On structure and twist in ZnS crystal whiskers

By S. MARDIX
Department of Electrical Engineering, University of Rhode Island, Kingston, Rhode Island 02881, U.S.A.

and A. R. LANG, G. KOWALSKI† and A. P. W. MAKEPEACE
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, England

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Abstract

ZnS crystal whiskers grown from the vapour at about 1450 K, with typical lengths of about 20 mm and diameters about 100 μm, have been studied by synchrotron X-ray topography. Crystallographic structure and texture have been compared with morphological and optical characteristics point-by-point along whisker axes. Using continuous radiation and cylindrical camera geometry, entire diffraction patterns from zones of {10T/1} type have been recorded, providing information on lattice symmetry and polytype order as well as on local lattice perfection in the whisker. The X-ray topographs spanned the three main types of structure in vapour-grown ZnS whiskers, namely an initial region of usually faulted 2H structure, a following region (of 'striated' appearance, optically) consisting of a stack of lamellae (average thickness a few μm) of polytypic structures with various c-axis repeat periods, and a third, following region containing long-period polytypes, all of the same order, in which individual structures can occupy lengths up to millimetre dimensions along the c axis and behave as perfect crystals except for the presence of a giant screw dislocation along the c axis. The third region exhibits the Eshelby twist expected from an axial screw dislocation with Burgers vector of magnitude equal to the axial length of the elementary stacking sequence of ZnS layers in the polytype structure, an equality accurately confirmed in two specimens by counter-diffractometer measurements with Cu Kα radiation. The region of thin lamellae can contain polytypes of high order equal or close to that found in the more perfect third region, but it shows inconstancy of polytype order along the c axis: from symmetry properties of the diffraction images on the X-ray topograph it is seen that all polytypes are of even order, changes of polytype order taking place by ±2m unit layers of ZnS structure (m being a small integer, frequently unity). In the four specimens studied, this lamellar region does not exhibit the expected Eshelby twist.

§1. Introduction

ZnS crystals grown from the vapour are remarkable for the variety of polytypes they exhibit when cooled down to room temperature. The simplest periodic structures of ZnS are wurtzite (hexagonal, 2H) and sphalerite (f.c.c., 3C), which are stable above and below about 1300 K, respectively. Less-simple periodically repeating stacking sequences of ZnS layers give rise to higher-order polytypes.

† On leave from Institute of Experimental Physics, University of Warsaw, Poland.
Much theoretical and experimental attention has been devoted to polytypism in ZnS. Such study has been assisted by the high degree of long-range order and large dimensions that domains of individual polytypes can exhibit, permitting analysis of their structures by conventional X-ray crystallographic techniques. To date about 200 different ZnS polytype structures have been identified (Mardix 1986a). Long periodicities of up to several tens of nanometres are found, the longest elementary stacking sequence so far reported containing 64 ZnS layers (Medizadeh and Mardix 1986).

It needs to be emphasized that regions containing large and rather perfect long-period polytypes constitute only one of several types of structure found in vapour-grown needle and blade-shaped ZnS crystals. Typically, such crystals contain three regions (Mardix 1986b), categorized as follows. Region 'a' comprises the initial growth which is hexagonal 2H, perfect or faulted, with the c axis parallel to the long axis of the crystal. Next along the direction of growth appears region 'b', which exhibits a 'striated' texture consisting of narrow bands transverse to the long axis of the crystal, the width of individual bands being of the order of a few μm measured parallel to the c axis. The bands vary in structure and may be cubic, hexagonal 2H, 4H, 6H or higher-order polytypes. Further along the crystal there may appear region 'c'. Here individual polytypes can extend up to millimetre dimensions along the c axis. They exhibit the diffraction behaviour of nearly perfect crystals, and contain a single axial screw dislocation of large Burgers vector coinciding with a hollow axial tube (Mardix, Lang and Blech 1971). The characteristics of regions of type 'a', 'b' and 'c' will be discussed more fully and will henceforth be referred to by a more descriptive notation: 'a' as IH (initial hexagonal), 'b' as SP (striated polytypic) and 'c' as MP (macroscopic polytypic).

