The question of why a dimeric tetrahydrate does not form should be asked. It may be that such a metastable polymorph does indeed exist, but has not yet been isolated or recognized. On the other hand it may be that in the absence of any non-bonded water molecules, the hydrogen bonding through the coordinated waters alone is not strong enough to hold the isolated units together, although it should be remembered that hydrogen bridging through the water molecule in both pentahydrates is not essential to their stability.

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New Families of ZnS Polytypes

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Seven ZnS polytypes belonging to hitherto unknown families, namely 44*L* − 132*R*; 38*L* − 114*R* and 18*L* − 54*R* have been found. The polytypes are 44*L* (37 7) and 44*L* (17 4 17 6) of the family 38*L* − 132*R*; 114*R* (29 9)$_3$, 114*R* (35 3)$_3$, 114*R* (21 9 6 2)$_3$ and 114*R* (13 5 2 2 6 2 6 2)$_3$ of the family 38*L* − 114*R* and 54*R* (10 8)$_3$ of the family 18*L* − 54*R*. Eighteen further new polytypes are reported: 12*H* (6 6), 12*L* (9 3) and 36*R* (8 4)$_3$ of the family 12*L* − 36*R*; 42*R* (12 2) of the family 14*L* − 42*R*; 20*H* (10 10), 20*L* (2 3 8 7), 20*L* (3 4 7 6), 60*R* (9 3 6 2)$_3$, 60*R* (17 3)$_3$, 60*R* (9 4 5 2)$_3$, 60*R* (10 3 5 2)$_3$, 60*R* (5 4 5 2 2 2)$_3$, 60*R* (6 3 3 3 3 2)$_3$, 60*R* (8 4 2 2 2 2)$_3$ of the family 20*L* − 60*R*; and 28*L* (23 5), 28*L* (2 2 21 3), 84*R* (25 3)$_3$ and 84*R* (11 8 4 5)$_3$ of the family 28*L* − 84*R*. X-ray oscillation photographs of their (10.*l*) or (40.*l*) row line are shown, and the calculated and observed intensities are compared.

During an investigation of ZnS polytypes, new polytypes were found, some of them belonging to hitherto unknown families (Steinberger & Mardix, 1967). The crystals investigated were ZnS platelets grown by sublimation at about 1200 C. Each crystal contains a large number of polytype regions having a common *c* axis. Most of the polytype regions investigated are wider than 0·1 mm. X-ray oscillation photographs about the *c* axis were taken with Cu *K* radiation. Photographs of the (10.*l*), or in some cases of (40.*l*) row line are given in Figs. 1 to 7. The structure was determined by a method given in a previous publication (Mardix, Alexander, Brafman & Steinberger, 1967). For the identification of the higher order polytypes an improved method was used (to be published). The observed and calculated intensities are given in Table 1.

In a few cases the width of the polytype region was smaller than 0·1 mm and a number of different regions were simultaneously in the X-ray beam. Thus spots appearing in a certain row line of the X-ray photograph may belong to two or three neighbouring regions. At first glance, the photograph may be thought to belong to a polytype of higher periodicity. An example is seen in Fig. 1(*a*), which is a photograph of the (40.*l*) row line of the polytype regions 12*H* (6 6) together with the two polytype regions 36*R* (8 4)$_3$ and 36*R* (2 10)$_3$. More examples are seen in Fig. 3; in Fig. 4 (*f*) which is a photograph of the (10.*l*) row line of the polytype regions 60*R* (9 4 5 2)$_3$ and 60*R* (5 4 5 2 2 2)$_3$; and in Fig. 5(*b*) where the two polytype regions 28*L* (23 5) and 84*R* (11 8 4 5)$_3$ are photographed simultaneously. However, the reflexions from different regions can be readily

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

Polytypes denoted by * have observed intensities symmetrical with respect to the zero line ($l=0$).

Polytypes of the family 12*L*

12*H* (6 6)*

l	I_{obs}		I_{calc}
0	*a*		0·00
1	*w*		8·38
2	*a*		0·00
3	*s*		44·98
4	*vvs*		100·00
5	*s*		41·81
6	*a*		0·00

12*L* (9 3)

l	I_{obs}		I_{calc}
0	*a*		0·00
1	*vw*		1·86
2	*w*		6·15
3	*m*		10·0
4	*m*	(4>3)	11·11
5	*m*	(5∼3)	9·29
6	*w*		6·13
−1	*vw*		1·86
−2	*w*		6·15
−3	*m*		10·00
−4	*vvs*		100·00
−5	*m*		9·29
−6	*w*		6·13

36*R* (8 4)$_3$

l	I_{obs}		I_{calc}
1	*w*		4·77
4	*vw*	(4>16)	2·61
7	*vw*		1·44
10	*vs*		62·61
13	*vvs*		100·00
16	*vw*	(16>7)	1·94
−2	*vvw*		0·60
−5	*vw*	(−5∼4)	3·08
−8	*m*	(−8>−17)	17·39
−11	*s*		29·16
−14	*s*		25·13
−17	*m*		11·26

Polytypes of the family 14*L*

42*R* (12 2)$_3$

l	I_{obs}		I_{calc}
1	*vw*		1·45
4	*vvw*		0·54
7	*a*		0·00
10	*w*		2·15
13	*vvs*		100·00
16	*vs*		38·06
19	*s*		6·80
−2	*w*		2·33
−5	*w*	(−5>−2)	3·03
−8	*w*		3·48
−11	*w*		3·65
−14	*w*		3·60
−17	*w*		3·41
−20	*w*		3·30

Polytypes of the family 18*L*

54*R* (10 8)$_3$

l	I_{obs}		I_{calc}
1	*w*	(1>10)	2·89
4	*vvw*		0·17
7	*w*	(7>1)	3·52
10	*w*		1·99
13	*m*		7·82
116	*vs*		54·30
19	*vs*	(19>16)	65·37
22	*s*		19·09
25	*a*		0·10
−2	*a*		0·04
−5	*w*	(−5∼1)	3·17
−8	*vw*		0·95
−11	*w*	(−11>−5)	5·28
−14	*m*	(−14>−26)	11·79
−17	*vvs*		100·00
−20	*vs*		63·43
−23	*vw*		0·73
−26	*m*		6·31

