

The regions 'a' to 'g' belong to the family 10L-20L-60R while region 'h' belongs to the family 18L-54R. 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 18L-54R. Only one other case of this kind has previously been reported. The polytype 14L (7 7) was found in a specimen containing polytypes of the family 6L-18R-24L-36R (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

BY S. MARDIX, I. KIFLAWI AND Z. H. KALMAN

*Department of Physics, The Hebrew University, Jerusalem, Israel*

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Regions of uniform birefringence in ZnS crystals were found to contain a great number of narrow domains (width  $\approx 1\mu$ ) 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  $36R(5\ 7)_3$  and  $36R(7\ 5)_3$ ,  $36R(3\ 4\ 2\ 3)_3$  and  $36R(5\ 2\ 2\ 3)_3$  and  $60R(9\ 6\ 2\ 3)_3$  and  $60R(8\ 7\ 2\ 3)_3$ , 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  $l=0 \pmod{3}$  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  $1200^\circ\text{C}$  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

(Mardix, Alexander, Brafman & Steinberger, 1967) consists of comparing the observed intensity distribution with that computed for all possible Zhdanov symbols having the appropriate number of Zhdanov numbers consistent with the birefringence measured (Brafman & Steinberger, 1966). A list of the polytypes found is given in Table 1. Two of the polytypes listed in Table 1 [ $6H(3\ 3)$  and  $60R(18\ 2)_3$ ] are known already, whilst the other six polytypes have not been reported before. Observed and calculated intensity distributions of the new polytypes are given in Table 2. It is to be noted that both specimens examined in this work contain single polytype regions as well as double polytype regions.

Table 1. *List of the polytypes found*

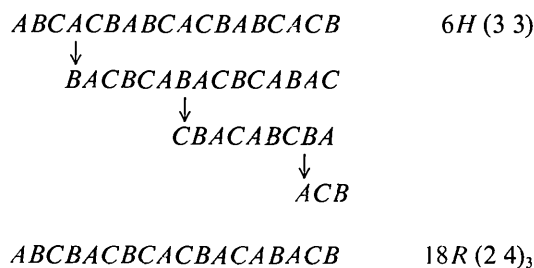
| Specimen No. | Region | Type of region | Polytypes                                    |
|--------------|--------|----------------|--|
| 155/51       | a      | double         | { $36R(5\ 2\ 2\ 3)_3$<br>$36R(3\ 4\ 2\ 3)_3$ |
|              | b      | single         | $36R(3\ 4\ 2\ 3)_3$                          |
|              | c      | double         | { $36R(7\ 5)_3$<br>$36R(5\ 7)_3$             |
|              | d      | single         | $6H(3\ 3)$                                   |
|              | e      | single         | $36R(10\ 2)_3^*$                             |
| 268/54       | a      | double         | { $60R(7\ 8\ 2\ 3)_3$<br>$60R(9\ 6\ 2\ 3)_3$ |
|              | b      | single         | $60R(18\ 2)_3^\dagger$                       |

\* X-ray photograph given in Fig. 2.

† Reported earlier (Mardix *et al.*, 1967).

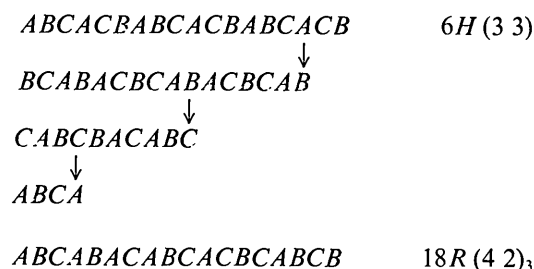
### Discussion

The formation of ZnS polytypes was explained by a p.s.p. which is periodically repeated along one direction of the crystal's  $c$  axis (Mardix, Kalman & Steinberger, 1968). If, however, a single p.s.p. propagates from the same layer (and at the same periodicity) in both directions of the  $c$  axis, two different polytypes may be formed. Let us look for example at the way the two polytypes  $18R(2\ 4)_3$  and  $18R(4\ 2)_3$  can be formed from the polytype  $6H(3\ 3)$ . If we start from the  $ABC$  sequence of the polytype  $6H(3\ 3)$  and perform one slip of the 4th layer of the unit cell at a periodicity of six, the polytype  $18R(2\ 4)$  will be formed:



