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New ZnS Polytypes of the Family 18L

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Abstract

ZnS crystals having wide polytypic regions were grown in sublimation. Twelve new polytypes of the family 18L were identified in one specimen. X-ray 10. *l* oscillation photographs are presented, the observed and calculated intensities are compared. A modified expression for intensity computations of rhombohedral polytypes is described.

Introduction

ZnS crystals grown by sublimation of a large number of adjacent regions stacked along their common *c* axis. Most of these regions are faulted 2H structures. A small number of specimens contain uniform polytypic regions, most of them less than 100 μm wide (along their *c* axis), wider regions are rare and regions of 500 μm are extremely rare (Alexander, Kalman, Mardix & Steinberger, 1970).

Experimental

The polytypes reported here were found in a platelet (specimen 17-1) grown by the static sublimation method (Pátek, 1961) with strict stabilization of temperature (± 0.02 K) and pressure (± 100 Pa) during growth. A peculiar characteristic of the crystals is the abundance of specimens with wide uniform polytypic regions: tens of specimens were found in each growth batch containing polytypic regions of 500 μm and wider.

* In partial fulfilment of requirements for the BS degree.

Cu *K* α radiation was used to take the 10. *l* row lines 10° *c*-axis oscillation photographs of the polytypes. These are presented in Fig. 1. A list of all currently identified ZnS polytypes of the family 18L is given in Table 1. Observed and calculated intensities of the 10. *l* reflections of the new polytypes are compared in Table 2. The calculated intensities are proportional to $|F|^2$, where *F* is the structure factor: they include the Lorentz and polarization factors and are normalized to give the strongest intensity as 100.000.

The method of identification used is the 'elimination method' reported previously (Mardix, Kalman & Steinberger, 1970).

The structure factor of rhombohedral polytypes

The expression for the structure factor of a ZnS polytype commonly used in computations is given by (Mardix, Kalman & Steinberger, 1970):

$$|F_{hk.l}|^2 = f^2 |\varphi_{hk.l}|^2$$

where

$$f^2 = f_{\text{Zn}}^2 + f_{\text{S}}^2 + 2f_{\text{Zn}} f_{\text{S}} \cos \frac{3\pi l}{2n}.$$

f_{Zn} and f_{S} are the atomic scattering factors of Zn and S, respectively, *n* is the number of layers in the unit cell.

For $h - k = 1 \pmod{3}$:

$$|\varphi_{hk.l}|^2 = \left[\sum_{z=1}^n \cos 2\pi \left(\frac{lz}{n} + \frac{\alpha_z}{3} \right) \right]^2 + \left[\sum_{z=1}^n \sin 2\pi \left(\frac{lz}{n} + \frac{\alpha_z}{3} \right) \right]^2.$$

The summation is over all layers in the unit cell; z is the cardinal number of the layer and α_z equals 0, 1 or 2 for A , B or C layers.

Table 1. List of currently identified polytypes of the family 18L

Structures	Reference
54R (10 8) ₃	(a)
54R (13 5) ₃	New
18L (15 3)	New
18L (5 5 4 4)	(b)
54R (5 5 5 3) ₃	(b)
18L (6 5 3 4)	(b)
54R (6 5 4 3) ₃	New
54R (6 5 5 2) ₃	New
18L (7 3 5 3)	New
54R (7 3 6 2) ₃	(b)
18L (7 5 2 4)	(b)
54R (7 5 3 3) ₃	(b)
18L (8 3 4 3)	New
54R (8 4 3 3) ₃	New
54R (8 5 2 3) ₃	New
18L (9 3 3 3)	New
54R (9 4 2 3) ₃	New
54R (4 3 4 3 2 2) ₃	New
18L (8 2 2 2 2 2)	New

References: (a) Kiflawi, Mardix & Steinberger (1969); (b) Kiflawi, Mardix & Kalman (1969).

