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New ZnS Polytypes

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Abstract. Fourteen new ZnS polytypes were identified, they are: 20*T*(5 4 2 3 3 3); 78*R*(10 8 5 3)$_3$; 26*T*(7 5 3 3 3 5); 26*T*(7 5 3 5 3 3); 78*R*(8 4 3 5 3 3)$_3$; 26*T*(8 5 3 3 2 5); 90*R*(7 7 5 5 2 4)$_3$; 36*T*(11 5 5 5 5 5); 108*R*(7 5 5 5 5 5 2 2)$_3$; 108*R*(11 5 3 3 5 2 4 3)$_3$; 40*T*(11 11 7 4 5 2); 120*R*(11 11 8 3 5 2)$_3$; 162*R*(50 4)$_3$; 64*T*(45 5 11 3). The last two polytypes have the largest elementary stacking sequence of any ZnS polytype identified so far. Cu *K* X-ray 10.*l* oscillation photographs are presented; observed and calculated intensities are compared.

Experimental. The polytypes reported here were found during a recent investigation. Information concerning the specimens and the regions in which they were found is given in Table 1. The letter following the number of layers in the unit cell of a polytype indicates its space group: *T* for *P*3*m*1, *H* for $P6_3mc$ and *R* for *R*3*m*1. It should be noted that in former publications the letter *L* was used to denote the *P*3*m*1 space group.

The crystals were grown in our laboratory by the static sublimation method (Reynolds & Czyzak, 1950) with strict stabilization of temperature and pressure (Mardix, 1984*b*). A detailed morphological and structural analysis of two of the specimens 18/14 and 18/16 was reported earlier (Mardix, 1984*a*,*b*, respectively). 15° X-ray oscillation photographs, using Cu *K* radiation, of the 10.*l* row line of the new polytypes are presented in Fig. 1. The photographs were taken on a flat film at a distance of 60 mm from the specimen.† Relative intensities were estimated from the photographs by observation and are given on the eight-grade scale: *vvs*, *vs*, *s*, *m*, *w*, *vw*, *vvw* and *a*; additional observed relations within each grade are specified. ZnS polytypes are crystallographically ideal crystals (Mardix, Lang & Blech, 1971), the intensities of the reflection spots are proportional to |*F*| where *F* is the structure factor (Farkas-Jahnke & Dornberger-Schiff, 1970). The calculated intensities are proportional to |*F*| and include the Lorentz and polarization factors; they are normalized to give the strongest intensity as 100·00. The elimination method (Mardix, Kalman & Steinberger, 1970) was used to identify the new polytypes. According to this method the number of hexagonally stacked layers in the elementary stacking sequence is determined from birefringence measurements. The reflections (10.*l*) are arranged according to decreasing observed intensity. Following this arrangement the theoretical intensities for each of the possible arrangements, for the observed unit cell and number of

Table 1. *List of the investigated specimens and their identified polytypes*

Specimen	Region	*c* dimension (mm)	Polytype
18/14	110	0·20	Cubic
	110	0·23	60*R*(18 2)$_3$*
	120	3·50	60*R*(18 2)$_3$*
	130	0·70	Cubic
	160	0·55	60*R*(9 5 3 3)$_3$†
	170‡	3·00	60*R*(5 1 1 5 5 3)$_3$
			60*R*(7 5 5 3)$_3$
			20*T*(5 7 5 3)$_3$
	180	0·40	20*T*(5 4 2 3 3 3)
	190	1·50	20*T*(5 4 2 3 3 3)
16/53	100	0·70	26*T*(7 5 3 5 3 3)
	110	0·50	78*R*(8 4 3 5 3 3)$_3$
	120	1·70	26*T*(7 5 3 3 3 5)
	130	0·80	26*T*(8 5 3 3 2 5)
	140	0·70	78*R*(10 8 5 3)$_3$
16/121	130	0·80	90*R*(7 5 5 2 4 7)$_3$
	140	1·00	Cubic
18/15	100	1·50	108*R*(11 3 4 2 5 3 3 5)$_3$
	110	1·00	36*T*(11 5 5 5 5 5)
	120	4·00	108*R*(7 5 5 5 5 5 2 2)$_3$
	130	0·35	36*T*(11 5 5 5 5 5)
18/20	110	0·50	40*T*(11 11 7 4 5 2)
	120	0·60	120*R*(11 11 8 3 5 2)$_3$
	180	0·70	40*T*(11 11 7 4 5 2)
18/16§	300	0·15	162*R*(50 4)$_3$
16/122	130	0·70	64*T*(45 3 11 5)

* Previously reported structure (Mardix, Alexander, Brafman & Steinberger, 1967).

† Previously reported structure (Kiflawi & Mardix, 1970).

‡ A double polytype region. Morphology and formation were discussed in a previous publication (Mardix, 1984*b*).

§ The morphology of this crystal was discussed in a previous publication (Mardix, 1984*b*).

* In partial fulfilment of requirements for the BS degree.