Polytypes of the family 18*L*
54*R* (10 8)$_3$

Polytypes of the family 20*L*

20*H* (10 10)*

l	I_{obs}		I_{calc}
0	*w*		2·16
1	*vvw*		0·76
2	*w*		2·67
3	*vw*		1·20
4	*w*	(4>5)	5·86
5	*w*	(5>2)	4·47
6	*vs*		77·64
7	*vvs*		100·00
8	*s*		19·07
9	*w*		2·27
10	*w*	(10>9)	4·11

20*L* (7 6 3 4)

l	I_{obs}		I_{calc}
0	*w*		2·40
1	*vw*		0·58
2	*m*	(2>9)	11·25
3	*vvw*		0·28
4	*w*	(4>0)	4·88
5	*vs*		52·01
6	*s*		30·69
7	*vvs*		88·34
8	*s*		34·30
9	*m*		8·99
10	*w*		4·57
−1	*w*		2·53
−2	*w*		2·71
−3	*w*	(−3>−1)	5·85
−4	*s*	(−4>−5)	20·88
−5	*s*		17·57
−6	*vs*		53·09
−7	*vvs*	(−7>7)	100·00
−8	*w*		2·10
−9	*s*	(−9>−4)	31·48
−10	*w*	(−10>−8)	4·57

20*L* (8 7 2 3)

l	I_{obs}		I_{calc}
0	*w*		2·31
1	*vw*		0·77
2	*m*		7·43
3	*vw*		0·61
4	*m*	(4>−1)	5·26
5	*vs*		27·44
6	*vvs*		97·39
7	*s*		19·83
8	*vs*	(8>5)	46·22
9	*s*		16·17
10	*s*		13·21
−1	*m*		4·40
−2	*w*		2·34
−3	*s*		18·50
−4	*w*		2·62
−5	*m*		10·85
−6	*vs*	(−6>8)	62·48
−7	*vvs*		100·00
−8	*m*	(−8>−9)	9·90
−9	*m*		7·26
−10	*s*		13·21

Polytypes of the family 20*L*

60*R* (17 3)$_3$

l	I_{obs}		I_{calc}
1	*a*		0·02
4	*vw*		0·34
7	*vw*	(7>4)	0·96
10	*w*		1·72
13	*w*	(13>10)	2·44
16	*m*		2·94
19	*m*		3·12
22	*m*		2·99
25	*m*		2·60
28	*w*		2·08
−2	*vvw*		0·09
−5	*vw*		0·52
−8	*w*		1·21
−11	*w*	(−11>−8)	1·98
−14	*m*		2·63
−17	*m*		3·04
−20	*vvs*		100·00
−23	*m*		2·89
−26	*m*		2·44
−29	*w*		1·88

60*R* (9 3 6 2)$_3$

l	I_{obs}		I_{calc}
1	*vvw*		0·71
4	*w*		2·26
7	*vw*		1·41
10	*w*	(10>4)	3·15
13	*m*		3·58
16	*vs*		19·39
19	*vvs*		100·00
22	*vs*		25·22
25	*vs*	(25>16)	23·77
28	*s*		5·25
−2	*vvw*		0·74
−5	*m*		4·76
−8	*w*		3·05
−11	*s*		5·10
−14	*s*		11·45
−17	*vw*		1·39
−20	*s*	(−20>−26)	15·79
−23	*vw*		1·32
−26	*s*		10·60
−29	*m*		4·90

60*R* (9 4 5 2)$_3$

l	I_{obs}		I_{calc}
1	*w*		2·37
4	*w*		2·42
7	*vw*		1·57
10	*s*		13·96
13	*w*		2·98
16	*s*		20·76
19	*s*		23·30
22	*m*		6·07
25	*s*		26·24
28	*vw*		2·15
−2	*m*	(−2>−14)	6·82
−5	*vvw*	(−5>−11)	0·38
−8	*vw*		1·25
−11	*vvw*		0·22
−14	*m*		5·77
−17	*vvs*		100·00
−20	*vs*		57·00
−23	*vs*	(−23>−20)	66·76
−26	*s*		11·67
−29	*s*		9·49

60*R* (10 3 5 2)$_3$

l	I_{obs}		I_{calc}
1	*vw*	(1>7)	1·21
4	*w*		1·85

Table 1 (*cont.*)

