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Scanning Electron Microscope Studies of Striations in ZnS

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ZnS platelets crossed by two orthogonal sets of striations were examined. Nomarski optical interference micrographs and scanning electron microscope (SEM) secondary electron micrographs showed that both sets of striations had associated surface topographical features. One set consisted of polytype or faulted bands, the other of thickness variations ("linear markings"). SEM cathodoluminescence micrographs showed that in some specimens certain lines in both sets were strong light sources. In other specimens only polytype interfaces were linear cathodoluminescent sources. SEM charge collection micrographs showed that many of the polytype or faulted bands could produce contrast possibly due to the separation of electron-hole pairs by internal electric fields associated with these defects. Transmission electron microscopy showed that there could be several different types of faulted stacking structures in areas a micron square in striated ZnS.

1. Introduction

ZnS platelet and needle crystals grown by vapour phase techniques are frequently found to be crossed by a system of fine striations, which are visible to the naked eye. An early suggestion was that the striations were alternations of the sphalerite (cubic) and wurtzite (hexagonal) phases [1]. The structure of striations has also been discussed in terms of stacking disorder theory [2-4]. Later evidence showed that striations were, in many cases, bands of different polytype structures [5-12]. It has also been shown that martensitic faulting processes can transform the wurtzite to the sphalerite structure [13-15] and one polytype to another [5, 16-17].

It has been suggested that striations are the sites of the electrical barriers which are believed to be responsible for the anomalous photovoltaic effect in ZnS [1]. This effect involves the generation of potential differences as great as hundreds of volts per cm normal to the striations when they are illuminated with monochromatic light. The anomalous photovoltage undergoes several reversals of sign as the wavelength of the illumination is changed [1, 18, 19]. Several detailed models have been proposed to account for this effect [20-22]. However, no direct evidence in support of any of the models has been produced although the occurrence of electrical field concentrations along striations has been demonstrated [23].

It has also been suggested that striations are the sites of the linear electroluminescent sources observed in some ZnS specimens [2, 24]. However, serious errors can arise in these observations due to the high refractive index of ZnS, and in luminescent powder particles at least, it has been shown that linear electroluminescent sources are not associated with striations [25, 26].

The use of a scanning electron microscope (SEM) makes it simple to observe localised variations in several important properties of striated ZnS platelets. The incident electron beam will induce a number of physical effects. Each of these can be detected, amplified and displayed to produce a different type of micrograph which will be described by the type of signal that is displayed. SEM cathodoluminescence (or SEBERR) micrographs will show any variations in cathodoluminescence intensity [27] or wavelength [28-30]. SEM charge collection (or SEBECC) micrographs [31] are produced by making one or two contacts to the sides of the specimen and operating the microscope in the conducting mode. Any internal electrical field

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regions at right angles to the line joining the contacts will appear bright in charge collection micrographs since strong local fields will efficiently separate the hole-electron pairs injected by electron bombardment, thus preventing their recombination and allowing them to be "collected" by the contacts as a relatively large current pulse [32]. SEM specimen current micrographs are obtained with one contact to the lower face of the specimen, using the "specimen current" from the beam to earth as video signal ([32], pp. 239-241). When the secondary electrons emitted from the specimen surface are used as video signal, micrographs are obtained which display the surface topography. Under appropriate conditions the potential difference between the specimen and the grid used to attract the secondary electrons to the detector, and therefore the fraction of the electrons attracted, is sensitive to the surface potential of the specimen. Thus "voltage contrast" can also be obtained in secondary electron SEM micrographs [(32], pp. 196, 203, 204 and 325). Obviously this group of micrographic techniques is a powerful tool for the investigation of phenomena like striations in ZnS. A preliminary survey of the results which can be obtained with some of these techniques is presented below.

Studies of the structure of striated ZnS platelets have employed X-ray diffraction [4, 6-10] and optical microscopy only. Transmission electron microscopy has, however, been used to study as-grown platelets which were thin enough to be electron transparent [11-13, 33-36]. Such platelets are thinner and less imperfect than typical striated platelets. The electron contrast effects to be expected at polytype interfaces have been calculated but no such observations have been made on ZnS [37]. A few transmission electron microscope observations on specimens thinned from thick striated platelets were therefore made and are also reported here.

2. Experimental Methods

The scanning electron microscope work was done on a Cambridge Instruments' Stereoscan with an additional photomultiplier mounted on a side port of the specimen chamber to detect the cathodoluminescent emission from the ZnS platelets. The photomultiplier was an EMI 9558B, low noise, S20 tube with a spectral sensitivity extending across the whole visible range. The specimens were examined without any conducting coating applied to the surface. No excessive electrostatic charging occurred.

