Low-order ZnS polytypes.

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ZnS polytypes having twenty or less layers in their elementary stacking sequence are referred to as low-order polytypes. Ten new low-order polytypes: $30R$ (6 4)$_3$, $10L$ (3 3 2 2), $30R$ (4 2 2 2)$_3$, $12L$ (4 4 2 2), $42R$ (9 5)$_3$, $42R$ (5 3 3 3)$_3$, $48R$ (6 4 3 3)$_3$, $48R$ (7 3 3 3)$_3$, $60R$ (9 3 5 3)$_3$ and $60R$ (9 5 3 3)$_3$ have been found. The observed and calculated intensities of the new polytypes are compared. A list of all low-order polytypes known so far is given.

The elementary stacking sequence of a polytype is the set of (00.1) planes contained in one period of a non-rhombohedral polytype, and the set of (00.1) planes contained in the third of a period of a rhombohedral polytype. A polytype having twenty or less layers in its elementary stacking sequence will be referred to as a low-order polytype.

Ten new low-order polytypes have been found in ZnS crystals grown from the vapour phase at a temperature of about 1250°C. X-ray oscillation photographs about the c axis of the crystals were taken using Cu K radiation. Row lines of the X-ray oscillation photographs are given in Fig. 1. The observed and calculated intensities are compared in Table 1. A full list of all known low-order polytypes found so far in vapour-phase-grown ZnS crystals is given in Table 2. It is to be noted that all polytypes listed in Table 2 are of even periodicity. This is a consequence of the growth mechanism of ZnS crystals around screw dislocations and the formation of polytypes, after the crystal's growth, by the movement of partial dislocations along the (00.1) planes (Mardix, 1969). Another property of the polytypes of vapour-grown ZnS crystals is the absence of the number 1 in their Zhdanov sequence. This property is presumably a consequence of the instability of two neighbouring hexagonal layers at a temperature below that of growth. Only one exception, $12R$ (3 1)$_3$, has been found so far. It is to be noted that the structures containing two neighbouring hexagonal layers are the $2H$ (1 1) having an elementary stacking sequence of order two, and the polytype $12R$ (3 1)$_3$ of order 4. These two elementary stacking sequences are the smallest possible. Thus it appears that the instability of two hexagonal neighbouring layers is somewhat dependent on the size of the elementary stacking sequence as well. The smallest elementary stacking sequences may still include the number 1 in the Zhdanov sequence, while this is impossible for higher polytypes. The reason for this dependence of the instability on the order of the polytype is not clear.

Table 1. *Comparison of observed and calculated intensities of the new polytypes mentioned in Table 2*

l	Observed		Calculated
$30R$ (6 4)$_3$			
1	vw		2·94
4	w		4·27
7	s	(7 > 13)	33·63
10	vs		51·15
13	s		31·13
−2	w	(−2 > −14)	8·26
−5	a		0·00

Table 1 (*cont.*)

