The two N–D distances in the ND_4 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 ND_4 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 ND_4 group perhaps has to move very little to accommodate the reversed $O_8(1)$ 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 ND_4 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 ND_4 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 [14*L* (7 7) and 24*L* (7 5 5 7)] have unit-cell dimensions identical with those of structures previously reported [14*L* (5 4 2 3) and 24 $L(5\ 3)_3$ 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

experimental and computational methods, were very similar to those presented by Brafman, Alexander & Steinberger (1967).

14*L* *polytype*

The (21.*l*) column is reproduced in Fig. 1. Table 1 shows the comparison of observed intensities with that of the only fitting sequence (7 7). Thus the *ABC* sequence (Ramsdell, 1947) is

ABCABCACBACBAC .

On hexagonal axes

$a = 3{\cdot}82$, $c = 43{\cdot}82$ Å .

The hexagonal unit cell has:

14 Zn at 0,0,0 r,s,z $s,r,2z$ 0,0,3z $r,s,4z$ $s,r,5z$ 0,0,6z $s,r,7z$ $r,s,8z$ 0,0,9z $s,r,10z$ $r,s,11z$ 0,0,12z $s,r,13z$

where $z = \frac{1}{14}$, $r = \frac{1}{3}$, $s = \frac{2}{3}$ and

14S, one above each Zn, at a distance $p = \frac{3}{56}$. Their coordinates are 0,0,p plus the coordinates of the corresponding *Zn* atoms.
Percentage of hexagonality: $\alpha = 14{\cdot}3$.
Birefringence: $\Delta n = 3{\cdot}5 \times 10^{-3}$.

Table 1. *Comparison of calculated and observed intensities for the* 14*L* (7 7) *polytype*

l	Calc.	Obs.
0	4112	*s*
1	1533	*vw*
2	6643	*s*
3	4719	*s*
4	80007	*vvs*
5	105564	*vvs*
6	22073	*vs*
7	3282	*w*
8	10515	*s*
9	28890	*vs*
10	18136	*s*
11	1217	*vw*
12	2213	*vw*
13	672	*a*

The observed intensities were symmetrical with respect to the zero layer ($l = 0$).

18*L* *polytype*

The (10.*l*) column is represented in Fig. 2. It was inferred from the distances between the spots and from the position of the zero layer that this was a rhombohedral 18*L* polytype; only sequences having rhombohedral symmetry were considered for the computations. Table 2 shows the comparison of the observed intensities with the only fitting sequence $(4\ 2)_3$. The *ABC* sequence is

ABCACBCABCBABCABAC .

On hexagonal axes

$a = 3{\cdot}82$, $c = 56{\cdot}34$ Å .

The hexagonal unit cell has:

6 Zn at 0,0,0 0,0,3z 0,0,7z 0,0,11z 0,0,14z 0,0,16z
6 Zn at $\frac{2}{3},\frac{1}{3},\frac{1}{3}$ plus the above coordinates
6 Zn at $\frac{1}{3},\frac{2}{3},\frac{2}{3}$ plus the above coordinates

where $z = \frac{1}{18}$ and

18S, one above each Zn at a distance $p = \frac{1}{24}$. Their coordinates are 0,0,p plus the coordinates of the corresponding Zn atoms.
Percentage of hexagonality: $\alpha = 33{\cdot}3$.
Birefringence: $\Delta n = 8{\cdot}3 \times 10^{-3}$.

Table 2. *Comparison of calculated and observed intensities for the* 18*L* $(4\ 2)_3$ *polytype*

l	Calc.	Obs.		Calc.	Obs.	Further observed relations between intensities
1	50104	*s*	$\bar{2}$	7474	*vw*	$10 > 7 \simeq 4$
4	77703	*s*	$\bar{5}$	287428	*vvs*	$4 > 1$
7	82537	*s*	$\bar{8}$	194083	*vs*	
10	108415	*s*	$\bar{11}$	28014	*w*	

24*L* *polytype*

The (21.*l*) column is represented in Fig. 3. Only Zhdanov sequences consisting of four elements were considered, as only these are compatible with the α values obtained from the observed birefringence (Brafman, Alexander & Steinberger, 1967). Table 3 shows the comparison of observed intensities with those of the only fitting sequence (7 5 5 7). The *ABC* sequence is

ABCABCACBACBCABCACBACBAC .

On hexagonal axes

$a = 3{\cdot}82$, $c = 75{\cdot}12$ Å .

