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Observation of polytypes and stacking faults in zinc sulphide by transmission electron microscopy

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Specimens of zinc sulphide have been examined by transmission electron microscopy after thinning by a specially developed chemical method. Observations were made of stacking faults and their thermal stability, and polytypes have been seen directly in the form of periodic fringe patterns.

1. Introduction

A considerable amount of work has been done by X-ray diffraction in discovering polytypes of zinc sulphide and elucidating their structure. Electron microscopical investigation of this material, however, seems to have been mainly confined to the examination of thin, as-grown, films, possibly because of the difficulties of thinning this material satisfactorily. Such films do not, in general, exhibit polytypism. Such work as has been done on thinned material has revealed dislocations and stacking faults [1], and in one case diffraction spots corresponding to the 6H polytype [2], but, as far as is known, no higher polytypes than this have been observed using electron microscopy.

This paper reports the results of an examination by transmission electron microscopy of thin foils of zinc sulphide prepared from vapour-grown platelets by a jetting and chemical polishing technique. In certain cases, polytypic areas were observed in the form of periodic fringe patterns. Heating experiments were also performed on randomly faulted specimens to investigate the stability of the faulting.

2. Experimental method

The starting material was in the form of platelets grown by vapour transport in Argon at 1150°C, their thickness being mostly in the range 50 to 300 μm.

Discs 2.3 mm in diameter were cut from these platelets using an "Airbrasive" unit, which cuts by the action of a jet of air-borne, fine abrasive particles.

The jetting technique of Holt *et al* [1] was used initially to produce thinned specimens, employing as reagent a solution of 1 g of chromium trioxide per 100 ml of concentrated hydrochloric acid. Unfortunately, the rate of attack was so rapid that it was found to be extremely difficult to stop the process sufficiently close to the point of perforation. Consequently, the area of material thin enough for electron microscopy was small, at most a micron or two around the edge of the hole, and also very wedge-shaped.

To overcome this, the jetting method was used only to produce dimples on the two faces of the initial disc of material, and this was followed by a thinning process which removed material at a much slower rate. The method eventually evolved for the final thinning was immersion of the specimen in a solution of 80 g of chromium trioxide per 100 ml of distilled water at about 85°C. To enable the specimen to be observed despite the opacity of this solution, the following arrangement was used.

The specimen was held in the centre of a pill-box shaped glass cell some 35 mm in diameter and 7 mm in depth. The top and bottom faces of this cell were optical flats, and the sides of the cell were provided with diametrically opposed inlet and outlet pipes for the passage of the solution, and a ground glass joint for the introduction of a rod carrying the specimen. The specimen lay in a recess provided in the flattened end of the rod, the recess having a central hole to permit ingress of the solution. The specimen was held in position by the weight of an annulus of glass resting on top of it and also within the recess.

The hot chromium trioxide solution was pumped through the cell by a glass centrifugal pump from an electrically heated reservoir whose temperature was thermostatically controlled at 95°C. Taps ("Teflon" barrelled) in the circuit were so arranged that the flow of hot reagent could be quickly replaced by one of cold distilled water when it was desired to stop the thinning.

The cell was placed on the stage of a polarizing microscope so that the process of thinning could be closely followed.

Specimens produced in this manner were examined in a Siemens Elmiskop Ia, using a double tilting stage or in certain cases a heating stage.

3. Results

It is already known that crystals grown under the conditions described are plate-like on $(2\bar{1}\bar{1}0)$, and this was confirmed for these specimens by electron diffraction.

Most of the specimens showed a random pattern of striations, an example being shown in Fig. 1a. Selected-area electron diffraction showed that these striations lie perpendicular to the *c*-axis. They are very similar to those observed by Chadderton *et al* [3], but occur in much greater density, as in a micrograph in the paper by Holt and Culpan [2]. Also, in contrast to the results of the former, no striations or fringe patterns were seen in any other orientation. These differences are probably due to the fact that their observations were on thin, as-grown crystals rather than thinned platelets. Selected thin crystals grown under the same conditions as the platelets used in this investigation have been examined, and gave results very similar to those of Chadderton *et al*, with a much lower density of striations, and also fringes attributable to stacking faults on prismatic planes.