† Observed and calculated intensities have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42638 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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hexagonal layers, are successively computed. A structure is rejected on the first case of discrepancy with the observed hierarchy. The final structure is determined by comparison of the observed to the computed intensity in the range $-N/2 \leq l \leq N/2$, where N is the number of layers in the elementary stacking sequence.

Discussion. Several of the specimens include groups of adjacent polytypes; they are: the narrow sub-regions in the double-polytype region 170 of specimen 18/14; regions 100, 110 and 130 of specimen 16/53; regions 110, 120 and 130 in specimen 18/15 and regions 110 and 120 in 18/20. The Zhdanov symbols of the polytypes in the adjacent regions are simply related to one another. This is a consequence of their formation mechanism and will be discussed in detail in a forthcoming publication.

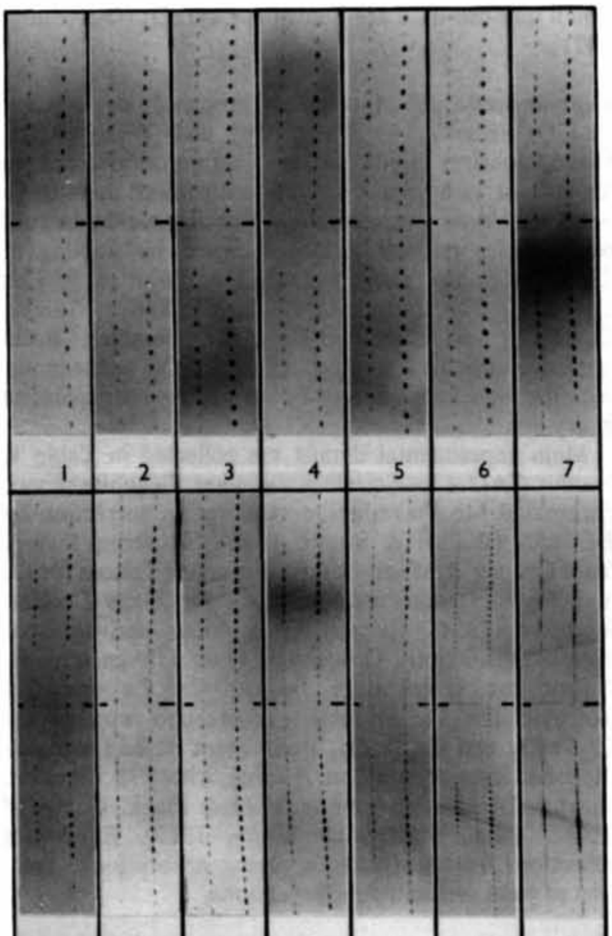

Fig. 1. The 10.l row lines of 15° c-axis Cu K X-ray oscillation photographs of the new polytypes recorded on a flat film at a distance of 60 mm from the specimen; collimator diameter: 0·2 mm. The zero layer is indicated by short segments on both sides of the $K\alpha$ and $K\beta$ row lines. The new polytypes are: (1) 20T(5 4 2 3 3 3); (2) 78R(10 8 5 3)$_3$; (3) 26T(7 5 3 3 3 5); (4) 26T(7 5 3 5 3 3); (5) 78R(8 4 3 5 3 3)$_3$; (6) 26T(8 5 3 3 2 5); (7) 90R(7 7 5 5 2 4)$_3$; (8) 36T(11 5 5 5 5 5); (9) 108R(7 5 5 5 5 5 2 2)$_3$; (10) 108R(11 5 3 3 5 2 4 3)$_3$; (11) 40T(11 11 7 4 5 2); (12) 120R(11 11 8 3 5 2)$_3$; (13) 162R(50 4)$_3$; (14) 64T(45 5 11 3).

The polytypic region which was identified as 162R(50 4) includes a very narrow unidentified sub-region. This may have contributed to the few slight discrepancies between the computed and observed intensities. There can, however, be no doubt as to the validity of the identification; birefringence measurement as well as the general distribution of intensities along the (10.l) row line show that the polytype has two hexagonally stacked layers in its elementary stacking sequence. There are only 18 such polytypes with the unit cell and space group 162R. The complete set of calculated intensities with $-79 \leq l \leq 80$ for all these polytypes was compared to the observed intensities in order to eliminate any doubt regarding the correctness of the identification.

The polytype 64T(45 5 11 3) has the largest elementary stacking sequence of any known ZnS polytype. Owing to the correlation of the elementary stacking sequence with the Burgers vector of the screw dislocation in the polytypic region (Mardix, Lang & Blech, 1971), one concludes that the magnitude of this Burgers vector is very close to 200 Å.

Specimen 16/122 includes a number of polytypes of the family 64T/192R which were not identified. The expected computation time was estimated to be unreasonably long by the current version of the elimination method. The percentages of hexagonally stacked layers in these regions were estimated from birefringence measurements (Brafman & Steinberger, 1966) to be 16% in some and 20% in the others. This corresponds to 10 or 14 Zhdanov elements in their elementary stacking sequences. Computer time necessary for identification goes up very rapidly with the number of layers and with the number of hexagonal layers in the elementary stacking sequence. Attempts are currently under way to increase the effectiveness of the elimination method in order to enable the identification of the above polytypes.

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