|		
−8	vs	71·03
−1	vvs	30·00
−1	w	1014·74
$10L$ (3 3 2 2)*		
0	w	10·90
1	m	23·58
2	vs	51·74
3	vvs (3 > 5)	100·00
4	m	24·57
5	vvs	90·07
$30R$ (4 2 2 2)$_3$		
1	m	24·77
4	vvw	0·47
7	s	47·34
10	w	12·32
13	w (13 > 10)	20·51
−2	vw	5·45
−5	a	0·00
−8	vvs	100·00
−11	w	11·02
−14	vs	61·78
$12L$ (4 4 2 2)*		
0	m	20·68
1	w	10·64
2	a	0·00
3	vvs	100·00
4	s	42·35
5	s (5 > 6)	53·12
6	s	39·42
$42R$ (9 5)$_3$		
1	vvw (1 > 4)	1·45
4	vvw	0·84
7	w	7·04
10	vw	3·78
13	vvs	100·00
16	vs	59·85
19	a	0·56
−2	vw	3·67
−5	a	0·25
−8	vw	5·47
−11	m	24·75
−14	s	35·33
−17	m	23·14
−20	vw	5·19
$42R$ (5 3 3 3)$_3$		
1	vw	0·66
4	vw	0·60
7	vs	31·14
10	w (10 > −2)	2·40
13	vs (13 > 7)	45·72
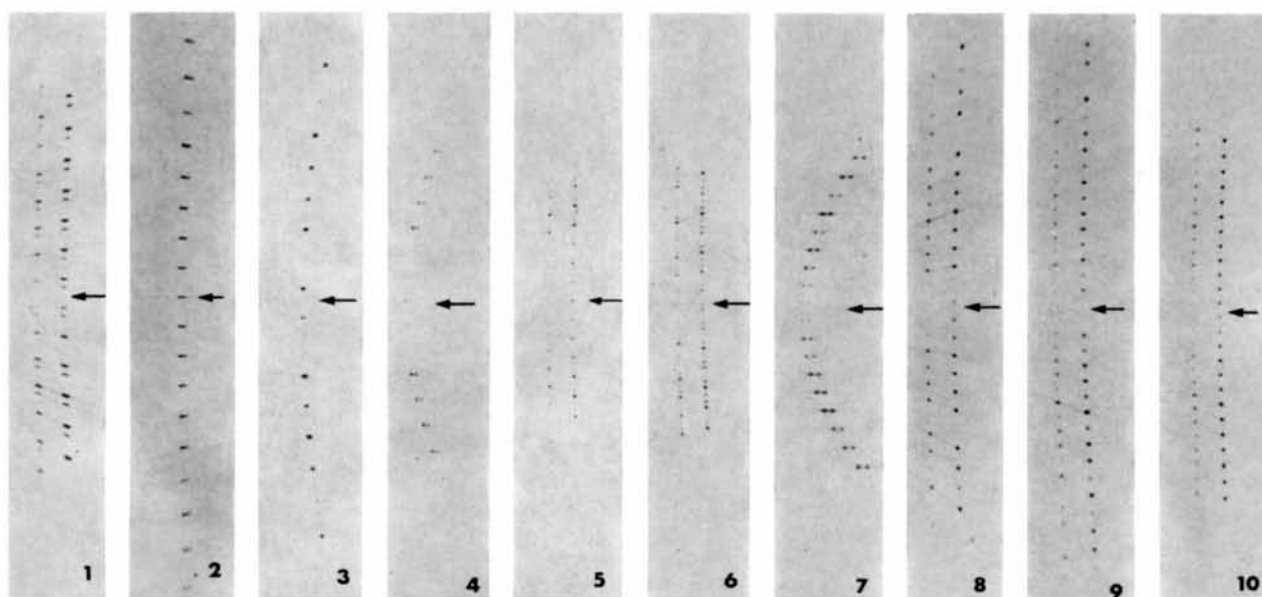
Fig. 1. Row lines of oscillation X-ray photographs about the c axis of the new polytypes. Cu K radiation, 60 mm diameter camera. Magnification $\times \sim 2.5$. The zero line is indicated by an arrow. (1) 10.l row line of the polytypes $30R$ (6 4)$_3$ and $30R$ (7 3)$_3$; (2) 10.l row line of the polytype $10L$ (3 3 2 2); (3) 20.l row line of the polytype $30R$ (4 2 2 2)$_3$; (4) 22.l row line of the polytype $12L$ (4 4 2 2); (5) 10.l row line of the polytypes $42R$ (9 5)$_3$ and $14R$ (7 7); (6) 10.l row line of the polytypes $42R$ (5 3 3 3)$_3$, $14L$ (4 4 3 3), and a few spots of the twin polytype of $42R$ (5 3 3 3)$_3$; (7) 10.l row line of the polytype $48R$ (6 4 3 3)$_3$; (8) 1 0.l row line of the polytype $48R$ (7 3 3 3)$_3$; (9) 10.l row line of the polytype $60R$ (9 3 5 3)$_3$; (10) 10.l row line of the polytype $60R$ (9 5 3 3)$_3$.

Table 1 (*cont.*)

16	s	(16>19)	20·38
19	s		15·70
−2	w		1·25
−5	m		7·00
−8	s	(−8>16)	30·51
−11	w		2·60
−14	vvs		100·00
−17	w		2·43
−20	s		28·97

48R (6 4 3 3)₃

1	vw		1·13
4	w		2·43
7	m	(7>13)	11·77
10	vs		32·57
13	m		6·96
16	vvs		79·05
19	m		6·55
22	s		30·37
−2	w		1·91
−5	m		9·79
−8	m		8·04
−11	vs		32·18
−14	vs	(−14>−11)	42·97
−17	vvs	(−17>−16)	100·00
−20	m		12·14
−23	s		16·31

48R (7 3 3 3)₃

1	vvw		0·34
4	a		0·00
7	m		13·83
10	m		13·46
13	w		5·02
16	vvs		100·00
19	w		4·72
22	m		12·55
−2	vw		0·79
−5	vw	(−5>−2)	1·33
−8	m	(−8>7)	19·93
−11	w		4·38
−14	m		17·76
−17	s		30·12
−20	a		0·00
−23	m	(−23~−8)	19·18

Table 1 (*cont.*)