Fig. 1b shows a diffraction pattern taken from the area shown in Fig. 1a, the relative orientation of the prints having been adjusted to correct for the rotation between them produced by the electron microscope. Fig. 1c is a key to Fig. 1b, and shows the major spots indexed.

In order to understand this better, a brief outline of the zinc sulphide structure follows. More detailed accounts may be found in the literature.

The zinc sulphide structure may be thought of as being built up of an assemblage of basic double close-packed layers. Each such double layer consists of a close-packed layer of zinc atoms lying "on top of" an identical close packed layer of sulphur atoms (or vice versa). These double layers then stack one on top of another in the same way as single layers stack to give cubic close packed or hexagonal close packed configurations. Denoting the position of a reference (double) layer by A, the layer above may then be added in one of two positions B or C, and similarly for subsequent layers. This normally results in either a cubic or hexagonal structure with one of the following layer sequences:

ABABABAB . . . hexagonal
or its equivalent
ACACACAC . . .

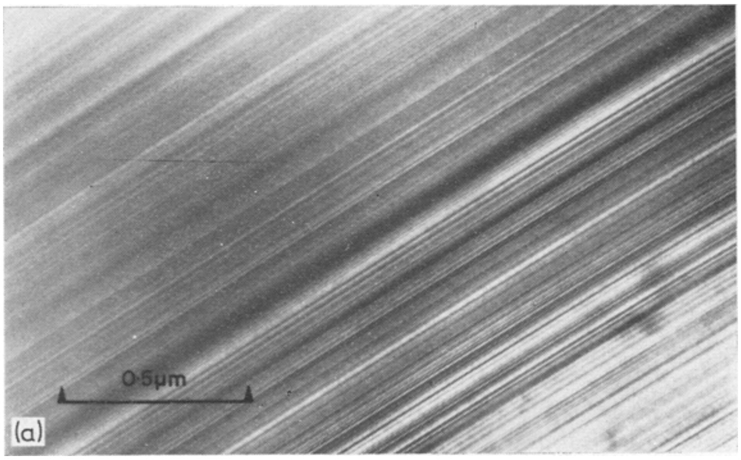
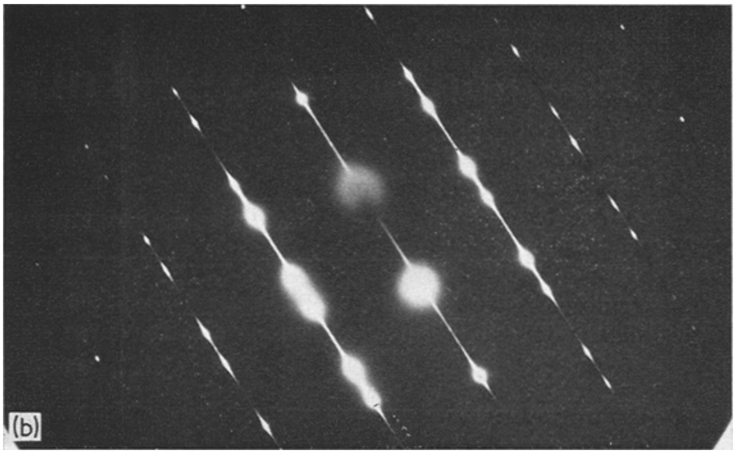


Figure 1(a)



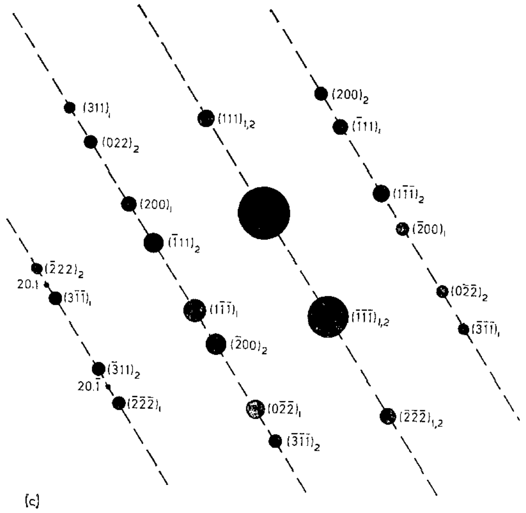


Figure 1 A randomly faulted area of ZnS. (a) Electron micrograph. (b) Electron diffraction pattern. (c) Key to (b), showing spots indexed; indices in brackets refer to the two cubic orientations, labelled 1 and 2; indices without brackets refer to the hexagonal orientation.