A review of past investigations of ZnS crystals shows that studies have tended to concentrate on one of the types IH, SP or MP according to the nature of the property investigated or the limitations of experimental technique employed. For example, photoelectronic effects such as the anomalous photovoltaic effect (Brafman, Alexander, Fraenkel, Kalman and Steinberger 1964), or the pyroelectric effect, have been investigated in SP crystals which produce large signals, whereas most of the structural analyses of ZnS and studies of optical properties have perfornre been executed on MP regions through the requirement for large and uniform specimens. This division has a serious drawback with regard to understanding the properties of ZnS since it presupposes that a given property in one type of crystal is the same in all types. The significant differences in crystal structure and texture represented by IH, SP and MP regions suggest that other properties may also differ from one type of region to another. It is desirable, therefore, that studies of ZnS should embrace all types of crystal. The reasons for the existence of IH, SP and MP regions and the circumstances leading to transition from one region to another are little understood. Here we report new observations on whisker crystals containing all three types of region, paying particular attention to structure and texture in the SP regions about which least was known. The principal technique applied to the whiskers was high-resolution synchrotron X-ray topography. This was supplemented by X-ray counter-diffractometer measurements of their 'Eshelby twist' (Eshelby 1953, 1958).

§2. GROWTH AND MORPHOLOGY OF CRYSTALS

The crystals studied in this investigation were grown by the static-sublimation method (Reynolds and Czyzak 1950) with strict stabilization of temperature and pressure in the growth tube (Mardix 1984). Growth starts with the formation of a
polycrystalline ZnS substrate on the walls of the quartz growth tube. The whiskers sprout from this substrate and extend in the c-axis direction defined by the IH structure, reaching lengths of 20 mm or more in a period of 48 h. Thickening of the whisker also takes place. Final diameters of whiskers average about 100 μm and they are generally close to a regular hexagon in cross-section. However, lateral, platelet-like secondary growths, with their principal surfaces containing the whisker axis, may develop from the main whisker. In some whiskers a hollow tube of diameter 1 μm or more, lying along the c axis, appears at a certain stage of growth. These tubes often gradually widen in later stages of growth. The type of structure in a whisker specimen is an indication of its growth stage. If growth is stopped at a very early stage of whisker development then only IH crystals will be found. If growth continues but the conditions are not suitable for the development of a hollow tube, then only IH and SP regions will be present. The MP regions always contain a hollow tube of diameter sufficient to be seen easily under the optical microscope except when the faces of the whisker prism are rough.

§3. X-RAY TOPOGRAPHIC METHOD

The synchrotron X-ray topographic experiments were performed at the SRS, Daresbury, using a camera specially designed for whisker studies; the camera was set up at Station 7.5, 65 m from the tangent point on the storage ring. The continuous X-ray spectrum was used. The camera design had to fulfil conflicting requirements: a specimen-to-film distance large enough to prevent overlapping of different Bragg reflections from adjacent crystal regions when working with unit cells of long c-axis dimension (> 10 nm), but not so large as to give unacceptably low geometric resolution in the topograph images. A semi-cylindrical film holder, radius 112 mm, was constructed. The area of pattern recorded measured 175 mm in the equatorial and 125 mm in the axial directions. The X-ray source at the tangent point is strongly elongated in the horizontal orbit plane, its full widths at half maximum intensity being about 12 mm in the horizontal and 0.3 mm in the vertical directions. With specimen-to-film distance 112 mm, the corresponding geometrical resolutions on the film are about 20 μm horizontally and about half a micron vertically. The whisker camera was oriented with its equatorial plane horizontal, with the whisker axis vertical, so as to provide high resolution where most needed, along the c-axis direction on the topographic images. However, the narrow divergence of the synchrotron X-rays above and below the orbit plane (of the order of $10^{-4}$ radians) causes a significant fall-off in intensity at the top and bottom of images of specimens of axial length exceeding about 12 mm. Therefore the goniometer head bearing the specimen was mounted on a vertical micrometer slide so that any desired level in a long whisker could be brought to the level of the orbit plane.

