 (%)	ΔF_c^2 (%)
131	3025	-7.3	-10.6	215	8100	4.4	9.0
331	676	30.6	25.4	615	3136	7.1	7.4
351	756	-21.8	-16.3	645	930	-6.6	-6.6
171	2601	7.8	7.7	675	1156	11.8	6.3
4,10,1	1190	-17.4	6.2	416	4900	-5.7	-8.5
512	1122	-17.9	-6.2	148	1560	-5.1	-9.3
222	9801	8.1	8.0	168	756	21.8	-6.6
342	1098	12.1	13.3	178	2070	-4.4	-8.9
382	552	8.5	-8.5	419	650	-15.5	-8.2
313	1332	5.5	12.9	429	1936	-9.1	-8.7
243	676	15.4	7.5	5,4,10	870	-6.8	-7.0
253	3660	9.9	6.6	2,1,11	1190	-5.8	-11.1
563	784	-14.3	-7.3	1,4,11	3844	6.4	6.4
373	1089	12.1	13.3	5,4,11	1332	5.5	6.6
114	5112	8.4	9.2	4,2,13	930	19.6	6.8
514	2652	11.6	7.8	1,6,14	812	7.0	7.8
174	2209	17.0	8.7	4,2,15	1296	-11.1	6.3

from our structure refinement. Table 4, model 1, shows the results assuming a wavelength of 5000 Å. It can be seen that there is a reasonable agreement (to within ± 0.02) between the published and calculated refractive indices. The calculated optical rotations are significantly smaller than those measured, especially for the [100] direction, although it is encouraging to note that the program immediately has given the correct signs of rotation.

Attempts were made to obtain better agreement between the magnitudes by varying the input polarizability volumes within acceptable limits [$O^{2-} = 0.5\text{--}3.2 \text{ \AA}^3$ and $NH_4^+ = 1.5\text{--}2.5 \text{ \AA}^3$, according to

Tessman, Kahn & Shockley (1953)]. Table 4 summarizes some of these calculations. Different polarizability volumes were allowed for water O atoms and sulphate O atoms and the NH_4^+ ion was assumed to have a polarizability volume centred on the N atom. Since the polarizability of sodium is small, it was kept constant at its literature value of 0.3 \AA^3 , so that only three parameters were varied in all.

It was found that the refractive indices and the birefringences were not very much affected by any reasonable variation of the polarizability volumes. An increase in the sulphate O and a decrease in the water oxygen resulted in a slight increase of all the refractive indices. A low polarizability volume for the NH_4^+ ion made $\rho[100]$ more negative and $\rho[001]$ more positive, whereas $\rho[010]$ was almost unaffected. A high polarizability volume for the NH_4^+ ion made $\rho[100]$ more negative, but $\rho[010]$ and $\rho[001]$ became more positive. Finally, giving a high polarizability volume to the water O resulted in $\rho[100]$ becoming positive and $\rho[010]$ and $\rho[001]$ becoming negative. Assigning different polarizabilities to O within the same group – between 1.8 and 2.2 \AA^3 – showed that they behaved slightly differently, but the signs of the rotation did not change. Treating the SO_4^{2-} tetrahedron as a unit gave good agreement with the refractive indices, but the wrong signs of rotation. It was not possible without relaxing the constraints used, and hence increasing the number of free variables, to achieve better agreement between the measured and calculated magnitudes of the rotatory power, the calculated values always remaining lower than the measured ones. This is not surprising, given the complexity of the crystal structure, in which all the atoms are in general positions, and therefore we need, for calculation purposes, to simplify the model. Despite this, it is encouraging that *OPTACT* successfully gave signs of ρ in agreement with our HAUP measurements using just the literature values of the

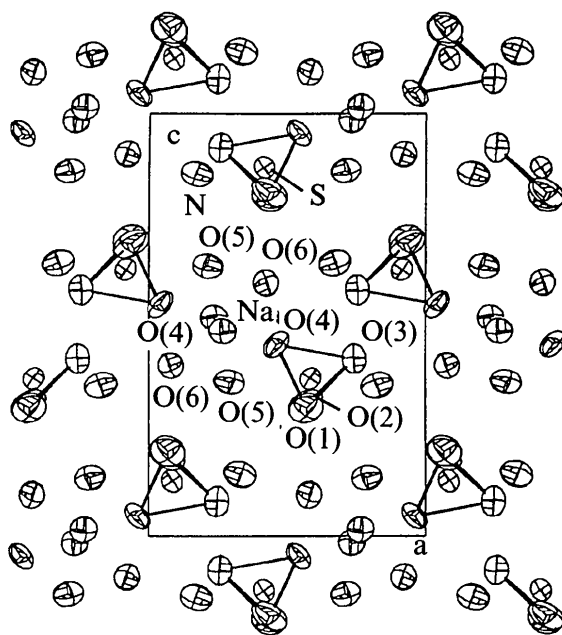


Fig. 4. Projection of the structure of SASD with thermal ellipsoids on (100).