$$\left.\begin{array}{l}\text{ABCABCABC}\ldots\text{ cubic}\\ \text{ACBACBACB}\ldots\text{ cubic}\end{array}\right\}\text{in twin relationship.}$$

The cubic and hexagonal sequences normally have quite different potential energies, the crystal growing in the form having the lowest energy under the particular conditions of growth (and occasional twinning of cubic forms being very common). In the case of zinc sulphide, however, the difference in energy between the two forms of stacking is very small indeed, so that the most common structure encountered is a largely random arrangement which is neither cubic nor hexagonal, but a mixture of the two.

Referring back now to Fig. 1c, it will be seen that the major spots in the diffraction pattern of Fig. 1b can be attributed to one or other of the cubic orientations. Two weak spots corresponding to hexagonal stacking are also indexed. This preponderance of the cubic forms of stacking was typical of all the randomly stacked specimens of zinc sulphide which were examined.

The streaks along the [1 1 1] directions in the diffraction pattern show that the unfaulted regions are of very limited extent in a direction parallel to the streaking, which agrees with the type of random structure just referred to.

The striations observed in the micrograph of Fig. 1a may also be attributed to these faults in the basal layer stacking sequence (Chadderton *et al*, loc. cit.), and this was borne out by the observation that the striations could no longer be seen when the specimen was oriented so that the reciprocal lattice vector, g, of the operative reflection was perpendicular to the striations. This implies that the displacement vector of the stacking fault responsible for the appearance of the striation lies in the basal plane.

A heating stage was used to examine the effect on the striations of heating to temperatures up to 500° C. Unfortunately, it was not possible to obtain an accurate correlation of the striations at different temperatures as the orientation of the specimens changed during the heating, presumably due to buckling. As the heating stage used did not permit of tilting, the change in orientation could not be corrected, and since the striations are sensitive to orientation this ruled out any detailed correlation. It was, however, observed that the striations in a specimen which had been heated to 500°C for an hour and then cooled again were identical before and after the heating.

This is in marked contrast to the thin, as-grown specimens, in which the heating caused by the electron beam was sufficient to cause movement of dislocations on the basal plane right across the specimen, leaving a stacking fault behind.

Certain specimens showed a periodic arrangement of striations, one example being shown in Fig. 2a. In spite of contrast differences arising from different thicknesses and perhaps orientations, a periodicity of some 16.7 nm can be seen to extend across the whole field of view. This periodicity was in fact observed to extend over an area of the order of a hundred microns square, being limited by the extent of the area thin enough for viewing in the electron microscope.

A diffraction pattern from the same area as Fig. 2a is shown in Fig. 2b, again in correct relative orientation. The orientation of the specimen in Fig. 2b is such that the beam is incident along [0 1.0] referred to hexagonal axes. This is the same orientation as that for Fig. 1b, with which it may be compared. It will be seen that the streaks which were present in Fig. 1b have now broken up into a close array of spots, though, owing to the difficulty of coping on a print with the large contrast range of the original plate, these spots are not visible