l	I_{obs}		I_{calc}
Polytypes of the family 20*L*			
60*R* (10 3 5 2)$_3$			
7	*vw*		0·78
10	*m*		3·11
113	*m*	(13 > 10)	5·71
16	*s*		15·87
19	*vvs*		100·00
22	*vs*		27·72
25	*s*	(25 > 28)	17·51
28	*s*		11·24
−2	*w*	(−2 > 4)	2·51
−5	*vvw*		0·25
−8	*m*	(−8 > 13)	6·54
−11	*m*	(−11 > −8)	7·46
−14	*vw*		1·28
−17	*s*		15·20
−20	*m*		4·37
−23	*m*	(−23 > −20)	5·78
−26	*s*		12·24
−29	*vvw*		0·30
60*R* (5 4 5 2 2 2)$_3$			
1	*m*		15·50
4	*a*		0·07
7	*vw*		1·38
10	*a*		0·00
13	*a*		0·004
16	*vvs*		100·00
19	*w*		5·90
22	*vs*	(22 > 28)	51·66
25	*m*		13·88
28	*vs*		33·14
−2	*w*	(−2 > −5)	3·25
−5	*w*		2·78
−8	*vvw*		0·54
−11	*s*		22·33
−14	*vvw*		0·42
−17	*vs*	(−17 > −26)	52·14
−20	*w*		3·69
−23	*m*		10·21
−26	*vs*		29·89
−29	*w*		2·07
60*R* (6 3 3 3 3 2)$_3$			
1	*vw*		0·71
4	*w*		2·38
7	*m*		5·27
10	*s*	(10 > 13)	20·18
13	*s*		13·35
16	*s*		20·47
19	*vvs*	(19 > −20)	100·00
22	*s*	(22 > 25)	22·92
25	*s*		15·24
28	*s*	(28 > 22)	28·11
−2	*vw*		0·67
−5	*w*		3·05
−8	*s*		16·35
−11	*s*	(−11 > −8)	27·62
−14	*w*		2·94
−17	*w*	(−17 > −14)	3·73
−20	*vvs*		64·82
−23	*w*	(−23 > −26)	3·54
−26	*w*		2·73
−29	*s*		26·52
60*R* (8 4 2 2 2 2)$_3$			
1	*s*		23·04
4	*vw*		4·25
7	*vvw*	(7 > −11)	1·50
10	*a*		0·00
13	*m*		13·11
16	*vvs*	(16 > 22)	100·00
19	*vs*		61·13
22	*vvs*		72·90
25	*s*		21·10
28	*m*		15·96
−2	*w*	(−2 > −20)	6·40
−5	*vw*	(−5 > −8)	4·23
−8	*vw*		3·11
−11	*vvw*		0·97
−14	*vs*		47·34
−17	*vs*	(−17 > −14)	62·96
−20	*w*		5·61
−23	*m*		17·30
−26	*m*		16·01
−29	*vs*		49·44
Polytypes of the family 28*L*			
28*L* (23 5)			
0	*vw*		0·47
1	*w*		0·65
2	*vw*	(2 > −3)	0·48
3	*vvw*		0·13
4	*a*		0·02
5	*w*		0·57
6	*m*		1·89
7	*s*		3·65
8	*s*	(8 > 7)	5·23
9	*s*		6·02
10	*s*		5·72
11	*s*	(11 < 8)	4·49
12	*m*	(12 > 6)	2·82
13	*w*		1·29
14	*vvw*		0·30
−1	*vvw*		0·14
−2	*a*		0·004
−3	*vw*		0·28
−4	*w*		0·86
−5	*w*	(−5 > −6)	1·30
−6	*w*	(−6 > −8)	1·11
−7	*vvw*		0·26
−8	*w*		0·98
−9	*vvs*		100·00
−10	*vs*		41·90
−11	*s*		5·83
−12	*w*		0·90
−13	*a*		0·002
−14	*vvw*	(−14 > −1)	0·30
28*L* (21 3 2 2)			
0	*vw*		0·48
1	*w*	(1 > 3)	1·11
2	*w*	(2 > 1)	1·51
3	*w*		0·86
4	*a*		0·03
5	*w*	(5 ∼ 3)	0·84
6	*m*	(6 > 9)	3·51
7	*m*	(7 > 6)	5·80
8	*m*	(8 ∼ 7)	5·41
9	*m*		2·71
10	*vw*		0·44
11	*vw*	(11 > 10)	0·75
12	*m*	(12 ∼ 9)	2·92
13	*m*		4·53
14	*m*		4·04
−1	*vw*		0·58
−2	*w*		1·02
−3	*w*	(−3 > −4)	1·02
−4	*w*		0·89
−5	*w*	(−5 > −3)	1·59
−6	*w*	(−6 > −5)	2·70
−7	*w*		2·30
−8	*w*		1·02
−9	*vvs*		100·00
−10	*vs*		37·90
−11	*m*		2·13
−12	*w*	(−12 ∼ −4)	0·93
−13	*m*	(−13 > −11)	3·20
−14	*m*	(−14 > −13)	4·04
84*R* (25 3)$_3$			
1	*a*		0·01
4	*vvw*	(4 > −2)	0·08
7	*vw*		0·24
10	*vw*	(10 > 7)	0·46
13	*w*		0·71
16	*w*	(16 > 13)	0·96
19	*w*	(19 > 16)	1·18
22	*w*	(22 > 19)	1·34
25	*w*	(25 ∼ 22)	1·43
28	*vvs*		100·00
31	*w*		1·38
34	*w*	(34 > 37)	1·26
37	*w*	(37 > 40)	1·09
40	*w*		0·91
−2	*vvw*		0·02
−5	*vvw*	(−5 > 4)	0·13
−8	*vw*		0·31
−11	*vw*	(−11 > −8)	0·54
−14	*w*		0·80
−17	*w*	(−17 > −14)	1·04
−20	*w*		1·24
−23	*w*	(−23 > −17)	1·38
−26	*w*		1·44
−29	*w*		1·43
−32	*w*		1·34
−35	*w*	(−35 > −38)	1·20
−38	*w*	(−38 > −41)	1·03
−41	*w*		0·85
84*R* (11 8 4 5)$_3$			
1	*w*	(1 > 13)	3·18
4	*w*	(4 > 13)	3·33
7	*vw*	(7 > 10)	0·79
10	*vw*		0·67
13	*w*	(13 > 16)	2·11
16	*w*		1·53
19	*w*		1·85
22	*s*		37·21
25	*s*		29·23
28	*s*		25·74
31	*vs*		70·39
34	*w*		2·55
37	*m*		7·00
40	*vw*		1·45
−2	*vvw*		0·15
−5	*vvw*		0·16
−8	*vw*	(−8 > 7)	1·19
−11	*vw*	(−11 > 7)	1·97
−14	*w*		2·62
−17	*s*		9·99
−20	*m*		4·77
−23	*w*	(−23 > 4)	3·62
−26	*vvs*		100·00
−29	*s*		23·79
−32	*vs*		54·40
−35	*m*		3·95
−38	*m*		4·02
−41	*m*		4·77

Table 1 (*cont.*)