The hexagonal unit cell has:

24 Zn at 0,0,0 r,s,z $s,r,2z$ 0,0,3z $r,s,4z$ $s,r,5z$ 0,0,6z $s,r,7z$ $r,s,8z$ 0,0,9z $s,r,10z$ $r,s,11z$ $s,r,12z$ 0,0,13z $r,s,14z$ $s,r,15z$ 0,0,16z $s,r,17z$ $r,s,18z$ 0,0,19z $s,r,20z$ $r,s,21z$ 0,0,22z $s,r,23z$

where $z = \frac{1}{24}$, $r = \frac{1}{3}$, $s = \frac{2}{3}$ and

24S, one above each Zn at a distance $p = \frac{1}{32}$. Their coordinates are 0,0,p plus the coordinates of the corresponding Zn atoms.
Percentage of hexagonality: $\alpha = 16{\cdot}7$.
Birefringence: $\Delta n = 4{\cdot}2 \times 10^{-3}$.

36*L* *polytype*

The (21.*l*) column is represented in Fig. 4. The distances between the spots and their position with respect to the zero layer yielded the information that the observed structure has rhombohedral symmetry; only sequences having this symmetry were considered for the computation. Table 4 shows the comparison of the observed intensities with the only fitting sequence $(6\ 2\ 2\ 2)_3$.

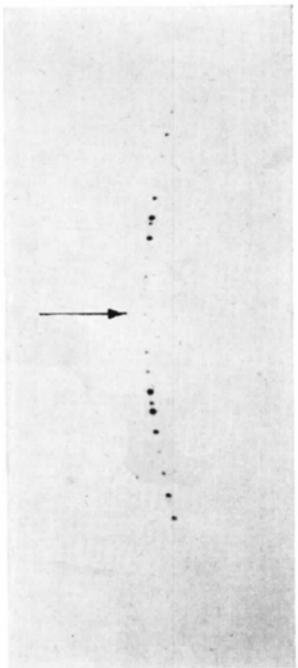

Fig. 1. (21. *l*) column of an oscillation photograph around the *c* axis of the 14*L* polytype. Cu $K\alpha$ radiation, 60 mm dia. camera, collimator 0·1 mm. The position of the zero layer is indicated by an arrow. Some spots belonging to an adjacent higher polytype are also seen (×3).

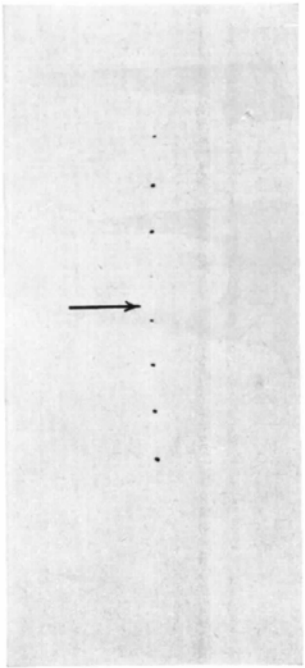

Fig. 2. (10. *l*) column for the 18*L* (rhombohedral) polytype, collimator 0·1 mm.

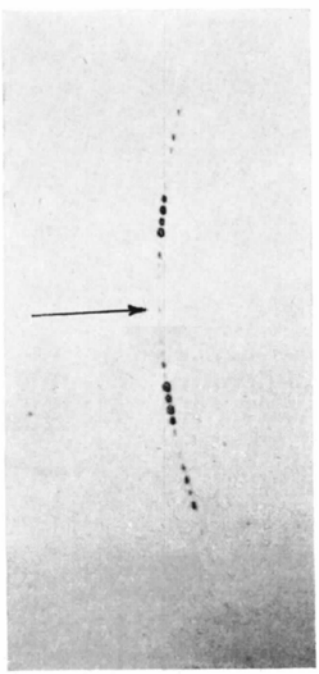

Fig. 3. (21. *l*) column for the 24*L* (7 5 5 7) polytype; collimator 0·4 mm.

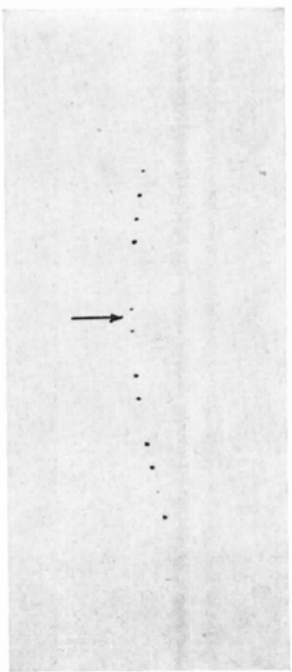

Fig. 4. (21. *l*) column for the $36L$ $(6\,2\,2\,2)_3$ polytype; collimator 0·1 mm.