In the Laue patterns, reflections from a given zone lie on a cone centred on the zone axis and containing the incident beam. With zone axes lying in the equatorial plane and making not more than about 20° with the direction of the incident beam, all reflections from the zone can be captured on a single cylindrical film of the size used, and they lie on an oval whose long diameter, parallel to the camera axis, exceeds its equatorial diameter by only a few per cent. This geometrical simplicity facilitates indexing of reflections, and is one of the advantages of cylindrical film compared with flat-plate recording as used in other synchrotron X-ray Laue topographic studies of polytypic crystals (Steinberger, Bordas and Kalman 1977, Fisher and Barnes 1984). The topograph shows segments of the nearly circular arrays of reflections from the (10T) planes of specimen 16/121, one of two whiskers containing IH, SP and MP regions of
Part of a continuous synchrotron-radiation topograph of whisker specimen 16/121. The whisker axis is vertical and the direction of growth points upwards. The field includes segments of the oval (nearly circular) arcs upon which reflections from planes of one zone, (101 /), fall. The print width corresponds to a width of 20 mm on the X-ray film, and the top edge of the field is just below the level of the equator of the diffraction pattern recorded from the lowest point in the whisker. The vertical sequence of numbers 1–9 identify bands in which lie reflections from correspondingly numbered whisker regions discussed in the text: region 1 is of IH type, 2–4 of SP type, and 5–9 of MP type. The numbers 5, 10, 15, 20 set along the lower edge of the pattern identify the / indices of the column of reflections above.
which many synchrotron radiation topographs were taken. Each whisker segment representing a particular crystal structure has its corresponding curved band on the topograph within which all its reflections lie. The sequence of bands on the topograph can be matched with the bands of different birefringence on an optical micrograph of the whisker. The matching is straightforward in MP regions but becomes less certain in SP regions when the spacing of striations falls below a few µm. Certain bands on the topograph are picked out by the numbers 1–9 and will be discussed below in §§ 4.1–4.3. The method and results of Eshelby-twist measurements are described in § 4.4.

§ 4. Observations

4.1. The MP region

Interpretation of the topograph can best commence with the MP region since the patterns of reflections in its well resolved bands can be readily related to prior experience in the diffraction patterns of high-order polytypes. In this specimen the start of the MP region is marked by simultaneous development (within topographic resolution limits) of both the Eshelby twist and a hollow tube of sufficient diameter to be visible under low-power optical magnification and radiographically in the topograph images. If the whisker has a uniform twist about its axis then the vertex angle of the cone on which reflections lie changes smoothly as the position of the point generating the reflections moves along the whisker axis. This leads to a sloping image as shown by bands 5 and above in the MP region. The technique of measuring the Eshelby twist of whiskers from the slope of their X-ray images in a Laue pattern has been used by Dragsdorf and Webb (1958). Such a procedure in the case of ZnS whiskers is complicated by their characteristic lack of straightness (Mardix, Kalman and Steinberger 1968). This problem is discussed in § 4.4. Here it is sufficient to note that the minor irregularities of slope exhibited in the images of bands 7 and above (but not the more noticeable departure from uniform slope between bands 5 and 6) are attributable to differing tilts of the physical axis of the whisker with respect to the crystallographic c axis.