The ZnS platelets examined here were obtained from three different sources and prepared as follows.

"*R*" *platelets* were prepared by *reacting* Zn and H_2S to produce platelets 50 to 100 μm thick. These were prepared at the Department of Electron Physics of the University of Birmingham by Dr B. Daniels. Several studies of the structure, deformation and luminescent properties of other platelets produced in the same way have been published by Dr Daniels and others [38-41]. These platelets were chemically thinned by immersion in hot chromic acid as previously described [42]. They were examined in transmission in an Hitachi HU-11 electron microscope.

"*A*" *platelets* were grown by sublimation in a stream of *argon* by Mr A. Custers of the Electrical Engineering Department, Imperial College. They were grown on the walls of silica tubes that had been flame polished to minimise the number of nucleation sites. The ZnS had been purified by pre-firing in argon.

"*A'*" *platelets* were also grown by sublimation in a stream of *argon* by Dr P. D. Fochs of the GEC Hirst Research Centre. A two-element furnace technique described in the literature for CdS growth was used [43, 44]. Although the starting material had been pre-fired in argon to purify it in this case also, spectroscopic analysis showed traces of Cu, Al, Si, Fe, and Cd to be present. (P. D. Fochs, private communication.)

The polarised light micrographs were taken on a Carl Zeiss Photo microscope and the Nomarski interference micrographs on a Reichert metallographic microscope.

Electrical contacts were made to the platelets for specimen current and charge collection micrography by applying colloidal silver paint. The contacts were therefore rectifying, not ohmic.

3. Results

3.1. Optical and Scanning Electron Microscopy

Fig. 1 is a set of optical and scanning electron micrographs of an A-type platelet. Fig. 1a is an optical micrograph taken with the platelet between a polariser and an analyser set at 45° to one another. Under these conditions different polytype slabs appear with different birefringence colours and therefore appear as dark and light bands in black and white micrographs [45]. The