Table 4. Results of calculations of refractive indices and optical rotatory power along [100], [010] and [001]

Model No.	Polarizability volumes [\AA^3]				n_α	n_β	n_γ	ρ ($^\circ \text{mm}^{-1}$)
	O(1)-O(4)	(O5)-(O6)	NH_4	Na				
1	2.0	2.0	2.0	0.3	1.4467	1.4704	1.4762	-0.3 +2.4 -1.3
2	2.0	2.0	1.5	0.3	1.4473	1.4717	1.4816	-0.9 +2.1 -0.6
3	2.0	2.0	2.5	0.3	1.4465	1.4696	1.4720	+0.2 +2.4 -1.8
4	2.0	0.5	2.0	0.3	1.4727	1.4777	1.4863	+2.2 +5.8 -0.6
5	2.0	3.2	2.0	0.3	1.4409	1.4707	1.4748	+0.6 +1.3 -1.9
6	0.5	2.0	2.0	0.3	1.4513	1.4554	1.4715	+1.8 +0.8 -1.0
7	3.2	2.0	2.0	0.3	1.4589	1.4773	1.4855	-1.5 +3.0 +0.9

polarizability volumes, even to the extent of agreeing that $\rho[010]$ should be largest. Fig. 5 shows a projection along [100] of the SASD structure in which anisotropic polarizability ellipsoids calculated for model 1 in Table 4 have been plotted by *OPTACT*.

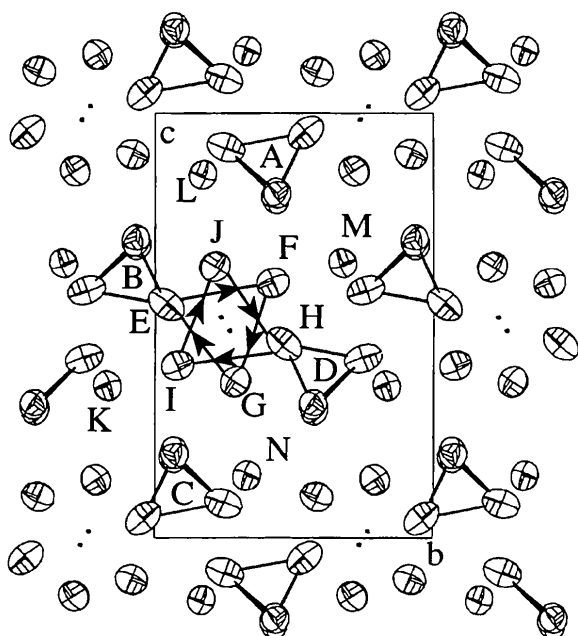


Fig. 5. Projection of the structure of SASD with polarizability ellipsoids as calculated with *OPTACT* on (100). The following helical arrangements are found: $RS1/4$ containing sulphate groups $ABCD$; $LS1/4$ containing NH_4 groups $KLMN$; two $LS1/3$ helices containing sulphate and water O-atoms EFG (fractional heights $x = 0.14, 0.16, 0.19$) and HIJ (fractional heights $x = 0.64, 0.66, 0.69$).

Finally, it is worth considering the role played by different structural units in determining the signs of the optical rotation. An approach that has proved successful in the past has been that of Glazer & Stadnicka (1986), who showed that the sense of optical rotation was usually determined by helical arrangements of anisotropically polarizable atoms. The closer together the atoms concerned, the greater the effect on the optical rotation. When atoms on a helix are polarizable more easily towards the centre of a helix, the plane of polarization of the light rotates in the opposite sense to the hand of the helix: when atoms are polarizable tangentially to the helix, the sense of optical rotation is the same as that of the helix. These simple rules seem to work in almost all cases, although when strong linear birefringence is also present they may not be so clear-cut.

The first thing to note is that, on comparing Figs. 4 and 5, generally speaking the thermal ellipsoids are seen to be perpendicular to the polarizability ellipsoids: this has been noted for other structures by Glazer & Stadnicka (1986) and results from the fact that atoms tend to vibrate more easily towards spaces between atoms, whereas polarizability tends to be largest towards other polarizable atoms.

For the (100) section (Figs. 4 and 5), it is possible to find a right-hand helix of four sulphate groups $ABCD$ [$RS1/4$ in the notation of Glazer & Stadnicka (1986)], two left-hand $LS1/3$ helices of water and sulphate O atoms EFG and HIJ , and a left-hand $LS1/4$ helix $KLMN$ of four NH_4 groups. The $LS1/3$ helices only extend a short distance along [100], with fractional heights of 0.14, 0.16 and 0.19 for EFG and 0.64, 0.66 and 0.69 for HIJ , and have their polarizability ellipsoids directed inwards to the

helix axes, thus contributing a rotation in the opposite sense, *i.e.* laevorotatory. The $RS1/4$ sulphate helix also contributes optical rotation in a laevorotatory sense, but because of the larger sulphate-sulphate distances, to a much lesser extent. The counteracting effect of the NH_4 helix is also small because of the greater NH_4 to NH_4 distances. Models 1 and 2 of Table 4 show that on reducing the polarizability of NH_4^+ , the optical rotation is increased, thus showing how they act in an opposite sense with respect to the other helices as far as the optics is concerned. Thus, despite the complexity of this structure, the simple theory seems to work well for the (100) section, which is also the section with the smallest linear birefringence.

It is far more difficult to apply the simple theory to the (010) and (001) sections, as these have large linear birefringences, which dominate over the optical rotation. While it is possible to find some evidence of helical arrangements of polarizable atoms in these sections, it is, therefore, far from clear how they relate to the sense of optical rotation.

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Structure of the Hofmann Clathrates $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6D_6$ and $Zn(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$

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Abstract

Rietveld analyses of the neutron powder diffraction patterns of $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6D_6$ and $Zn(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ have been performed. The space

group $P4/m$ is confirmed for $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6D_6$ with $a = 7.2196$, $c = 8.1007$ Å at 25 K, $a = 7.2358$, $c = 8.3104$ Å at 300 K. The same space group is found for $Zn(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ with $a = 7.3294$, $c = 8.0722$ Å at 25 K. The effects of