The lowest whisker segments in the MP region, numbers 5 and 6, have cubic structure. All the higher-order polytypes further up the whisker belong to the same family (Mardix, Alexander, Brafman and Steinberger 1967); that is, they all include the same number of layers in their elementary stacking sequence (in this case 30). In identifying reflections in the topograph we shall throughout employ hexagonal indices, indicating in a following parenthesis the number of layers in the relevant unit cell. Columns of 10f I/30L reflections for which l = 5, 10, 15 and 20 are identified by these them, based on a 30L hexagonal cell. (The purpose of the three arrows placed in band 6, pointing to reflections in the MP bands above, is explained in the text.) For regions 1–4, the zone axis made 19°1' with the direct beam. The Bragg angle decreases along the arcs from upper left to lower right. The abrupt weakening of intensity in the pattern in the area where the numbers 1–4 are inserted, and above, is due to increased specimen absorption for wavelengths shorter than the Zn K absorption edge, λ = 0.1283 nm. The pattern was recorded on Agfa-Gevaert Strukturix Type D2 X-ray film, double coated, one coat being removed before enlargement. The storage ring operated at 2 GeV energy and the exposure was approximately 50 beam mA h.
numbers placed under them. Some strong higher-order reflections \( n0l \) (30L) appear interleaved between the 10l / (30L) reflections. For example, the reflection seen strongly in the IH and some of the SP bands at the position corresponding to \( l = 7.5 \), half-way between the \( l = 5 \) and \( l = 10 \) columns, is predominantly 20215 (30L).

Only three images appear in the cubic bands, 5 and 6. The lowest-order reflections (hexagonally indexed) and the wavelengths producing them are as follows. At position \( l = 5 \) (30L) is 202 1 (3L), reflecting \( \lambda = 0.084 \) nm. At position \( l = 10 \) is 303 3 (3L), reflecting \( \lambda = 0.051 \) nm, and appearing weak because at this short wavelength the flux from the source is relatively low. Note that 303 3N (NL) is a special case of reflections for which \( h-k=0 \) mod 3 (Verma and Krishna 1966). These reflections are allowed and have the same intensities for all polytypes, irrespective of their stacking sequence, as long as \( l = mN \), where \( N \) is the number of layers in the unit cell of the polytype and \( m \) is an integer. Hence reflections occur in this position from the whole whisker. Lastly, at \( l = 20 \) is 101 2 (3L), reflecting \( \lambda = 0.116 \) nm. Distinction is made between bands 5 and 6 because of the irregular displacements in the topograph image that appear between them. The diffraction pattern demonstrates that a similarly oriented cubic structure (that is, free from twinning) persists throughout whisker segments 5 and 6 and the transition region between them. However, optical microscopy shows, firstly, that the whisker segments 5 and 6 have slightly different tilts with respect to the \( c \) axis, implying that different groups of partial dislocations were responsible for their transformation to cubic structure by the periodic-slip process (Mardix et al. 1968) and, secondly, at the location corresponding to the irregular topograph image, the whisker is divided into lamellae parallel to the basal plane. Irregular changes of tilt between each lamella are seen, but are on too small a scale to account geometrically for the image irregularities. It is concluded that a number of twist boundaries lie in basal planes in this region. The overall twist needed to account for the overall topograph-image offsets between bands 5 and 6 is of the order of one milliradian. No measurable offsets attributable to misorientation boundaries occur elsewhere in the pattern.

Next consider the interpretation of the multiplicity of images given by the various polytypes of the family 30L which occupy the whisker above the cubic segments 5 and 6. The longest segment, number 8, has been identified as the 90R (755247) polytype in a previous study of this specimen (Medizadeh and Mardix 1986). To understand the relative positioning of reflections from different polytypes along the 10l / arcs, recall that their structures can be classified into three types of unit cell, non-rhombohedral, rhombohedral cyclic and rhombohedral anticyclic (Mardix et al. 1968, Mardix, Steinberger and Kalman 1970), all of which occur in this crystal. Instead of conventionally indexing reflections from the rhombohedral structures with respect to a 90L cell, it is convenient to retain the 30L \( c \)-repeat here and admit fractional indices \( l \pm \frac{1}{2} \). By way of illustration, consider the reflections to which the group of three arrows placed in band 6 on the topograph point. The middle arrow points to reflection 10l 14 (30L) of the non-rhombohedral polytypes in bands 7 and 9, whereas the arrows on either side point to reflections from rhombohedral regions which we can index as 10l 14 ± \( \frac{1}{4} \) (30L). In parts of the photograph where the density of reflections is high the staggering of images along the 10l / arcs can give the impression that the elementary stacking sequences belong to a 90L rather than a 30L family. Noting again that the reflection 202 2l + 1 of the harmonic \( \lambda/2 \) will fall between 10l / and 10l / + 1, all images of high-order polytypes in the MP region can be accounted for on the basis of a 30L family. Sometimes the ‘harmonic’ reflections appear as strong as the ‘fundamentals’; for example, near 10l 20 (30L) in band 7.
4.2. The IH region