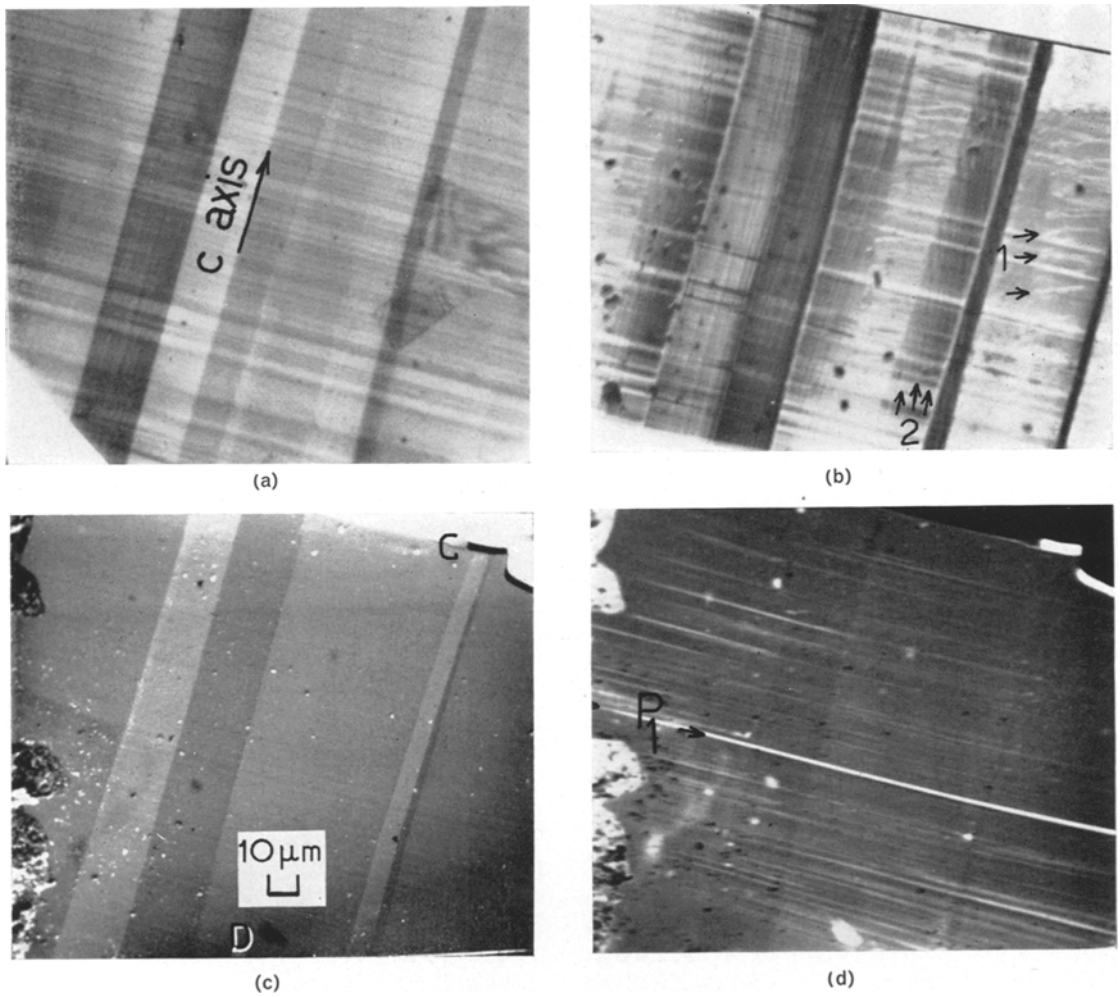

Figure 1 Micrographs of the same area of a ZnS platelet grown by sublimation in a stream of argon. (a) Polarised light micrograph. (b) Nomarski optical interference micrograph. (c) SEM secondary electron micrograph. The detector was in a position above the top of this micrograph. (d) One-contact SEM charge collection micrograph. (e) Two-contact charge collection micrograph. (f) SEM cathodoluminescence micrograph. The detector was in a position to the right of this micrograph. P indicates polytype or faulted bands, I is a "linear marking" [17] and two sets of growth steps are marked 1 and 2. The common *c*-axis of the bands is also marked.

set of fine lines perpendicular to the polytype bands were called linear markings by Mardix *et al* [17] who showed them to run parallel to the common *c*-axis of the hexagonal polytypes which coincides with a $<111>$ axis in the sphalerite slabs. Fig. 1a however, shows an unusual structure in which the polytype or faulted bands are very narrow. Consequently the birefringence effects are less pronounced than effects due to thickness (overgrowth effects) parallel to the linear markings, and the otherwise characteristic kinking of the linear markings where they cross polytype bands [17] is not visible, making interpretation difficult. The structural interpretation of this specimen is represented by the *c*-axis direction that is marked (I. T. Steinberger,* private communication). Linear markings run parallel to the *c*-axis and faulted regions and polytype bands run perpendicular to the *c*-axis. Fig. 1b was taken with the Nomarski optical interference microscopy technique [46] which reveals steps down to about 30 Å in height. Both the polytype bands and the linear markings at right angles to the bands are visible and there-

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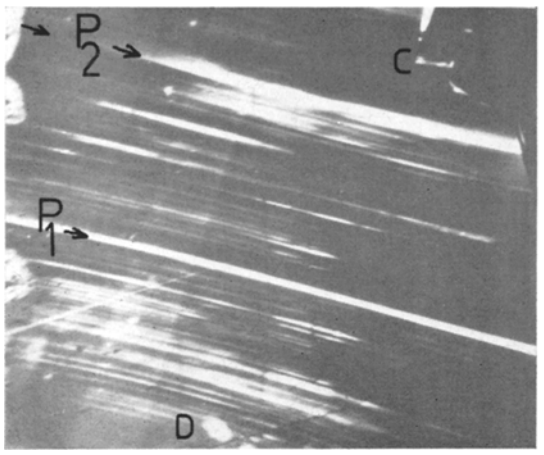
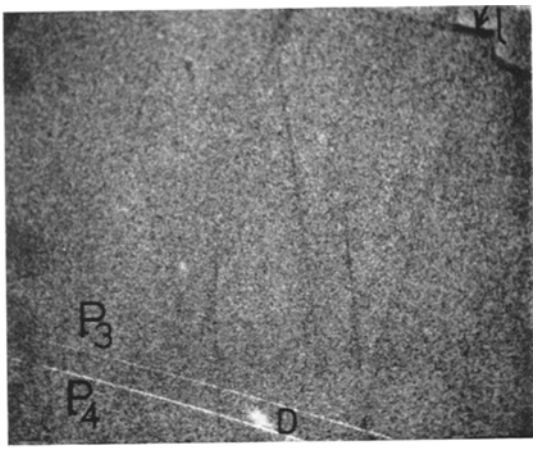
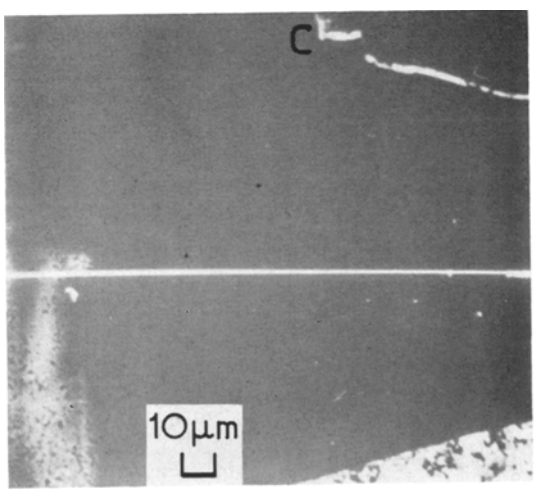