If we let the same p.s.p. propagate at the same periodicity along the other direction of the  $c$  axis the poly-

type  $18R(4\ 2)_3$  will be formed:



In this particular case the two polytypes are twins. In general the two polytypes formed by this process will have the following two properties: (a) Only one pair of successive Zhdanov numbers will be different in the Zhdanov symbols of the elementary stacking sequence of either of the two polytypes. Let us denote by  $I_K, J_K$  and  $I'_K, J'_K$  the different pairs in the Zhdanov symbols, referring to the two polytypes. Then the relation  $I_K - I'_K = J'_K - J_K = \pm 2$  holds. Obviously  $I_K + J_K$  must equal  $I'_K + J'_K$ . (b) The two regions will be tilted in opposite directions in the same tilt plane (Mardix *et al.*, 1968) and will have the same angle of tilt with respect to the  $c$  axis.

It should be mentioned that similar situations are frequently encountered in single regions. In these cases two adjacent regions are found, each region being a single polytype, with both structure and tilt of the two polytypes fulfilling conditions (a) and (b) mentioned above. In some cases a third polytype region, the 'parent' polytype, was also found adjacent to one of the 'derived' polytype regions [e.g. Mardix *et al.*, 1968, where three consecutive regions were found to have the structures  $6H(3\ 3)$ ,  $18R(2\ 4)_3$  and  $18R(4\ 2)_3$ ].

The formation of double polytype regions can be explained by assuming the above mentioned process to begin at a great number of places in a single polytype region. The polytypes  $36R(5\ 7)_3$  and  $36R(7\ 5)_3$  can be formed from the polytype  $12H(6\ 6)$  by a single slip of the 7th layer and propagation at a periodicity of twelve in both directions of the  $c$  axis. The polytypes  $36R(5\ 2\ 2\ 3)_3$  and  $36R(3\ 4\ 2\ 3)_3$  can be formed from the polytype  $12L(4\ 3\ 2\ 3)$  by a single slip of the 5th layer and periodicity twelve. Also, the polytypes  $60R(7\ 8\ 2\ 3)_3$  and  $60R(9\ 6\ 2\ 3)_3$  can be formed in the same way by a single slip of the 9th layer of the polytype  $20L(8\ 7\ 2\ 3)$  with periodicity twenty. It is easily verified that all pairs of polytypes identified here obey condition (a) mentioned above.

Condition (b), *i.e.* the tilt of the various domains, could not be measured because of their small width. However, it was observed that double regions did present a somewhat wobbly surface under the microscope, in contrast to the smooth surfaces found in single polytype regions.

It was assumed that although the p.s.p. begins at a great number of places, it always begins at the same

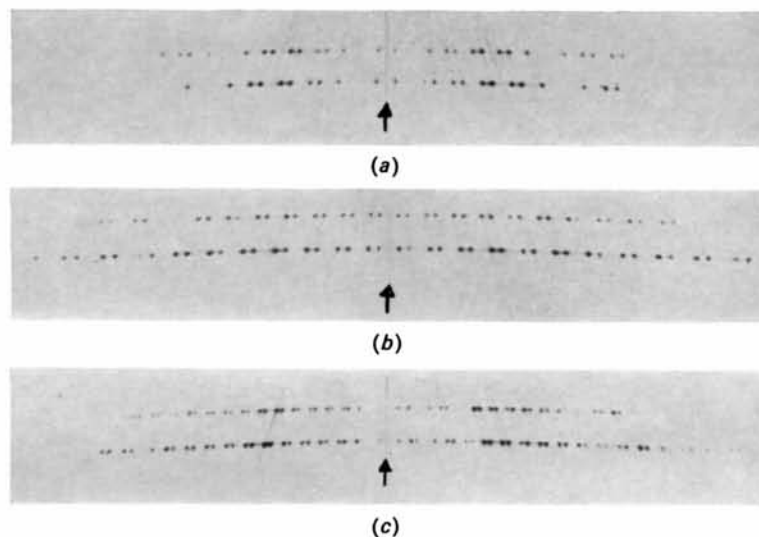


Fig. 1. (10.*l*) row lines of oscillation photographs about the *c* axis of the double polytype regions. Cu *K* radiation, 60 mm diameter camera. Magnification  $\times 3$ . The zero line is indicated by an arrow. (a) The double polytype region  $36R(7\ 5)_3$  and  $36R(5\ 7)_3$ ; (b) the double polytype region  $36R(5\ 2\ 2\ 3)_3$  and  $36R(3\ 4\ 2\ 3)_3$ ; (c) the double polytype region  $60R(9\ 6\ 2\ 3)_3$  and  $60R(7\ 8\ 2\ 3)_3$ .