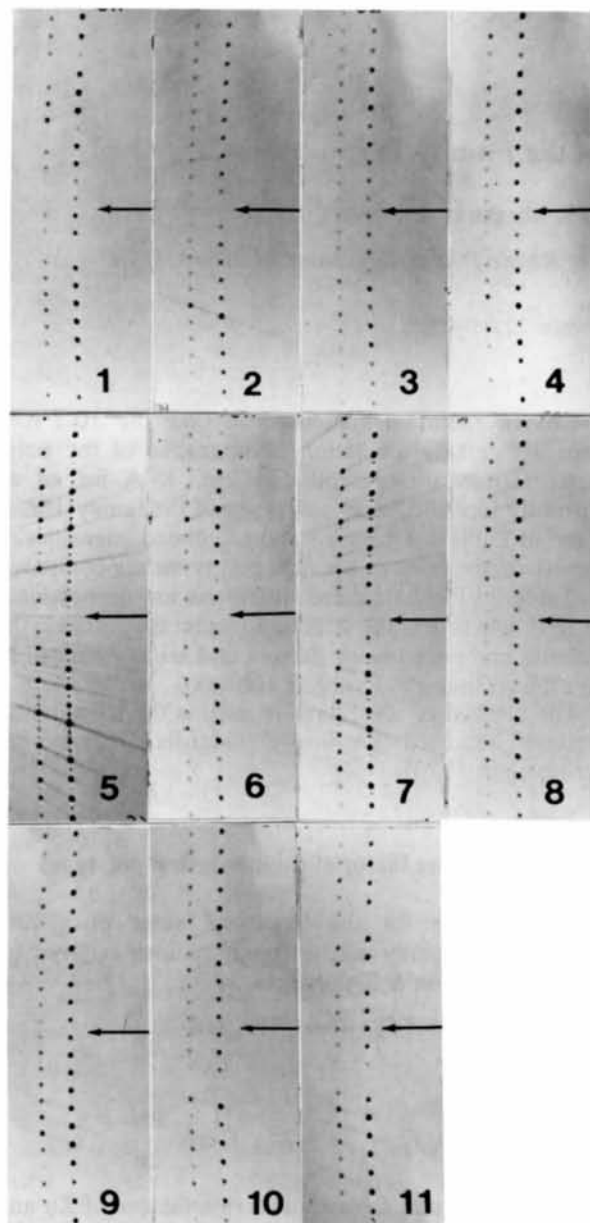


Fig. 1. $10.l$ row lines of 10° c axis Cu K oscillation X-ray photographs of the new polytypes. Collimator 0.2 mm; recorded on a flat film at a distance of 60 mm from the specimen. The zero line is indicated by an arrow. Magnification: $\times 2$. (1) 54R (13 5)₃; (2) 18L (15 3); (3) 54R (6 5 4 3)₃; (4) 54R (6 5 5 2)₃; (5) 18L (7 3 5 3) and two unidentified 54R rhombohedral polytypes; (6) 18L (8 3 4 3); (7) 54R (8 4 3 3)₃ and 18L (9 3 3 3); (8) 54R (8 5 2 3)₃; (9) 54R (9 4 2 3)₃; (10) 54R (4 3 4 3 2 2)₃; (11) 18L (8 2 2 2 2 2).

For hexagonal polytypes (space groups $P3m1$ and $P6_3mc$) $n = m$, where m is the number of layers in the elementary stacking sequence, while for rhombohedral polytypes (space group $R3m$) of the same family (Mardix, Alexander, Brafman & Steinberger, 1967) $n = 3m$. As a result two separate computer programs for hexagonal and rhombohedral polytypes are needed in the 'elimination method'.

The expression for the structure factor of rhombohedral polytypes can be rewritten to include sums of terms related to layers in the elementary stacking sequence rather than in the rhombohedral unit cell. The expression is correct only for those reflections which are not typical extinctions for the rhombohedral cell, namely $l = 3r - 1$, and $l = 3r + 1$ for cyclic and anti-cyclic structures, respectively, where r is an integer ($l = 3r$ for an n -layered hexagonal polytype). But certainly, only the intensities of the non-extinct reflections have to be calculated.

The modified expression for $|\varphi_{hk,l}|^2$ for hexagonal or rhombohedral polytypes is given by (for $h - k = 1 \pmod{3}$):

$$|\varphi_{hk,l}|^2 = \left[\sum_{z=1}^m \cos 2\pi \left(\frac{rz}{m} + \frac{\alpha_z + tz/m}{3} \right) \right]^2 + \left[\sum_{z=1}^m \sin 2\pi \left(\frac{rz}{m} + \frac{\alpha_z + tz/m}{3} \right) \right]^2,$$

where t equals 0, -1 and $+1$ for hexagonal rhombohedral and rhombohedral anti-cyclic polytypes, respectively.