The initial region of faulted 2H structure, band 1 in the topograph, extends only 0.5 mm along the whisker axis. Its lowest segment appearing in the picture, corresponding to an axial distance of about 60 μm, is very highly faulted, the reflections being smeared sufficiently so as to merge into a continuous arc. This local strong disorder was probably introduced when the whisker was broken away from its substrate. The degree of disorder in the rest of band 1 is typical of 2H regions which have had lengthy storage at room temperature. The development of stacking disorder in 2H regions can be monitored X-ray topographically day-by-day (Mardix 1986b). Band 1 shows no overall twist about the c axis.

4.3. The SP region

The diffraction patterns of the MP region described in §4.1 serve as an ideal model with which those of the much less perfect SP region can be compared. SP regions are of prime interest since they contain the crystal growth immediately preceding the appearance of a single family of long-period polytypes, together with an axial screw dislocation whose Burgers vector corresponds to the length of the elementary stacking sequence of the polytype family (Mardix et al. 1971) but whose origin is open to conjecture. To date, very little information is available concerning the structure and lattice imperfections in SP regions because of the difficulty of studying their narrow bands by conventional X-ray diffraction techniques. By contrast, the synchrotron-radiation topographs provide a wealth of new data. The imaging of all the SP bands in one exposure is informative as well as convenient. The following features stand out in the synchrotron-radiation topographs:

1. Long-period polytypes do occur in the SP region and can be of as high an order as in the MP region.
2. In contrast to the MP region, there is instability of polytype order: one encounters an irregular sequence of polytypes of order $N \pm 2m$, where $m$ is unity or a small integer.
3. There is not present the Eshelby twist expected on the basis that the whisker contains axial or near-axial dislocations with a resultant axial Burgers vector of magnitude equal to the elementary stacking sequence of the high-order polytypes.

Consider now the sequence of structures appearing in the topograph. By definition, the SP region commences with the first non-2H structure, represented in this specimen by a ½ mm-wide band consisting principally of cubic lamellae with repeated twinning on the plane normal to the c axis interspersed with a few very narrow (thickness a few μm) polytypes of family 6L. The repeatedly twinned cubic lamellae are seen very strongly diffracting immediately above the weak harmonic reflection of the IH band in the $l=10$ column. (The whole diffraction pattern was used for their identification, however.) In the next band, extending axially about 1 mm and indicated by the arrow 2, there is no dominant polytype family, and identification of polytype order is rendered difficult by the presence of higher diffraction orders and by uncertainty in the assignment of diffraction spots to individual lamellae in the whisker. However, in a region about 2 mm higher up in the crystal (mid-level of its band of reflections indicated by arrow 3) one polytype family is clearly dominant. It is of order 28L, as shown by the 14-fold subdivision of the range $l=10$ to $l=15$ (of the 30L unit cell) by the columns of
reflections (including those from both rhombohedral and non-rhombohedral structures) in this band. The observation that columns of reflections from polytypes in the SP region diverge or converge symmetrically around the columns with \( l = 5, 10, 15 \) and 20 is not trivial and will be discussed in §5. Here we just note its convenience in establishing the polytype family \( N_\alpha L \) of any segment, \( s \), of the SP region. If \( n_s \) is the number of columns of reflections the segment produces in an arc length corresponding to an increment in \( L/30L \) of 5, then \( N_\alpha = 30n_s/(3 \times 5) = 2n_s \), the dividing factor 3 taking account of the presence of both rhombohedral and non-rhombohedral structures. (In this count, interleaved harmonic reflections, which are usually weak, are excluded; they can be identified by reference to corresponding occurrences in the simpler patterns from MP regions.)