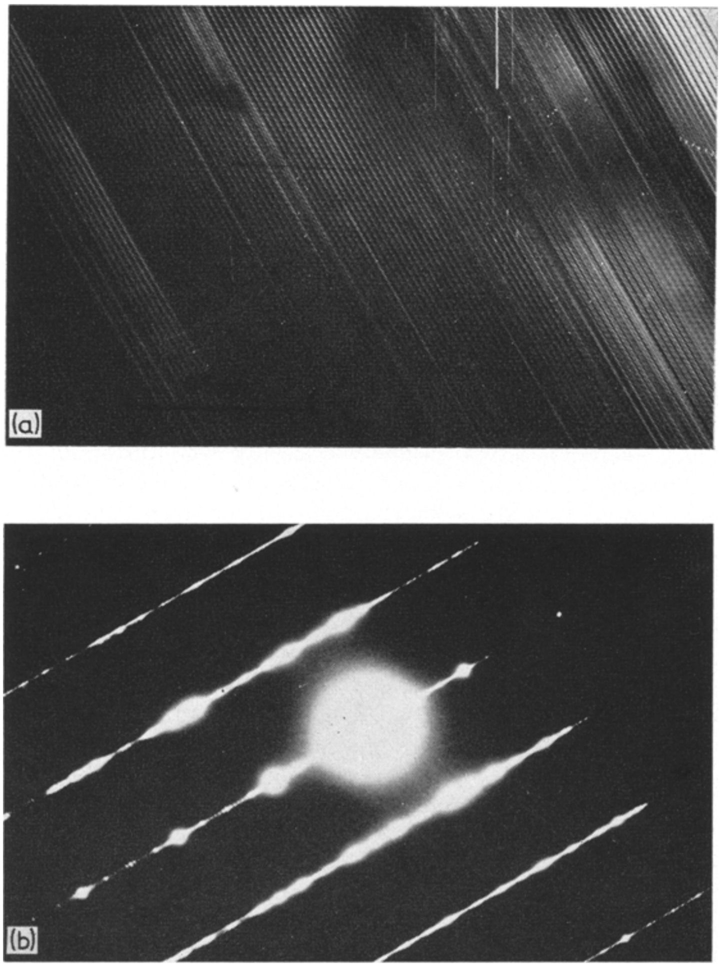


Figure 2 A polytypic area in ZnS showing a periodicity of 16.7 nm (fifty layers). (a) Electron micrograph. (b) Diffraction pattern.

in all regions. As before, the intense spots along the line passing through the origin are produced by diffraction from adjacent close-packed (double) layers. Between each of these intense spots one may count forty-nine subsidiary spots, and this spacing also obtains along the other lines. These must therefore be due to either a 50-layer hexagonal polytype or a 150-layer rhombohedral polytype. (For a discussion of polytype structures and diffraction therefrom see Verma and Krishna [4].) Both types have a repetition period of fifty layers (although this is a subsidiary repeat in the case of the rhombohedral polytype) and, since the distance between these layers in zinc sulphide is known to be 0.312 nm, this corresponds to a periodicity of 15.6 nm. The periodicity of 16.7 nm shown in Fig. 2a compares reasonably with this figure, especially as the magnification of this micrograph is not known to better than ±10% as a result of the tilting. Fig. 2a may therefore be said to show directly either a 50H or a 150R polytype in zinc sulphide.

It may be remarked in passing that, theoretically, these polytype spots should not appear in the diffraction pattern in the line passing through the origin, or in the lines ±3, ±6, etc. from this line. Their presence in the diffraction pattern actually observed must be attributed to the effect of multiple diffraction, which is to be expected on account of the thickness of the specimen (several extinction distances).

It should also be pointed out that Fig. 2a and b were not in fact taken in exactly the same orientation, as the contrast of the striations is improved by tilting slightly from the symmetrical position of Fig. 2b about an axis in the [1 0.0] direction. Tilting about the orthogonal [0 0.1] axis causes the polytype spots to disappear, confirming that they are due to a one-dimensional stacking configuration.

Fig. 3 shows a periodic fringe pattern observed in another specimen, the repeat distance being indicated by the two arrows. There is here a much more extensive fringe system within the repeat distance, but, although this appears constant across the field of view of Fig. 3, observations outside this field show that this fringe system varies, presumably as a result of thickness and orientation differences. The same periodicity persists, however.

The repeat distance is 82 nm, which corresponds to 263 layers in the polytype, with a possible variation of up to 10% on account of uncertainties in the magnification. The corresponding diffraction pattern unfortunately does not have sufficient resolution to show all the polytype spots, though enough can be seen to confirm that the number of spots is of the right order. This is believed to be the longest period polytype yet reported for zinc sulphide.

4. Discussion

Both polytpes and randomly faulted structures were found in material from the same production batch. Any variations in environment responsible for the appearance of one rather than the other must therefore be minor variations occurring within the preparation tube.

All the specimens appeared very similar under the optical microscope, with the usual bands of apparently uniform birefringence perpendicular to the *c*-axis. As polytypes were only found in two cases out of twenty examined, this suggests strongly that random stacking can give rise to areas of uniform birefringence. Since birefringence can be related to the ratio of cubic and hexagonal stacking present this implies that the random stacking is subject to a longer range regularity in this ratio, at least within limits. This is presumably in response to some constraint imposed during growth or subsequent cooling, and one is tempted to wonder whether it is a similar constraint which in other cases gives rise to the formation of polytypes.