The above expression can be easily derived by first summing triplets of terms of $|\varphi_{hk,l}|^2$ with $z_1 = \beta$, $z_2 =$

Table 2. Observed and calculated intensities for the new polytypes

(1) 54R (13 5) ₃			(2) 18L (15 3)			(7) 54R (8 4 3 3) ₃			(8) 18L (9 3 3 3)		
<i>l</i>	Observed	Calculated	<i>l</i>	Observed	Calculated	<i>l</i>	Observed	Calculated	<i>l</i>	Observed	Calculated
25	<i>w</i>	3.905	9	<i>w</i>	2.189	26	<i>s</i>	22.714	9	<i>s</i>	13.681
22	<i>m</i>	11.207	8	<i>w</i> (8>9)	2.967	23	<i>w</i>	3.996	8	<i>m</i>	4.635
19	<i>s</i> (19≈16)	17.095	7	<i>w</i> (7≈5)	3.645	20	<i>s</i>	26.485	7	<i>m</i> (7>8)	5.695
16	<i>s</i>	16.351	6	<i>w</i> (6>5)	4.000	17	<i>vs</i>	45.606	6	<i>s</i>	25.000
13	<i>m</i>	9.367	5	<i>w</i> (5>4)	3.870	14	<i>vw</i>	0.703	5	<i>m</i> (5>4)	6.046
10	<i>w</i> (10>4)	2.249	4	<i>w</i>	3.229	11	<i>s</i>	23.307	4	<i>m</i>	5.046
7	<i>a</i>	0.009	3	<i>vw</i> (3>2)	2.225	8	<i>m</i>	8.839	3	<i>s</i>	13.905
4	<i>w</i>	1.341	2	<i>vw</i>	1.141	5	<i>vw</i> (5>14)	1.477	2	<i>w</i>	1.782
1	<i>ww</i>	1.771	1	<i>vvw</i>	0.310	2	<i>vvw</i>	0.241	1	<i>vw</i>	0.485
-2	<i>vvw</i> (-2≈-5)	0.385	0	<i>a</i>	0.000	-1	<i>w</i> (-1>5)	2.472	0	<i>a</i>	0.000
-5	<i>vvw</i>	0.350	-1	<i>vvw</i>	0.310	-4	<i>vw</i> (-4≈5)	1.743	-1	<i>vw</i> (-1≈1)	0.485
-8	<i>w</i>	2.800	-2	<i>vw</i>	1.141	-7	<i>m</i> (-7<-10)	7.863	-2	<i>w</i> (-2≈2)	1.782
-11	<i>w</i> (-11>-8)	3.685	-3	<i>vw</i> (-3>-2)	2.225	-10	<i>m</i> (-10>-25)	8.604	-3	<i>s</i>	13.905
-14	<i>vvw</i>	0.193	-4	<i>w</i>	3.229	-13	<i>s</i>	19.773	-4	<i>m</i>	5.046
-17	<i>vvs</i>	100.000	-5	<i>w</i> (-5>-4)	3.870	-16	<i>vs</i>	44.604	-5	<i>m</i> (-5>-4)	6.047
-20	<i>vs</i>	51.753	-6	<i>vvs</i>	100.000	-19	<i>vvs</i>	100.000	-6	<i>vvs</i>	100.000
-23	<i>w</i>	3.116	-7	<i>w</i> (-7>-8)	3.645	-22	<i>m</i> (-22>-25)	9.794	-7	<i>m</i> (-7>-8)	5.695
-26	<i>vw</i>	0.214	-8	<i>vw</i> (-8>-9)	2.967	-25	<i>m</i>	5.351	-8	<i>m</i>	4.635
			-9	<i>vw</i>	2.189				-9	<i>s</i>	13.681
(3) 54R (6 5 4 3)			(4) 54R (6 5 5 2) ₃			(9) 54R (8 5 2 3) ₃			(10) 54R (9 4 2 3) ₃		
<i>l</i>	Observed	Calculated	<i>l</i>	Observed	Calculated	<i>l</i>	Observed	Calculated	<i>l</i>	Observed	Calculated
25	<i>m</i> (25>4)	10.452	26	<i>w</i> (26>2)	1.064	25	<i>s</i>	24.663	26	<i>s</i> (26<23)	17.823
22	<i>s</i>	28.122	23	<i>s</i> (23>20)	24.366	22	<i>s</i> (22>25)	33.008	23	<i>s</i> (23≈17)	28.298
19	<i>vs</i> (19>13)	56.222	20	<i>s</i> (20≈14)	14.173	19	<i>m</i>	6.643	20	<i>w</i> (20≈-1)	1.502
16	<i>s</i>	15.529	17	<i>vs</i>	35.723	16	<i>vs</i> (16>-20)	65.047	17	<i>s</i>	28.921
13	<i>vs</i>	49.613	14	<i>s</i> (14>11)	15.495	13	<i>s</i> (13>25)	29.650	14	<i>vs</i>	41.636
10	<i>vw</i>	0.575	11	<i>s</i>	10.453	10	<i>vw</i>	1.103	11	<i>w</i> (11>5)	3.997
7	<i>w</i> (7>-5)	3.739	8	<i>m</i>	3.763	7	<i>w</i> (7>4)	3.671	8	<i>w</i> (8>11)	4.179