60R (9 3 5 3)₃

1	vvw		0·09
4	w	(4>28)	1·32
7	vw		0·54
10	s		10·17
13	w		1·37
16	s	(16>10)	11·34
19	s	(19>16)	12·06
22	w		1·69
25	s		15·36
28	w		1·17
−2	vvw		0·05
−5	m		3·08
−8	vw	(−8>7)	0·68
−11	s		7·63
−14	s	(−14>−11)	10·17
−17	w	(−17>−23)	1·71
−20	vvs		100·00
−23	w	(−23>4)	1·63
−26	s	(−26>−29)	9·41
−29	s		7·33

60R (9 5 3 3)₃

1	vw		0·71
4	vw		0·85
7	w		1·67
10	s	(10>−11)	17·19
13	m		4·23
16	m	(16>13)	7·32
19	vvs		100·00
22	vs		46·51
25	s		12·99
28	m	(28~13)	5·19
−2	w		1·37
−5	w	(−5>−2)	2·60
−8	w	(−8>−5)	3·02
−11	s	(−11>−17)	14·16
−14	s		11·58
−17	s	(−17>−14)	12·07
−20	vs		55·22
−23	s	(−23>−26)	11·47
−26	s		10·72
−29	s	(−29>−23)	13·60

* The observed intensities are symmetrical with respect to the zero line $l=0$.

Table 2. *List of low order polytypes*

Number of layers in elementary stacking sequence	Polytype found	References*
4	4H (2 2)	l
	12R (3 1)₃†	
6	6H (3 3)	l
	18R (4 2)₃	a
8	8H (4 4)	b
	24R (5 3)₃	c
	24R (6 2)₃	b
10	10H (5 5)†	
	30R (6 4)₃	d
	30R (7 3)₃	c
	10L (8 2)	new
	10L (3 3 2 2)	new
	30R (4 2 2 2)₃	new
12	12H (6 6)	e
	12L (9 3)	e
	12L (4 4 2 2)	new

Table 2 (*cont.*)

	$36R$ (7 5)$_3$	f
	$36R$ (8 4)$_3$	e
	$36R$ (10 2)$_3$	f
	$36R$ (4 3 3 2)$_3$	f
	$36R$ (5 3 2 2)$_3$	f
	$36R$ (6 2 2 2)$_3$	a
14	$14H$ (7 7)	a
	$42R$ (8 6)$_3$	g
	$42R$ (9 5)$_3$	new
	$42R$ (11 3)$_3$	g
	$42R$ (12 2)$_3$	e
	$14L$ (4 4 3 3)	g
	$42R$ (5 3 3 3)$_3$	new
	$14L$ (5 4 2 3)	c
	$42R$ (5 4 3 2)$_3$	g
	$42R$ (6 4 2 2)$_3$	g
16	$16H$ (8 8)	h
	$48R$ (9 7)$_3$	h
	$48R$ (10 6)$_3$	k
	$48R$ (12 4)$_3$	h
	$48R$ (13 3)$_3$	k
	$16L$ (14 2)	k
	$16L$ (5 5 3 3)	k
	$48R$ (6 4 3 3)$_3$	new
	$48R$ (7 3 3 3)$_3$	new
	$48R$ (7 4 2 3)$_3$	h
	$48R$ (8 4 2 2)$_3$	k
	$16L$ (3 3 3 3 2 2)	k
	$48R$ (4 3 3 2 2 2)$_3$	h
18	$54R$ (10 8)$_3$	e
	$18L$ (5 5 4 4)	g
	$54R$ (5 5 5 3)$_3$	g
	$18L$ (6 5 3 4)	g
	$54R$ (7 3 6 2)$_3$	g
	$18L$ (7 5 2 4)	g
	$54R$ (7 5 3 3)$_3$	g
20	$20H$ (10 10)	e
	$60R$ (11 9)$_3$	d
	$60R$ (12 8)$_3$	d
	$20L$ (13 7)	d
	$60R$ (17 3)$_3$	e
	$60R$ (18 2)$_3$	h
	$20L$ (7 6 3 4)	e
	$20L$ (7 7 3 3)	d
	$20L$ (8 7 2 3)	e
	$60R$ (9 7 3 2)$_3$	f
	$60R$ (9 3 5 3)$_3$	new
	$60R$ (9 3 6 2)$_3$	e
	$60R$ (9 4 5 2)$_3$	e
	$60R$ (9 5 3 3)$_3$	new
	$60R$ (9 6 2 3)$_3$	f
	$60R$ (10 3 5 2)$_3$	e
	$60R$ (11 4 3 2)$_3$	h
	$20L$ (5 3 3 4 2 3)	h
	$60R$ (5 3 5 2 2 3)$_3$	h
	$60R$ (5 4 5 2 2 2)$_3$	e
	$20L$ (5 5 3 2 2 3)	d
	$20L$ (6 3 2 2 5 2)	h
	$60R$ (6 3 3 3 3 2)$_3$	e
	$60R$ (7 4 2 3 2 2)$_3$	d
	$60R$ (8 4 2 2 2 2)$_3$	e

* (*a*) Mardix, Brafman & Steinberger (1967), (*b*) Mardix & Kiflawi (1970), (*c*) Brafman, Alexander & Steinberger (1967), (*d*) Kiflawi & Mardix (1969), (*e*) Kiflawi, Mardix & Steinberger (1969), (*f*) Mardix, Kiflawi & Kalman (1969), (*g*) Kiflawi, Mardix & Kalman (169), (*h*) Mardix, Alexander, Brafman & Steinberger (1967), (*k*) Mardix & Brafman (1967), (*l*) Strock & Brophy (1955).