Proceeding upwards, next seen is a jump to a 30L family, identified by a 15-fold subdivision of the arc range between, for example, \( l = 10 \) and \( l = 15 \). This family dominates up to a distance of about \( \frac{1}{4} \) mm from the boundary between the SP and MP regions; arrow 4 points to a region where its dominance is most clearly evident. Note that a sequence of small positive increments in polytype order (for example, in steps with \( \Delta n = 1 \)) leads to a progressive contraction in spacing between columns of reflections (and, conversely, decrements in polytype order lead to expansion). It follows that, even when polytype regions are too small to be matched individually with their corresponding arcs of reflections, a progressive increase or decrease in polytype order can be detected by the convergence or divergence, respectively, of the columns of reflections close on either side of a column that does not shift with change of polytype order. This situation is exemplified at the approach to the SP/MP boundary. Here we see a divergence of the columns on either side of the \( l = 15 \) column (for example) which reveals a progressive reduction of polytype order, taking place by two, or perhaps three, minimum steps. Scrutiny of the whole SP-region pattern suggests that some other changes up or down of polytype order, by minimum steps, take place in addition to those mentioned.

The second whisker studied by synchrotron X-ray topography, specimen 17B11, was similar in length and diameter to specimen 16/121 and contained IH, SP and MP regions. The topographs of 17B11 exhibited features broadly similar to that of 16/121. Thus, in the MP region a single polytype family (34L), low fault density and the Eshelby twist were seen, but a high fault density, no overall twist, and some variation in polytype order relative to a dominant 30L family were found in the 2.5 mm-long SP region. One difference between the SP regions in the two crystals worthy of note was that in specimen 17B11 the introduction of long-period polytypes was quite abrupt, no low-order polytypes being detectable between the faulted 2H structure of the IH region and the structure immediately succeeding it, a polytype of order 34L.

### 4.4. Measurements of twist

In order to measure the Eshelby twist from the slope of images of equatorial reflections in the synchrotron X-ray topographs allowance must be made for the whisker’s lack of straightness. This can be done by reference to a radiographic silhouette of the whisker recorded on the same film. After removing the direct beam trap, an exposure of about 1 s duration through a thin lead-foil filter gave silhouettes of suitable density and contrast. The silhouette needed is obtained by rotating the specimen about the \( c \) axis so that the direct-beam radiograph corresponds to a silhouette of the specimen projected along the diffracted-beam direction of the
equatorial reflection used for twist measurement. However, the method chosen for accurate measurements of Eshelby twist employed a conventional source of Cu Kα, X-rays and a topograph camera operated as a counter diffractometer in the equatorial plane. The whiskers were scanned axially in 100 μm steps with a slit of opening 150 μm measured along the whisker. For each measurement, the whisker was translated in the equatorial plane by the small distance needed (a few μm) to place the axial segment under measurement symmetrically in the ribbon incident beam which was of width similar to the whisker diameter. Although this method involved taking hundreds of measurements per whisker, it yielded data free from need of correction for whisker tilt with respect to the c axis. The angular settings for Bragg reflection from the whisker at each step in the axial scan were measured to within a few seconds of arc. Results from three whiskers are given in the table, presented as a comparison between the Burgers vector of the axial screw dislocation needed to produce the observed twist according to Eshelby's calculation (1953, 1958) and the Burgers vector which would generate the observed polytype family of order N via the periodic-slip process. The latter Burgers vector magnitude, b, is simply \( b = Nc_0 \), where \( c_0 = 0.3128 \) nm. In the table, 2R is the overall diameter of the regular-hexagonal whisker cross-section, measured by an optical microscope. The Eshelby twist \( \alpha \) is expressed as rotation in milliradians per millimetre length of whisker, and is connected with the Burgers vector by the relation \( \alpha = \frac{\kappa b}{A} \) (Eshelby 1958) in which the regular cross-section area \( A = (3/8)R^2 \) and the constant \( \kappa = 1.015 \), appropriate for a regular hexagon. Crystal 16/122 fell short of regularity in cross-section, and the value of 2R quoted for it is an estimated mean. In the other specimens, measurements of 2R had a precision of about 1 μm. In general, the whiskers exhibit a gradual increase of R with distance from whisker root. This leads to a corresponding gradual decrease in \( \alpha \). The rate of diameter increase was less than 2 μm per 10 mm axial length in the specimens investigated. The values of \( \alpha \) and 2R quoted in the table apply to measurements made at the same position along the whisker. The modification needed in the expression for \( \alpha \) when the whisker has a hollow core was discussed by Eshelby (1958). The whiskers listed in the table all contained axial hollow tubes, but the tube diameters were sufficiently small fractions of 2R for the correction to the simple expression for \( \alpha \) to be insignificant. Equally insignificant was correction for non-coincidence of the tube axis with the geometric axis of the whisker. Tube diameters and off-centring were of similar magnitudes (about 2 μm). The uncertainty in value of \( b(P) \) is merely that in the value of \( c_0 \). The uncertainty in \( b(E) \) should be within a few percent for specimens 16/121 and 18/16, and for these specimens the agreement between \( b(E) \) and \( b(P) \) is excellent. In SP regions, twist measurements give differing results. As already described, specimens 16/121 and 17B11 show no overall twist. Specimens 18/16 and 16/122 did show twists, less regular than in the MP regions, about one-third the strength of the MP-region twist, and in the opposite sense.