The absence of unfaulted regions is in complete contrast with the findings of Steinberger *et al* [5], who deduced, from X-ray observations and from the study of etch pit distributions on the surface, that the bands of uniform birefringence in their specimens corresponded to crystallographically uniform regions (cubic, hexagonal or polytypic), virtually free of dislocations and faults.

The obvious conclusion from this is that their material is in fact different from that used in this investigation, presumably owing to slight differences in preparation technique. However, there does remain the possibility that the results here reported arise from preferential thinning of the heavily faulted areas.

The heating experiments show that the more ordered and, therefore, presumably more stable, polytypic structure cannot be produced from the random one by heating *in vacuo* at up to 500°C, which is about the limit set by sublimation of the specimen. This could, however, be as well due to the stabilizing influence of

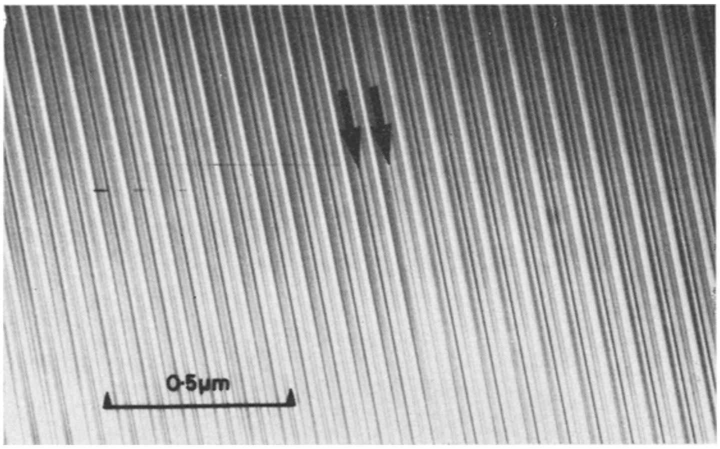


Figure 3 Electron micrograph of a polytypic area in ZnS showing a periodicity of 82 nm (263 layers). The two arrows delineate one cycle.

surface layers produced during thinning or subsequently as to any intrinsic thermal stability of the structure itself.

An important advantage of being able to observe polytypes directly in the electron microscope rather than detecting them by X-ray diffraction is that it should be possible to observe very much smaller polytypic areas with the electron microscope, although in fact the ones observed in this work were large enough to have been detected by the X-ray method also.

Close examination of Fig. 1a actually reveals small regions, up to about 30 nm in extent, which contain a regular arrangement of striations. Whilst these could be due to the presence of a very narrow polytypic region, this cannot be inferred with any certainty for such a narrow region, since such an effect might also be produced by interference between beams which have suffered one or more phase changes on crossing the boundary of such a region. Such interference fringes are well understood for stacking faults inclined at greater than about 10 degrees to the foil normal, but the situation is much more complicated in the present case because of the stacking faults being nearly normal to the foil, and also because of their proximity to each other.

Efforts to identify the precise structure of the polytype shown in Fig. 2 on the basis of the intensity distribution in the diffraction pattern have so far proved unsuccessful. Amongst the methods tried, the "Direct Method" of Dornberger-Schiff and Farkas-Jahnke [6] did not work, presumably because it requires fairly accurate intensity data, whereas the intensities observed would have been "smeared out" by the multiple diffraction which has already been referred to. The "Elimination Method" of Mardix *et al* [7] cannot be used on its own for such long period polytypes, as the number of possible structures increases too rapidly with increasing number of layers in the polytype. The number of possibilities can be reduced by making use of other data, namely the number of Zdhanov symbols in the polytype sequence, deduced from the optical birefringence, and the cyclicity. The first of these was not available in this case, as the position of final thinning was too random to permit correlation with prior observations of birefringence, and the second, whilst it could be deduced from the diffraction data, was not sufficient to allow of a solution.

If thinner specimens could be obtained, it might be possible to apply the first of the methods referred to, but it is also proposed to attempt a combination of the two methods using the existing diffraction data.

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