4	<i>m</i>	7.120	5	<i>m</i> (5>8)	4.859	4	<i>w</i>	3.107	5	<i>w</i> (5>2)	2.549
1	<i>w</i>	2.583	2	<i>w</i>	2.960	1	<i>w</i> (1>4)	4.115	2	<i>w</i> (2≈-1)	1.480
-2	<i>vw</i>	0.784	-1	<i>m</i> (-1≈5)	4.307	-2	<i>vw</i> (-2>10)	1.797	-1	<i>w</i>	1.873
-5	<i>w</i> (-5>1)	3.093	-4	<i>w</i>	1.125	-5	<i>w</i> (-5<1)	2.417	-4	<i>m</i> (-4>-7)	6.871
-8	<i>m</i>	6.198	-7	<i>w</i> (-7>-4)	1.593	-8	<i>s</i>	18.982	-7	<i>m</i>	5.060
-11	<i>s</i> (-11≈-23)	25.002	-10	<i>m</i>	4.169	-11	<i>w</i> (-11≈4)	3.393	-10	<i>m</i> (-10≈-13)	9.211
-14	<i>m</i> (-14>-8)	7.480	-13	<i>m</i> (-13>5)	8.887	-14	<i>m</i> (-14>19)	9.750	-13	<i>m</i>	9.474
-17	<i>vvs</i>	100.000	-16	<i>vvs</i>	100.000	-17	<i>vvs</i>	100.000	-16	<i>vs</i> (-16>14)	51.348
-20	<i>vs</i> (-20≈13)	41.546	-19	<i>w</i> (-19≈-7)	1.678	-20	<i>vs</i>	52.107	-19	<i>vvs</i>	100.000
-23	<i>s</i>	26.580	-22	<i>vs</i> (-22>17)	56.935	-23	<i>m</i> (-23>-14)	11.648	-22	<i>m</i> (-22<-13)	8.168
-26	<i>m</i> (-36>-14)	9.272	-25	<i>m</i>	5.362	-16	<i>w</i> (-26>-11)	4.074	-25	<i>w</i>	1.406
(5) 18L (7 3 5 3)			(6) 18L (8 3 4 3)			(11) 54R (4 3 4 3 2 2) ₃			(12) 18L (8 2 2 2 2 2)		
<i>l</i>	Observed	Calculated	<i>l</i>	Observed	Calculated	<i>l</i>	Observed	Calculated	<i>l</i>	Observed	Calculated
9	<i>m</i>	3.420	9	<i>s</i>	10.261	25	<i>m</i>	5.209	9	<i>vs</i>	36.034
8	<i>s</i>	10.881	8	<i>vw</i> (8<1)	0.559	22	<i>s</i> (22>19)	37.276	8	<i>m</i>	7.235
7	<i>s</i> (7>8)	13.368	7	<i>vs</i> (7>4)	22.093	19	<i>s</i>	27.037	7	<i>w</i> (7>2)	3.216
6	<i>m</i> (6>-2)	6.250	6	<i>m</i> (6≈2)	6.250	16	<i>w</i> (16≈1)	3.183	6	<i>a</i>	0.000
5	<i>vs</i>	21.357	5	<i>s</i>	9.993	13	<i>vs</i> (13>-11)	78.184	5	<i>s</i> (5>4)	28.312
4	<i>w</i>	0.609	4	<i>vs</i>	17.283	10	<i>vvw</i>	0.076	4	<i>s</i> (4>0)	27.818
3	<i>s</i> (3≈7)	13.905	3	<i>a</i>	0.000	7	<i>w</i>	1.272	3	<i>a</i>	0.000
2	<i>vvw</i>	0.215	2	<i>m</i>	6.295	4	<i>s</i> (19>4)	17.529	2	<i>w</i> (2>-1)	2.782
1	<i>w</i> (1>4)	1.713	1	<i>vw</i> (1>-2)	0.802	1	<i>w</i>	3.305	1	<i>m</i>	5.331
0	<i>a</i>	0.000	0	<i>a</i>	0.000	-2	<i>w</i> (-2>1)	4.746	0	<i>s</i>	19.174
-1	<i>w</i> (-1>4)	1.139	-1	<i>w</i>	1.882	-5	<i>w</i> (-5≈-2)	4.226	-1	<i>w</i>	2.271
-2	<i>m</i>	4.184	-2	<i>vw</i>	0.215	-8	<i>m</i> (-8>-14)	9.126	-2	<i>vw</i>	0.336
-3	<i>m</i> (-3≈-9)	3.476	-3	<i>s</i> (-3≈-4)	10.429	-11	<i>vs</i>	40.544	-3	<i>a</i>	0.000
-4	<i>vs</i> (5≈-4)	17.823	-4	<i>s</i>	11.844	-14	<i>m</i> (-14>-23)	6.661	-4	<i>m</i> (-4>1)	7.876
-5	<i>vw</i> (-5≈-7)	0.729	-5	<i>w</i> (-5≈-7)	2.829	-17	<i>vvs</i>	100.000	-5	<i>vvs</i>	100.000
-6	<i>vvs</i>	100.000	-6	<i>vvs</i>	100.000	-20	<i>s</i> (-20≈19)	27.135	-6	<i>vs</i>	39.020
-7	<i>vw</i>	0.687	-7	<i>w</i>	2.665	-23	<i>m</i>	5.598	-7	<i>s</i> (-7≈4)	26.665
-8	<i>s</i>	16.373	-8	<i>s</i> (-8≈-9)	10.881	-26	<i>vs</i> (-26>-11)	54.470	-8	<i>s</i> (-8>-7)	16.982
-9	<i>m</i>	3.420	9	<i>s</i>	10.261				-9	<i>vs</i>	36.034