[*To face p.* 806

Table 3. *Comparison of calculated and observed intensities for the* 24 *L*(7 5 5 7) *polytype*

l	Calc.	Obs.	Further observed relations between intensities
0	11848	*w*	$0>3\simeq4$
1	4467	*vw*	$4>6\simeq13$
2	822	*a*	$5>14$
3	9430	*w*	$7>9$
4	10360	*w*	$8>10$
5	28032	*s*	$11>13$
6	8712	*w*	$17\simeq15>14$
7	224506	*vvs*	
8	87986	*vs*	
9	168355	*vvs*	
10	67189	*vs*	
11	14848	*w*	
12	3175	*vw*	
13	9573	*w*	
14	28892	*s*	
15	52026	*s*	
16	21939	*w*	
17	51653	*s*	
18	2074	*a*	

The observed intensities were symmetrical with respect to the zero layer ($l=0$).

Table 4. *Comparison of calculated and observed intensities for the* 36*L* (6 2 2 2)$_3$ *polytype*

l	Calc.	Obs.	*l*	Calc.	Obs.	Further observed relations between intensities
2	113252	*w*	$\bar{1}$	98018	*w*	$17>20$
5	7778	*a*	$\bar{4}$	868	*a*	
8	264459	*s*	$\bar{7}$	8696	*vw*	
11	186264	*w*	$\bar{10}$	978728	*vvs*	
14	9614	*a*	$\bar{13}$	281988	*s*	
17	287051	*s*	$\bar{16}$	440683	*vs*	
20	247545	*s*	$\bar{19}$	214106	*w*	
23	80458	*vw*				

The *ABC* sequence is

ABCABCBABCBABCABCACBC-
ACBCABCABACABAC .

On hexagonal axes

$$a=3{\cdot}82\,, \quad c=112{\cdot}68\ \text{Å}\,.$$

The hexagonal unit cell has:

12 Zn at 0,0,0 0,0,3*z* 0,0,7*z* 0,0,11*z* 0,0,14*z*
0,0,17*z* 0,0,21*z* 0,0,25*z* 0,0,28*z*
0,0,30*z* 0,0,32*z* 0,0,34*z*

12 Zn at $\frac{1}{3},\frac{2}{3},\frac{1}{3}$ plus the above coordinates.
12 Zn at $\frac{2}{3},\frac{1}{3},\frac{2}{3}$ plus the above coordinates.

where $z=\frac{1}{36}$ and

36S, one above each Zn at a distance $p=\frac{1}{48}$. Their coordinates are 0,0,*p* plus the coordinates of the corresponding Zn atoms.
Percentage of hexagonality: $\alpha=33{\cdot}3$.
Birefringence $\Delta n=8{\cdot}4\times10^{-3}$.

Discussion

Among the four crystal structures reported in the present work, two [14*L* (7 7) and 24*L* (7 5 5 7)] are of the same cell dimensions as previously determined structures [14*L* (5 4 2 3) and 24*L* (5 3)$_3$, (Brafman, Alexander & Steinberger, 1967)]. The structures, however, differ in the stacking order of the sequences. Similar cases, *i.e.* polytypes having the same unit-cell dimensions but differing in layer sequence, are known for SiC as well (*e.g.* Krishna & Verma, 1965).

The structures identified here do not seem to have known SiC counterparts; moreover they are not expected to exist on the basis of Krishna & Verma's (1965) theory for polytypism in SiC. The need for a theory on polytypism in ZnS is again stressed by this fact.

One way of polytype formation in ZnS has been described recently (Mardix & Steinberger, 1966). It was reported that in ZnS crystals a tilt of external faces is often observed, though the orientation of the *c* axis is the same throughout the crystal. At the plane where the tilt begins, the structure changes as well. It was also demonstrated that the tilt and the corresponding structure change could be induced by applying mechanical stresses to the crystal.

It is, however, not yet known to what extent this mechanism is a common one in polytype formation. It is hoped that structure determinations of further polytypes will facilitate solving this and other problems of ZnS polytypism.

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