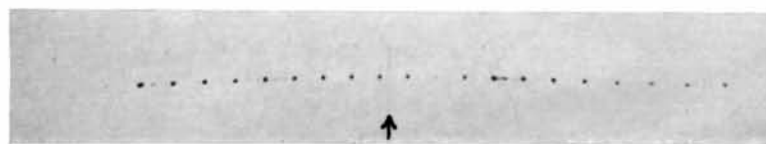


Fig. 2. (10.*l*) row line of oscillation photograph about the *c* axis of the polytype  $36R(10\ 2)_3$ . Cu *K* radiation, 60 mm diameter camera. Magnification  $\times 3$ .

atomic layer of the unit cell. This may be connected with an instability of specific layers in the unit cell.

The order of magnitude of the width of the domains in a double polytype region can be estimated from the X-ray photographs. The regions were photographed

using fine grain films, and the reflexions formed on the film seemed to be uniformly blackened even under high magnification. From this it was concluded that the domains' width must be smaller than about  $5\mu$ . On the other hand it would appear from the fact that

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

| 36R (7 5) <sub>3</sub>     |                            |                      |            |   |                      |
|----------------------------|----------------------------|----------------------|------------|---|----------------------|
| <i>l</i>                   | Observed intensity         | Calculated intensity | <i>l</i>   | Observed intensity  | Calculated intensity |
| 1                          | <i>w</i>                   | 5.945                | $\bar{2}$  | <i>a</i>  | 0.190                |
| 4                          | <i>vw</i>                  | 0.901                | $\bar{5}$  | <i>w</i>  | 7.458                |
| 7                          | <i>w</i> (7 > 1)           | 10.06                | $\bar{8}$  | <i>w</i>  | 9.031                |
| 10                         | <i>s</i>                   | 46.18                | $\bar{11}$ | <i>vs</i>   | 100.0                |
| 13                         | <i>s</i>                   | 52.70                | $\bar{14}$ | <i>vs</i>   | 65.74                |
| 16                         | <i>m</i>                   | 19.64                | $\bar{17}$ | <i>a</i>  | 0.108                |
| 36R (10 2) <sub>3</sub>    |                            |                      |            |   |                      |
| 1                          | <i>w</i>                   | 2.965                | $\bar{2}$  | <i>vw</i>   | 1.456                |
| 4                          | <i>m</i>                   | 4.189                | $\bar{5}$  | <i>vw</i>   | 0.153                |
| 7                          | <i>m</i> (7 > 4)           | 4.932                | $\bar{8}$  | <i>vw</i>   | 1.433                |
| 10                         | <i>m</i> (10 > 7)          | 5.161                | $\bar{11}$ | <i>vs</i>   | 100.0                |
| 13                         | <i>m</i>                   | 4.988                | $\bar{14}$ | <i>vs</i>   | 40.48                |
| 16                         | <i>m</i>                   | 4.691                | $\bar{17}$ | <i>m</i> ( $\bar{17}$ > 4)                                | 7.009                |
| 36R (3 4 2 3) <sub>3</sub> |                            |                      |            |   |                      |
| 1                          | <i>vw</i>                  | 5.669                | $\bar{2}$  | <i>vw</i>   | 1.998                |
| 4                          | <i>m</i>                   | 19.74                | $\bar{5}$  | <i>w</i>  | 14.29                |
| 7                          | <i>s</i>                   | 31.42                | $\bar{8}$  | <i>s</i>  | 39.56                |
| 10                         | <i>m</i> (10 > 4)          | 25.01                | $\bar{11}$ | <i>vs</i>   | 100.0                |
| 13                         | <i>vs</i>                  | 55.77                | $\bar{14}$ | <i>m</i> ( $\bar{14}$ > 4)                                | 23.66                |
| 16                         | <i>w</i>                   | 7.989                | $\bar{17}$ | <i>vs</i> ( $\bar{17}$ > 13)                              | 62.30                |
| 36R (5 2 2 3) <sub>3</sub> |                            |                      |            |   |                      |
| 1                          | <i>w</i> (1 > 4)           | 10.33                | $\bar{2}$  | <i>w</i>  | 9.317                |