$\beta + m$ and $z_3 = \beta + 2m$, where $1 \leq \beta \leq m$, and then performing the summation from 1 to m .

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Patterson Search – an Alternative to Direct Methods

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Abstract

On the basis of the solution of six unknown structures by a real-space Patterson search the merits and limitations of the method are discussed. It is shown how chemical information can be used to provide a reliable starting point for direct methods when there is no automatic solution. Two examples demonstrate the potential usefulness of force-field calculations for generating the geometries of appropriate search fragments in the absence of related crystal structures. The further discussion deals with future applications of the vector search method to determine large structures. A Patterson search program, which incorporates all necessary features of a modern program and is compatible with *SHELX* 84, is being developed.

Introduction

Nowadays the overwhelming majority of light-atom structures are determined by direct methods, many of them automatically. Although these techniques have proved extremely powerful, they cannot solve all structures and even less complex problems still resist solution, sometimes for reasons not obvious to the investigator. The principal weakness of the method lies in its dependence on a few key reflections during the early stages of phase determination. If some of them are measured incorrectly (*e.g.* weak data from very small crystals, or poor resolution arising from solvent disorder), an inappropriate starting set may be chosen and thus the whole chaining process can go wrong. Current research activities in this field centre on how to

improve this situation (Furusaki, 1979; Jia-Xing, 1981; Hull, Viterbo, Woolfson & Shao-Hui, 1981; Schenk, 1983). Furthermore, direct methods are based on a random distribution of atoms, so that structures which deviate considerably from this assumption (*e.g.* those containing planar rings) often present problems.

Difficult structures may eventually be solved by varying one or several parameters that govern the phasing procedure. If this does not work either, the problem reduces to an often frustrating trial-and-error approach in which many phase sets are tested. On the other hand, valuable chemical information, which for most (organic) structures is at least partially present, is not fully used by direct methods. It seems paradoxical, especially to a chemist, that even crystal structures of molecules whose total geometry is well known cannot be determined. Therefore, instead of using chemical knowledge only indirectly, *e.g.* to modify *E* values or recognize correct electron-density maps, one should try to use it directly in those cases where direct methods fail.

The Patterson function differs from the statistical methods in that all data are used simultaneously and independently of each other; it is therefore less sensitive to a few incorrectly measured or missing reflections. Since the resulting vector map contains in principle the whole structural information, attempts have been made to solve light-atom structures semi-automatically from Patterson syntheses (Mighell & Jacobson, 1963; Gorres & Jacobson, 1964; Simpson, Dobrott & Lipscomb, 1965). However, considering the expected vector peak density it is quite hopeless to unravel more complex problems *ab initio*, *i.e.* without additional information. If part of the molecular geometry is