Polytypes of the family 38*L*

114*R* (29 9)$_3$

l	I_{obs}		I_{calc}
1	*vvw*		0·02
4	*vw*		0·22
7	*vw*	(7>4)	0·33
10	*vvw*	(10>1)	0·14
13	*a*		0·003
16	*vw*		0·26
19	*w*	(19>22)	0·59
22	*w*		0·42
25	*a*		0·01
28	*w*		0·66
31	*m*		3·32
34	*s*	(34∼40)	7·07
37	*s*	(37>40)	9·49
40	*s*	(40>43)	8·81
43	*s*		5·58
46	*m*		2·08
49	*vw*		0·22
52	*vvw*		0·10
55	*w*		0·52
−2	*vvw*	(−2>−11)	0·07
−5	*vw*		0·29
−8	*vw*		0·29
−11	*vvw*	(−11>−14)	0·06
−14	*vvw*	(−14>−26)	0·05
−17	*vw*	(−17>−23)	0·40
−20	*w*		0·60
−23	*vw*		0·26
−26	*vvw*	(−26∼1)	0·03
−29	*w*		1·33
−32	*m*		4·55
−35	*s*		8·15
−38	*vvs*		100·00
−41	*s*		7·92
−44	*m*		4·32
−47	*w*		1·23
−50	*vvw*		0·03
−53	*vw*		0·24
−56	*w*		0·59

114*R* (35 3)$_3$

l	I_{obs}		I_{calc}
1	*vvw*		0·002
4	*vw*		0·02
7	*vw*	(7>4)	0·07
10	*w*		0·14
13	*w*	(13>10)	0·22
16	*w*	(16>13)	0·31
19	*w*		0·41
22	*w*	(22>19)	0·50
25	*w*	(25∼22)	0·58
28	*w*	(28>25)	0·65
31	*m*		0·70
34	*m*		0·73
37	*m*		0·74
40	*m*		0·72
43	*w*	(43>46)	0·69
46	*w*	(46>49)	0·64
49	*w*	(49>52)	0·58
52	*w*	(52>55)	0·52
55	*w*		0·45
−2	*vvw*		0·01
−5	*vw*	(−5>4)	0·04
−8	*w*		0·09
−11	*w*	(−11>−8)	0·16
−14	*w*	(−14>−11)	0·25
−17	*w*	(−17>−14)	0·34
−20	*w*	(−20>−17)	0·44
−23	*w*		0·53
−26	*w*		0·61
−29	*w*		0·67
−32	*m*		0·71
−35	*m*	(−35>−32)	0·74
−38	*vvs*		100·00
−41	*m*		0·71
−44	*m*		0·68
−47	*w*		0·62
−50	*w*	(−50>−53)	0·56
−53	*w*	(−53>−56)	0·50
−56	*w*		0·43

114*R* (21 9 6 2)$_3$

l	I_{obs}		I_{calc}
1	*vw*		0·20
4	*w*	(4>5)	0·60
7	*m*		1·40
10	*vw*r		0·17
13	*vvw*		0·10
16	*vw*	(16>1)	0·27
19	*w*	(19>28)	0·98
22	*vw*	(22>16)	0·43
25	*vw*	(25∼16)	0·26
28	*w*	(28>4)	0·82
31	*s*	(31>43)	14·23
34	*s*	(34>31)	18·99
37	*vvs*		100·00
40	*vs*		30·48
43	*s*		9·90
46	*s*	(46∼31)	14·88
49	*m*		2·31
52	*m*		2·37
55	*w*		0·47
−2	*vw*		0·24
−5	*w*	(−5>55)	0·51
−8	*m*	(−8>7)	2·06
−11	*w*		0·64
−14	*m*		1·14
−17	*vw*	(−17>−2)	0·36
−20	*w*	(−20∼19)	1·05
−23	*m*	(−23>−8)	2·33
−26	*w*		0·95
−29	*s*	(−29>−47)	5·19
−32	*s*		4·45
−35	*s*	(−35>−29)	12·12
−38	*vs*		23·75
−41	*s*	(−41∼−35)	11·78
−44	*s*	(−44>−32)	4·22
−47	*s*	(−47>−44)	4·84
−50	*w*		0·88
−53	*m*		2·19
−56	*w*	(−56>−50)	1·02

114*R* (13 5 2 2 6 2 6 2)$_3$

l	I_{obs}		I_{calc}
1	*vw*	(1>13)	0·76
4	*m*		3·48
7	*vw*		0·88
10	*vvw*	(10>−14)	0·13
13	*vvw*	(13>10)	0·46
16	*vw*	(16>19)	1·15
19	*vw*		1·08
22	*vw*		1·18
25	*vw*		1·50
28	*a*		0·08
31	*s*		10·98
34	*vvs*		100·00
37	*vs*		16·70
40	*vs*	(40>37)	22·16
43	*s*		11·19
46	*vs*		18·28
49	*vs*	(49>46)	23·94
52	*a*		0·06
55	*vvw*		0·82
−2	*w*	(−2>−20)	1·86
−5	*vw*		0·79
−8	*m*	(−8>−11)	4·04
−11	*m*		3·47
−14	*vvw*		0·10
−17	*vw*		0·56
−20	*w*		1·31
−23	*m*		2·80
−26	*s*		11·07
−29	*m*		3·70
−32	*m*	(−32>−29)	7·17
−35	*s*		13·44
−38	*m*	(−38>−41)	6·69
−41	*m*		4·62
−44	*w*		2·00
−47	*m*		4·25
−50	*m*		5·76
−53	*s*		11·98
−56	*a*		0·03