Comparison of magnitudes of axial screw dislocation Burgers vectors derived from Eshelby twist, \( b(E) \), and from order of polytype family, \( b(P) \).

<table>
<thead>
<tr>
<th>Crystal</th>
<th>N</th>
<th>2R (μm)</th>
<th>( \alpha ) (mrad mm(^{-1}))</th>
<th>( b(E) ) (nm)</th>
<th>( b(P) ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16/121</td>
<td>30</td>
<td>75</td>
<td>2.66</td>
<td>9.58</td>
<td>9.38</td>
</tr>
<tr>
<td>18/16</td>
<td>54</td>
<td>112</td>
<td>2.14</td>
<td>16.7</td>
<td>16.89</td>
</tr>
<tr>
<td>16/122</td>
<td>64</td>
<td>104</td>
<td>3.13</td>
<td>21.5</td>
<td>20.02</td>
</tr>
</tbody>
</table>
§ 5. DISCUSSION

Firstly we refer to the observation, noted in §4, that throughout the diffraction pattern all columns of reflections diverge or converge relative to the columns at \( l \) values (referred to the 30-layer trigonal or hexagonal cell) for which \( l = 5k \), where \( k = 0, \pm 1, \pm 2 \), etc. It will now be shown that this property holds only if all polytype families in the crystal have an even value of \( N \). Use the \( l \) values of non-rhombohedral 30L polytypes to define the scale along the \( 10\overline{1}l \) reciprocal lattice row (restricting use of the symbol \( l \) to a measure of the position of a reflection on this row). Reflections of a non-rhombohedral polytype with \( N \) layers in its elementary stacking sequence will fall at the positions \( l = 30n/N = 10 \times 3n/N \), and the reflections of rhombohedral polytypes with the same length of elementary stacking sequence will fall at positions \( l = 10(3n+1)/N \) and \( l = 10(3n-1)/N \), \( n \) being an integer. Now \( 3n, 3n+1 \) and \( 3n-1 \) embrace all integers; they must include \( mN \), where \( m \) is an integer. Consequently, coincidences of columns (that is, integral \( l \) values) will certainly occur at \( l = 10m \), whether or not 10 and \( N \) have a common factor. Only if \( N \) is even do coincidences occur at \( l = 5m \), and in consequence neighbouring columns diverge or converge symmetrically about these columns when \( N \) changes, as is observed.