| 4                          | <i>w</i>                   | 8.115                | $\bar{5}$  | <i>w</i> ( $\bar{5}$ > $\bar{2}$ )                        | 9.667                |
| 7                          | <i>m</i>                   | 20.71                | $\bar{8}$  | <i>s</i>  | 30.89                |
| 10                         | <i>vs</i>                  | 63.41                | $\bar{11}$ | <i>vs</i>   | 100.0                |
| 13                         | <i>a</i>                   | 3.698                | $\bar{14}$ | <i>s</i> ( $\bar{14}$ > $\bar{8}$ )                       | 33.19                |
| 16                         | <i>s</i> (16 > 17)         | 42.32                | $\bar{17}$ | <i>s</i> (17 > $\bar{14}$ )                               | 39.32                |
| 60R (7 8 2 3) <sub>3</sub> |                            |                      |            |   |                      |
| 1                          | <i>vw</i> (1 > 4)          | 1.320                | $\bar{2}$  | <i>w</i> ( $\bar{2}$ > $\bar{8}$ )                        | 4.856                |
| 4                          | <i>vw</i>                  | 1.192                | $\bar{5}$  | <i>vw</i>   | 1.821                |
| 7                          | <i>s</i> (7 $\approx$ 13)  | 14.11                | $\bar{8}$  | <i>w</i>  | 4.222                |
| 10                         | <i>m</i>                   | 6.017                | $\bar{11}$ | <i>m</i>  | 7.215                |
| 13                         | <i>s</i> (13 > 16)         | 13.49                | $\bar{14}$ | <i>vw</i> ( $\bar{14}$ > $\bar{5}$ )                      | 2.477                |
| 16                         | <i>s</i>                   | 10.25                | $\bar{17}$ | <i>vs</i>   | 100.00               |
| 19                         | <i>vs</i>                  | 85.72                | $\bar{20}$ | <i>vs</i> ( $\bar{20}$ > $\bar{23}$ )                     | 59.18                |
| 22                         | <i>vs</i>                  | 53.68                | $\bar{23}$ | <i>vs</i> ( $\bar{23}$ > $\bar{26}$ )                     | 43.34                |
| 25                         | <i>s</i> (25 $\approx$ 16) | 9.089                | $\bar{26}$ | <i>vs</i>   | 23.71                |
| 28                         | <i>m</i> (28 > 10)         | 7.259                | $\bar{29}$ | <i>s</i> ( $\bar{29}$ > 13)                               | 16.58                |
| 60R (9 6 2 3) <sub>3</sub> |                            |                      |            |   |                      |
| 1                          | <i>vw</i> (1 > $\bar{2}$ ) | 0.2923               | $\bar{2}$  | <i>vw</i>   | 0.2102               |
| 4                          | <i>m</i> (4 > 10)          | 5.0884               | $\bar{5}$  | <i>m</i> ( $\bar{5}$ > $\bar{8}$ )                        | 6.2316               |
| 7                          | <i>vw</i>                  | 0.4743               | $\bar{8}$  | <i>m</i>  | 5.096                |
| 10                         | <i>m</i>                   | 4.117                | $\bar{11}$ | <i>m</i> ( $\bar{11}$ > $\bar{5}$ )                       | 8.098                |
| 13                         | <i>w</i>                   | 1.201                | $\bar{14}$ | <i>m</i>  | 6.290                |
| 16                         | <i>vs</i> (16 > 19)        | 43.73                | $\bar{17}$ | <i>s</i> ( $\bar{17}$ > 22)                               | 18.54                |
| 19                         | <i>vs</i> (19 > 28)        | 41.19                | $\bar{20}$ | <i>vs</i>   | 100.00               |
| 22                         | <i>s</i>                   | 7.144                | $\bar{23}$ | <i>s</i> ( $\bar{17} \approx \bar{23} \approx \bar{29}$ ) | 17.62                |
| 25                         | <i>vs</i>                  | 31.09                | $\bar{26}$ | <i>m</i>  | 5.822                |
| 29                         | <i>s</i>                   | 8.762                | $\bar{29}$ | <i>s</i>  | 7.774                |

spots from mixed regions are quite sharp, that the widths of most of the domains are not much less than about  $1\mu$ . Some smearing out along the columns in the X-ray photographs is observed which indicates some one-dimensional disorder.