Polytypes of the family 44*L*

44*L* (37 7)

l	I_{obs}		I_{calc}
0	*w*		0·19
1	*vw*	(1>3)	0·07
2	*a*		0·001
3	*vw*		0·05
4	*w*		0·20
5	*w*	(5>−1)	0·33
6	*w*	(6∼5)	0·33
7	*w*	(7∼4)	0·18
8	*vvw*		0·02
9	*vw*		0·07
10	*w*	(10>6)	0·52
11	*m*		1·44
12	*m*	(12>11)	2·66
13	*m*	(13>12)	3·82
14	*m*		4·56
15	*m*		4·62
16	*m*	(16>17)	4·00
17	*m*		2·91
18	*m*		1·71
19	*w*	(19>6)	0·73
20	*w*	(20∼4)	0·16
21	*a*		0·0003
22	*vw*		0·12
−1	*w*	(−1>4)	0·25
−2	*w*		0·20
−3	*vw*	(−3>3)	0·09
−4	*a*		0·003
−5	*vw*		0·05
−6	*w*		0·23
−7	*w*		0·43
−8	*w*	(−8∼10>−9)	0·49
−9	*w*	(−9>−6)	0·32
−10	*vw*		0·06
−11	*vw*	(−11>−10)	0·10
−12	*m*		1·34
−13	*s*		6·33
−14	*vs*		41·10
−15	*vvs*		100·00
−16	*m*		1·45
−17	*vw*		0·05
−18	*w*		0·58
−19	*w*	(−19>−18)	0·86
−20	*w*		0·74
−21	*w*		0·41
−22	*a*		0·0003

Figs. 1 to 7. (10.l) or (40.l) row lines of oscillation photographs about the c axis of the various polytype regions. Cu K radiation, 60 mm diameter camera. Magnification × 3. The zero line is indicated by the arrow.

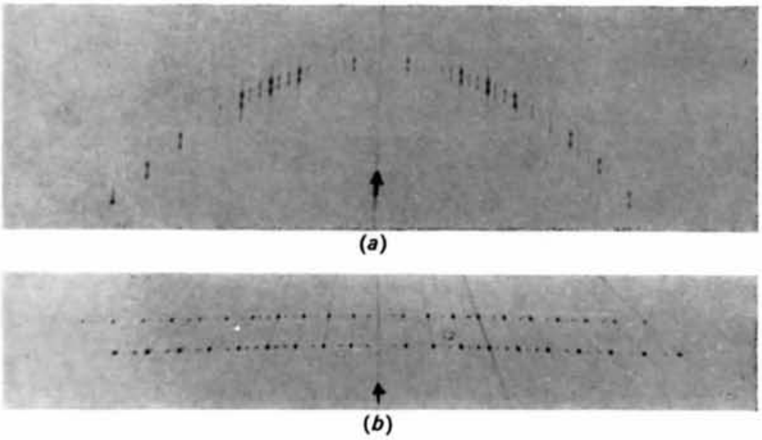

Fig. 1. (*a*) (40.l) row line of the polytypes $12H$ (6 6); $36R$ $(8\ 4)_3$ and $36R$ $(2\ 10)_3$, photographed simultaneously. (*b*) (10.l) row line of the polytypes $12L$ (9 3); $36R$ $(10\ 2)_3$ and $3R$ $(7\ 5)_3$, photographed simultaneously.

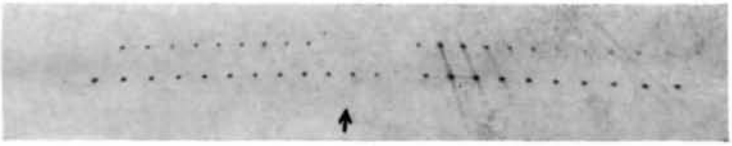

Fig. 2. (10.l) row line of the polytype $42R$ $(12\ 2)_3$.

Fig. 3. (10.l) row line of the polytype $54R$ $(10\ 8)_3$, and unidentified polytype regions belonging to the family $18L$–$54R$.