† Hitherto found in natural ZnS crystals only.

Low order ZnS polytypes can be identified by any of the usual methods of polytype identification: for example the method described by Mardix, Alexander, Brafman & Steinberger (1967). This method consists in comparing the calculated intensity distributions of all possible polytypes with the experimental intensity distribution. It should be noted that the number of possible structures, the intensity distributions of which have to be calculated, can be reduced by using readily available preliminary information:

(a) The order of the polytype can easily be determined from X-ray oscillation photographs. Also, by observing systematic absences in these photographs it can be determined whether or not the polytype is rhombohedral (Verma & Krishna, 1966).

(b) Using the linear dependence of the birefringence on the percentage of hexagonality (Brafman & Steinberger, 1966) and the value 24×10^{-3} for the percentage of hexagonality of the hexagonal $2H$ structure, the number of Zhdanov numbers in the elementary stacking sequence can be determined by measuring the birefringence of the polytypic regions. The birefringence can almost always be measured when the specimens are platelets. In the case of needle-shaped specimens, most of which are hollow, the birefringence measurement is not feasible (Kiflawi, Mardix & Kalman, 1969).

(c) It is an experimental fact that polytypes found in ZnS crystals grown by sublimation do not have the number 1 in their Zhdanov sequences.

According to Verma & Krishna (Verma & Krishna, 1966), and also from our experience, there is no need for a quantitative determination of the intensities of reflexion spots. In no case was there any ambiguity in polytype identification as a result of visual determination of the intensities. In all cases, on comparison of the observed intensity distribution of the polytype to be identified with the calculated intensities of all possible structures, only one calculated intensity distribution was found to fit. The calculated intensity distribution of all other possible structures differed considerably from that observed.

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The crystal structure of 2,6-dichloro-4-diazo-2,5-cyclohexadien-1-one. By C. TRAVIS PRESLEY and RONALD L. SASS,

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The crystal structure of 2,6-dichloro-4-diazo-2,5-cyclohexadien-1-one has been determined. Observed unit-cell constants are $a = 13 \cdot 29$ (1), $b = 10 \cdot 36$ (1), $c = 10 \cdot 83$ (1) Å and $\beta = 103 \cdot 07$ (05)°. The space group is $C_{2h}^5 - P2_1/c$ with 8 molecules per unit cell. Three-dimensional visual data were collected. The structure was refined by least squares to a final conventional R index of $10 \cdot 5\%$. Even though the asymmetric unit contains two independent molecules, no evidence of a molecular complex was observed.

The structure of 2,6-dichloro-4-diazo-2,5-cyclohexadien-1-one, $C_6H_2N_2OCl_2$, has been determined by single-crystal X-ray diffraction methods. The compound was prepared by Dr James Perry of Rice University by diazotizing the corresponding dichloroaminophenol with acidic sodium nitrite at zero degrees centigrade. The single crystals used in this study were obtained by recrystallization from hot ethyl acetate as light orange needles. Shortly after the initial X-ray study had begun, it was observed that the crystals were affected by extended periods of exposure to X-rays, the color of the crystals gradually changing to a deep red. Changes were also observable on X-ray photographs as a broadening of the diffraction spots. For this reason, it was necessary to use several different crystals in the collection of the intensity record.

Equi-inclination Weissenberg photographs (Cu $K\alpha$, $\lambda = 1 \cdot 5418$ Å) indicated the space group to be $C_{2h}^5 - P2_1/c$ (systematic absences: $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). The unit-cell dimensions are $a = 13 \cdot 29$ (1), $b = 10 \cdot 36$ (1), $c = 10 \cdot 83$ (1) Å and $\beta = 103 \cdot 07$ (05)°. The observed density, determined by flotation in a mixture of carbon tetrachloride and methylene chloride, is $1 \cdot 72$ g.cm^{-3}; the calculated density, based on eight molecules per unit cell, is $1 \cdot 71$ g.cm^{-3} Since the space group has fourfold symmetry, the asymmetric unit contains two crystallographically independent molecules.

The intensity data for this compound were collected by multiple-film equi-inclination Weissenberg photography and were estimated visually by comparison with standard intensity exposures in the usual way. Data were collected