Past investigations of polytypism in ZnS have concentrated on MP regions. In studies of hundreds of polytype structures in these regions it was found that all were of even order. This property constitutes one of the major pieces of experimental evidence supporting the role of axial screw dislocations in the formation mechanism of polytypes in MP regions of ZnS crystals. The same property has now been found to hold for tens of polytype structures in the SP regions of the two crystals we have examined by synchrotron X-ray topography. This leads us to believe that the basic mechanism of a dislocation-controlled thermodynamically driven process (Mardix 1986a) for high-order polytype formation takes place in SP as well as in MP regions, albeit with some important variations. In the MP regions the hollow tube enclosing all axial Burgers vectors creates the basal-plane topology of a single giant screw dislocation. In SP regions the topology is not so simple; the frequent changes of polytype family show that the total strength of axial screw dislocations active in the periodic-slip process is variable. This can occur either by elementary screws joining or leaving the crystal at various levels or by their failing to contribute to the propagation of the periodic slip over a certain range along the axis. If the dislocations are in one central cluster the second alternative appears less likely. The existence of the IH region, which, despite demonstrated availability of Shockley partials, does not transform to give identifiable polytypic regions, suggests that whatever axial screws are present in this region have zero resultant Burgers vector; there may just be a single pair of screw dislocations, of opposite sign.

The evidence described above points against a single giant axial screw dislocation, of fixed Burgers vector, being present in the whisker right from the inception of its growth from the substrate. We shall interpret the boundary between IH and SP regions as being the point where imbalance of sense of axial Burgers vectors first develops, and the SP/MP boundary as the last point where change of resultant axial Burgers vector occurs. Frank (1987) has proposed a natural mechanism for development of a large resultant axial Burgers vector by the self-trapping of screw dislocations of like sign in the presence of the Eshelby twist. The pattern of gradual development of high-order polytypes seen in the topograph reproduced here, implying accretion of Burgers vectors of like sign over an axial distance of about 1.5 mm, is well fitted by Frank’s model, but less evidently well fitted in the pattern of specimen 17B11 described at the
end of §4.3. In order to initiate the easily visible tube at the SP/MP boundary we may
suppose that the inward-sloping sides of a central dimple on the growing whisker tip
reach a certain critical steepness at which they lock on to facets of pyramidal planes.
The latter then expand outwards to form the base of the tube. There is some
microscopic evidence for faceted bottoms on tubes. Remarkable though the changes in
structure and lattice defect content are at IH/SP and SP/MP boundaries, it would
appear likely that neither transition requires for its initiation more than chance
fluctuations in the growth process at the whisker tip.

The data in the table show that MP regions have supported the stress field of a giant
axial screw dislocation since growth (albeit relieved by a hollow core). The SP regions,
on the other hand, are divided by dislocation-containing basal planes into lamellae
whose average thickness is very much less than the present whisker diameter. We
assume that low yield stress with respect to shear parallel to their basal-plane
boundaries allowed stress relaxations to take place in the lamellae similar to those
occurring in a surface-stress-free disc with a screw dislocation along its axis (Eshelby
and Stroh 1951). In this state the Eshelby twist, with its containing effect on a cluster of
similar screw dislocations, as discussed by Frank, is lost, but so too is long-range
repulsion between like axial screw dislocations. At what stage in the whisker’s history
the breakdown of the SP region took place is not known. For the Frank trapping
mechanism to operate, freedom from basal-plane slip must have been maintained
below the growing whisker tip over axial lengths many times greater than the initial
whisker diameter. Breakdown of the SP region would become more elastically
favourable following the whisker thickening that takes place after the initial relatively
rapid axial growth. (Observations on products of interrupted whisker growth
experiments suggest that the initial diameters of whisker regions such as those
discussed here were 20 µm or less, rather than their present 100 µm diameter.)

The calculation of Eshelby and Stroh (1951) shows that, in the presence of an axial screw
dislocation, the elastic energy per unit axial length of a disc of thickness 2d compared
with that of a long cylinder, radius R, is lower in the ratio \( \ln(d/2-24r_i)/\ln(R/r_i) \), where \( r_i \)
is the inner cut-off radius and \( R \gg d \), neglecting the relatively small fractional reduction
of energy of the cylinder provided by the Eshelby twist.

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