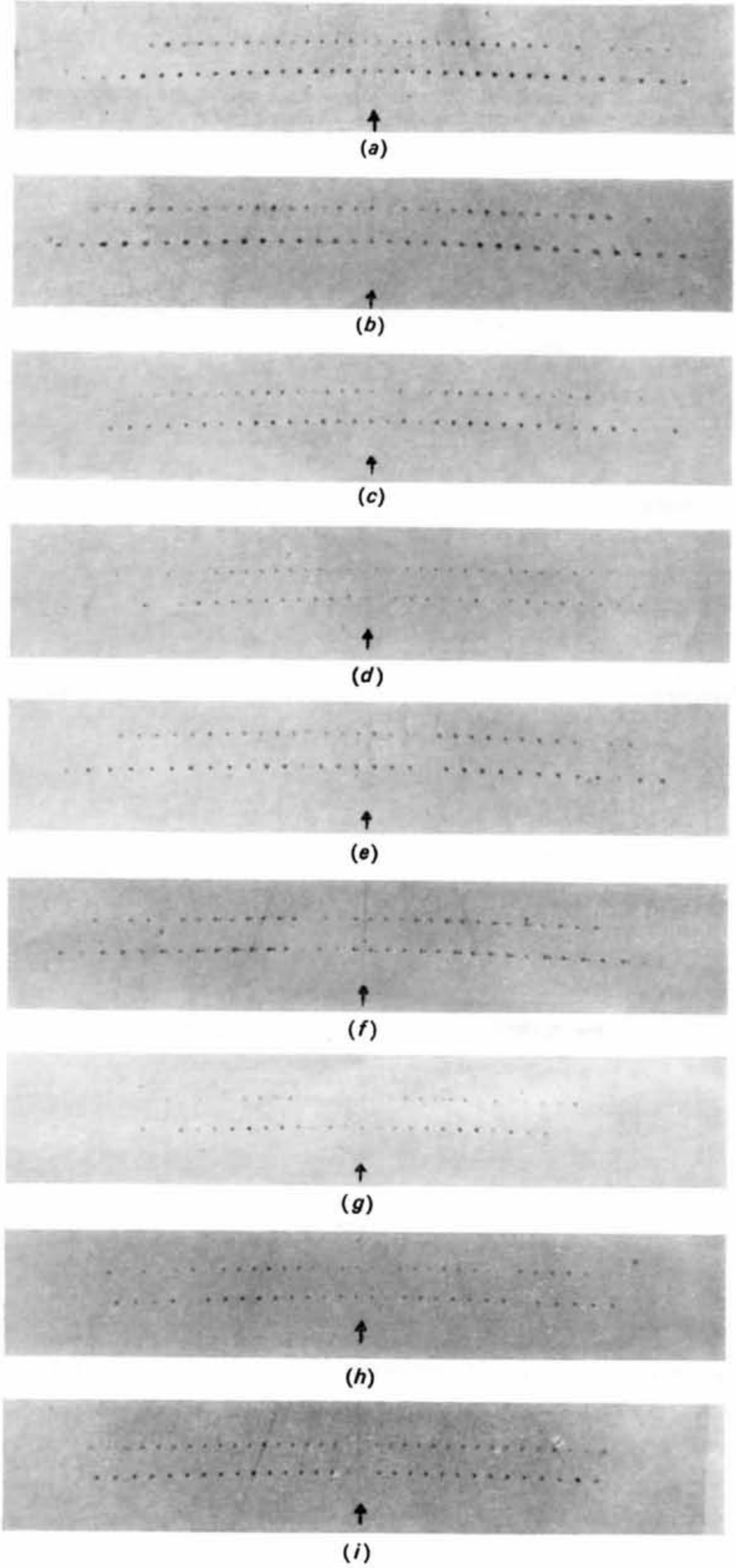

Fig. 4. (*a*) (10.*l*) row line of the polytype 60*R* $(9\ 3\ 6\ 2)_3$. (*b*) (10.*l*) row line of the polytype 20*H* (10 10). (*c*) (10.*l*) row line of the polytype 20*L* (2 3 8 7). (*d*) (10.*l*) row line of the polytype 60*R* $(6\ 3\ 3\ 3\ 3\ 2)_3$. (*e*) (10.*l*) row line of the polytype 60*R* $(8\ 4\ 2\ 2\ 2\ 2)_3$. (*f*) (10.*l*) row line of the polytypes 60*R* $(9\ 4\ 5\ 2)_3$ and 60*R* $(5\ 4\ 5\ 2\ 2\ 2)_3$, photographed simultaneously. (*g*) (10.*l*) row line of the polytype 20*L* (3 4 7 6). (*h*) (10.*l*) row line of the polytype 60*R* $(10\ 3\ 5\ 2)_3$. (*i*) (10.*l*) row line of the polytype 60*R* $(17\ 3)_3$.

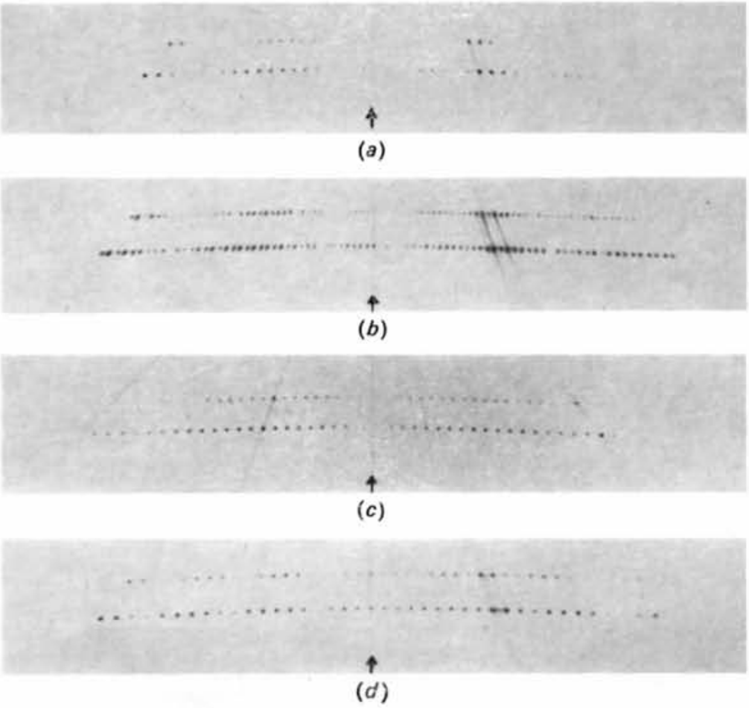
(*a*)
(*b*)
(*c*)
(*d*)

Fig. 5. (*a*) (10.*l*) row line of the polytype 28*L* (23 5). (*b*) (10.*l*) row line of the polytypes 84*R* (11 8 4 5)$_3$ and 28*L* (23 5); photographed simultaneously. (*c*) (10.*l*) row line of the polytype 84*R* (25 3)$_3$. (*d*) (10.*l*) row line of the polytype 28*L* (2 2 21 3); the additional spot between *l* = 9 and *l* = 10 belongs to a cubic region.

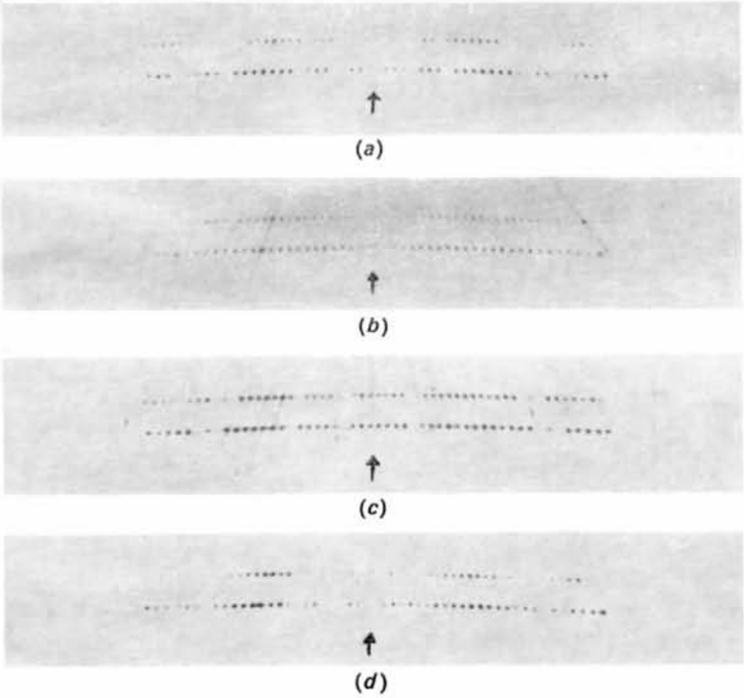
(*a*)
(*b*)
(*c*)
(*d*)