The authors wish to express their sincere thanks to Professors E. Alexander and I. T. Steinberger for many helpful discussions and suggestions.

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## The Crystal Structure of 1,8-Dichloro-9-methylanthracene

BY ROBERT J. DELLACA, BRUCE R. PENFOLD AND WARD T. ROBINSON

*Chemistry Department, University of Canterbury, Christchurch, New Zealand*

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1,8-Dichloro-9-methylanthracene,  $C_{15}H_{10}Cl_2$ , crystallizes in the orthorhombic space group *Pnma* with  $a = 7.13$ ,  $b = 19.46$ ,  $c = 8.76$  Å,  $Z = 4$ ,  $D_{obs} = 1.42$  and  $D_{calc} = 1.43$  g.cm<sup>-3</sup>. Thus a crystallographic mirror plane is imposed on the separate molecular units. The intensities of 772 reflexions were estimated visually from integrated Weissenberg photographs. Atomic parameters have been refined by full-matrix least-squares procedures to a conventional *R* index of 0.092. The chlorine and methyl carbon atoms were assigned anisotropic thermal parameters; the other atoms isotropic parameters. All hydrogen atoms have been located. There is a pronounced distortion of the anthracene skeleton, C(9) being displaced by 0.19 Å from the mean molecular plane. The methyl carbon displacement is 0.80 Å on the same side of the plane as C(9), while the chlorine displacement is 0.33 Å on the opposite side.

### Introduction

There are now a number of structural data available relating to the molecular distortions which arise when naphthalene is *peri*-substituted. (For a review see Balasubramanian, 1966.) Hitherto, however, there appears to have been no structure analysis which could cast light on the related problem in the *peri*-substitution of anthracene.

The electronic absorption spectrum of 1-chloro-9-methylanthracene relative to that of 1-chloro-10-methylanthracene has been interpreted by Bouas-Laurent & Lapouyade (1965) as being consistent with distortions of the ground state molecular configuration of the 1,9(*peri*) substituted compound. In particular, the shift to longer wave-lengths of the band in the 3900 Å region, which accompanies *peri*-substitution, is believed to reflect the reduction in energy difference between the ground and excited electronic states to be expected as the result of molecular distortion. With a view to establishing the extent of such distortions, we began X-ray studies on crystals of 1-chloro-9-methylanthracene and 1,8-dichloro-9-methylanthracene. The relatively poor quality of the diffraction data obtainable from the monochloro compound at room temperature (22°C) caused us to abandon further work on it in favour of the dichloro compound in which the distortions would be expected to be even greater.

### Experimental

A sample of 1,8-dichloro-9-methylanthracene was kindly supplied by Professor Henri Bouas-Laurent of the University of Bordeaux, France. Suitable crystals were mounted on glass fibres and appeared to be stable in air and to X-rays.

#### Crystal data

1,8-Dichloro-9-methylanthracene,  $C_{15}H_{10}Cl_2$ ,  $M = 261.2$ . Orthorhombic with  $a = 7.13(1)$ ,  $b = 19.46(3)$ ,  $c = 8.76(1)$  Å. ( $\lambda = 1.5418$  Å for Cu  $K\alpha$  radiation. The numbers in parentheses here and elsewhere are estimated standard deviations in the least significant figures quoted).  $U = 1215$  Å<sup>3</sup>,  $D_{obs} = 1.42(2)$  g.cm<sup>-3</sup> (by flotation).  $Z = 4$ ,  $D_{calc} = 1.43$  g.cm<sup>-3</sup>,  $F(000) = 536$ ,  $\mu(\text{Cu } K\alpha) = 45.4$  cm<sup>-1</sup>,  $\mu(\text{Mo } K\alpha) = 5.1$  cm<sup>-1</sup>. Systematic absences:  $0kl$  for  $(k+l)$  odd,  $hk0$  for  $h$  odd.

Unit-cell dimensions were obtained from zero-level precession photographs with Polaroid film (Swink & Carpenter, 1967). Systematic absences of X-ray reflexions were consistent with space groups *Pnma* (which requires molecular symmetry *m*) and *Pn2<sub>1</sub>a* (which requires no molecular symmetry). Intensity statistics (Wilson, 1949; Howells, Phillips & Rogers, 1950) favoured centrosymmetric *Pnma* and the structure has been solved and refined in this space group.