Fig. 6. (*a*) (10.*l*) row line of the polytype 114*R* (29 9)$_3$. (*b*) (10.*l*) row line of the polytype 114*R* (35 3)$_3$. (*c*) (10.*l*) row line of the polytype 114*R* (13 5 2 2 6 2 6 2)$_3$. (*d*) (10.*l*) row line of the polytype 114*R* (21 9 6 2)$_3$.

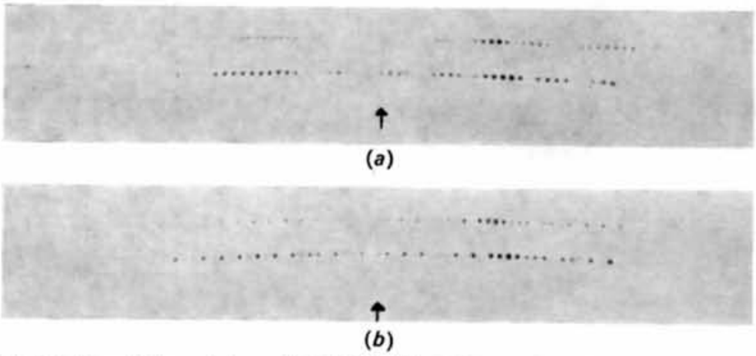

Fig. 7. (*a*) (10.*l*) row line of the polytype 44*L* (37 7). (*b*) (10.*l*) row line of the polytype 44*L* (17 4 17 6).

Table 1 (*cont.*)

l	$I_{\rm obs}$	$I_{\rm calc}$
Polytypes of the family 44*L*		
44*L* (17 4 17 6)		
0	*vw*	0·25
1	*a*	0·03
2	*vw* (2 > 4)	0·50
3	*vw*	0·21
4	*vw* (4 > 0)	0·31
5	*w*	0·64
6	*a*	0·003
7	*w*	0·53
8	*w* (8 > 5)	1·09
9	*vvw*	0·11
10	*m*	4·66
11	*a*	0·04
12	*s*	9·48
13	*vw*	0·36
14	*s* (14 > 12)	12·44
15	*vw* (15 > 13)	0·49
16	*s*	11·46
17	*vw* (17 ~ 13)	0·23
18	*s*	7·38
19	*a*	0·0002
20	*m*	2·99
21	*vw*	0·23
22	*vw* (22 > 21)	0·47
−1	*w* (−1 ~ 5)	0·64
−2	*a*	0·02
−3	*w* (−3 > −1)	1·31
−4	*a*	0·01
−5	*w*	0·92
−6	*a*	0·01
−7	*vvw*	0·03
−8	*a*	0·01
−9	*w*	1·17
−10	*vvw* (−10 > −7)	0·06
−11	*m*	7·09
−12	*a*	0·01
−13	*vs*	25·12
−14	*vs* (−14 > −16)	24·67
−15	*vvs*	100·00
−16	*vs*	18·49
−17	*w*	1·00
−18	*w* (−18 > −17)	2·67
−19	*w* (−19 > −21)	1·83
−20	*vvw*	0·09
−21	*w*	0·91
−22	*w*	0·47

distinguished by the shape of the spots. This is particularly easy if the regions photographed belong to the same family but to different space groups; *i.e.* one hexagonal and the other rhombohedral.

Some of the new polytypes found belong to hitherto unknown families, namely 44*L*–132*R*; 38*L*–114*R* and 18*L*–54*R*. The other polytypes belong to the family 12*L*–36*R*; 14*L*–42*R* (Mardix, Brafman & Steinberger, 1967); 20*L*–60*R* (Mardix, Alexander, Brafman & Steinberger, 1967): and 28*L*–84*R* (Brafman, Alexander & Steinberger, 1967). A list of the new polytypes is given in Table 2. It is to be noted that the polytypes 44*L* (37 7) and 44*L* (17 6 17 4) have the largest elementary stacking sequence identified in ZnS.

A rare case of polytypes belonging to two different families was found in the specimen 220/69. A microphotograph of the specimen is given in Fig. 8. The polytypes found in this crystal are listed in Table 3.

Table 3. *Polytypes found in crystal No.* 220/69

Region	Polytype
a	10*H* (5 5)
b	60*R* (5 4 5 2 2 2)$_3$
c	60*R* (9 4 5 2)$_3$
d	60*R* (18 2)$_3$
e	60*R* (6 3 3 3 3 2)$_3$
f	60*R* (8 4 2 2 2 2)$_3$
g	3*C*
h	54*R* (10 8)$_3$

Table 2. *List of the polytypes found*

Polytype families	Specimen No.	New polytypes found	Other polytypes found
12*L*–36*R*	209/52	12*H* (6 6)	6*H* (3 3)
		12*L* (9 3)	36*R* (10 2)*
		36*R* (8 4)$_3$	36*R* (7 5)$_3$*
14*L*–42*R*	220/70	42*R* (12 2)$_3$	
18*L*–54*R*	220/69	54*R* (10 8)$_3$	
20*L*–60*R*	220/69	60*R* (9 4 5 2)$_3$	10*H* (5 5)
		60*R* (5 4 5 2 2 2)$_3$	60*R* (18 2)$_3$†
		60*R* (6 3 3 3 3 2)$_3$	
		60*R* (8 4 2 2 2 2)$_3$	
	175/79	20*L* (3 4 7 6)	
		60*R* (17 3)$_3$	
		60*R* (10 3 5 2)$_3$	
	220/62	20*H* (10 10)	20*L* (13 7)*
		20*L* (2 3 8 7)	60*R* (11 9)$_3$*
		60*R* (9 3 6 2)$_3$	20*L* (5 3 3 4 2 3)†
28*L*–84*R*	248/51	28*L* (23 5)	
		84*R* (11 8 4 5)$_3$	
	217/54	28*L* (21 3 2 2)	
		84*R* (25 3)$_3$	
38*L*–114*R*	175/95	114*R* (29 9)$_3$	
		114*R* (35 3)$_3$	
		114*R* (21 9 6 2)$_3$	
		114*R* (13 5 2 2 6 2 6 2)$_3$	
44*L*–132*R*	217/55	44*L* (37 7)	
		44*L* (17 4 17 6)	

* These polytypes were already found in other crystals also, their characteristic intensities and X-ray photographs are to be published.

† Already reported (Mardix *et al.*, 1967).

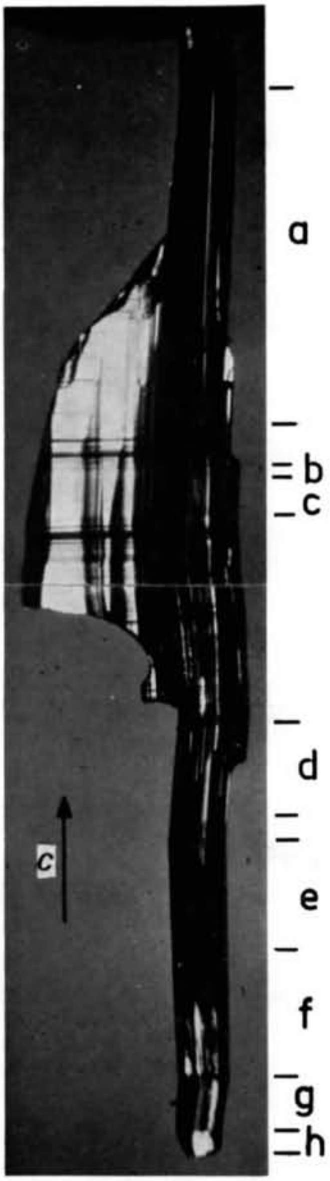

Fig. 8. ZnS crystal No. 220/69 seen under partially crossed polarizers, *c* axis direction and polytype region are indicated. Magnification × 20.

The regions '*a*' to '*g*' belong to the family 10*L*–20*L*–60*R* while region '*h*' belongs to the family 18*L*–54*R*. More regions belonging to this family were observed at the very end of the specimen, adjacent to region '*h*'. These regions are very narrow and it is difficult to identify the polytypes, but, from the distance between the few spots belonging to these regions and appearing on the X-ray photograph (Fig. 3), it was concluded that they belong to the family 18*L*–54*R*. Only one other case of this kind has previously been reported. The polytype 14*L* (7 7) was found in a specimen containing polytypes of the family 6*L*–18*R*–24*L*–36*R* (Mardix, Alexander, *et al.* 1967). It is to be noted that in both cases the regions belonging to the different families were found in two different parts of the specimen; no polytype of one family was found between polytype regions of the other family. This fact may be due to secondary growth on the main crystal, but it may also indicate some specific mechanism of transformation governing the formation of polytypes. This point must be further investigated.

All polytypes reported here are of even periodicity and do not contain the number 1 in their Zhdanov sequence. These properties are characteristic of ZnS polytypes grown by sublimation (Steinberger & Mardix, 1967).

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Double Polytype Regions in ZnS Crystals

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Regions of uniform birefringence in ZnS crystals were found to contain a great number of narrow domains (width $\simeq 1\mu$) of two different polytypes each. Three such regions were found in two specimens. From X-ray oscillation photographs the structures of these three regions were identified and found to consist of 36*R* $(5\ 7)_3$ and 36*R* $(7\ 5)_3$, 36*R* $(3\ 4\ 2\ 3)_3$ and 36*R* $(5\ 2\ 2\ 3)_3$ and 60*R* $(9\ 6\ 2\ 3)_3$ and 60*R* $(8\ 7\ 2\ 3)_3$, polytypes respectively. These polytypes were unknown so far. The formation of such double polytypes is discussed.

Introduction

During investigation of ZnS crystals containing polytypes, some regions of uniform birefringence were found whose X-ray oscillation photographs indicated that these regions consisted of a single polytype with a periodicity of $3n$ layers. Reflexions having $l = 0$ (mod 3) were systematically absent. The polytype was first assumed to be primitive hexagonal. However, it was found that no stacking sequence of $3n$ layers resulted in a calculated intensity distribution similar to the experimental one.

On a second trial it was assumed that each of these regions consisted of a mixture of two rhombohedral polytypes of equal cell height ($3n$ layers per unit cell along the threefold axis), and those could actually be identified. Such regions will be referred to as 'double polytype regions'. These mixed regions contain domains of a single polytype which are thinner by one or two orders of magnitude than the single polytype regions encountered so far in similar crystals.

Their formation is discussed in terms of a periodic slip process (p.s.p.).

Results

The crystals used were grown by sublimation at approximately 1200°C from pure ZnS powder. Under suitable magnification a great number of parallel striations can be seen on the crystal's faces. These striations form the borderlines of regions of uniform birefringence which indicates a uniform percentage of hexagonality within each region (Brafman & Steinberger, 1966).

Three cases of double polytype regions were examined. Their X-ray oscillation photographs are shown in Fig. 1(*a*) to (*c*). The polytypes could be identified by assuming that each of these photographs consists of reflexions from two rhombohedral polytypes having the same periodicity. The procedure of identification