(e)

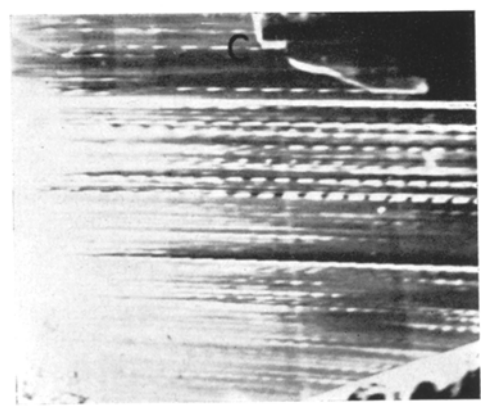


(f)

fore have associated surface steps. Two additional types of steps are also visible. The first, marked 1 in fig. 1b, run at about 20° to the linear markings, only appear in certain of the regions separated by the markings parallel to the *c*-axis, and are not straight. The second, marked 2, appear in other regions parallel to the *c*-axis, are straight and run at about $\pm 10°$ to the linear markings. Both these sets of additional lines are probably growth steps. Fig. 1c is a secondary electron micrograph. It shows the surface topography again but reveals less detail than fig. 1b. Neither of the two additional sets of lines of fig. 1b is visible in fig. 1c. The contrast of the bands parallel to the *c*-axis probably arises from small tilts of the surface of the platelet occurring at certain of the linear markings. A piece of the platelet cracked away leaving a corner C which, with a dust particle marked D, serves as a landmark for comparison with subsequent micrographs. Silver paint making one of the electrical contacts flowed irregularly over the edge of the platelet at the left. The second contact was made to the parallel edge off the field of view to the right. Fig. 1d was obtained by using the current to earth from the left-hand (visible) contact as video signal with the other contact disconnected. Certain of the (horizontal) polytype or faulted



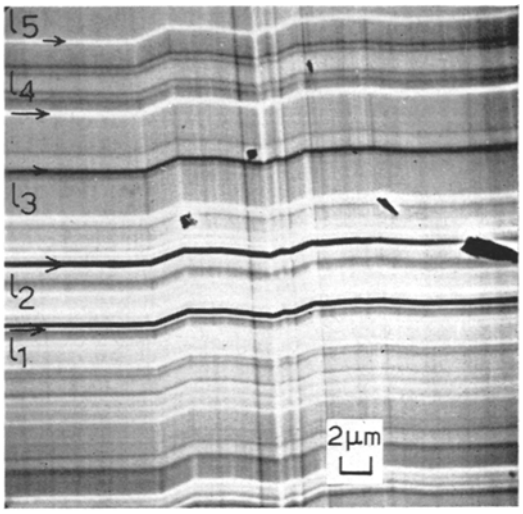
(a)



(b)

Figure 2 SEM charge collection micrographs of the platelet shown in fig. 1. The direction in which the electron beam scanned across the specimen was (a) parallel to the polytype bands (the bright horizontal line is a multiply exposed scan line) and (b) at an angle of $3\frac{1}{2}°$ to the polytype bands. Compare fig. 1d in which the scan direction was at a large angle to the polytype bands.

(a)



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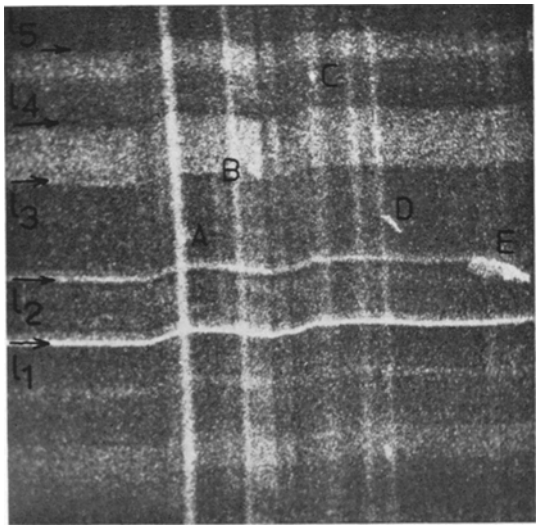


(c)

Figure 3 ZnS platelet grown by sublimation in a stream of argon (a) SEM secondary electron micrograph. (b) Specimen current micrograph. (c) Cathodoluminescence micrograph. Dust particles are marked A to E. L_1 to L_5 are linear markings and B_1 and B_2 are polytype bands.

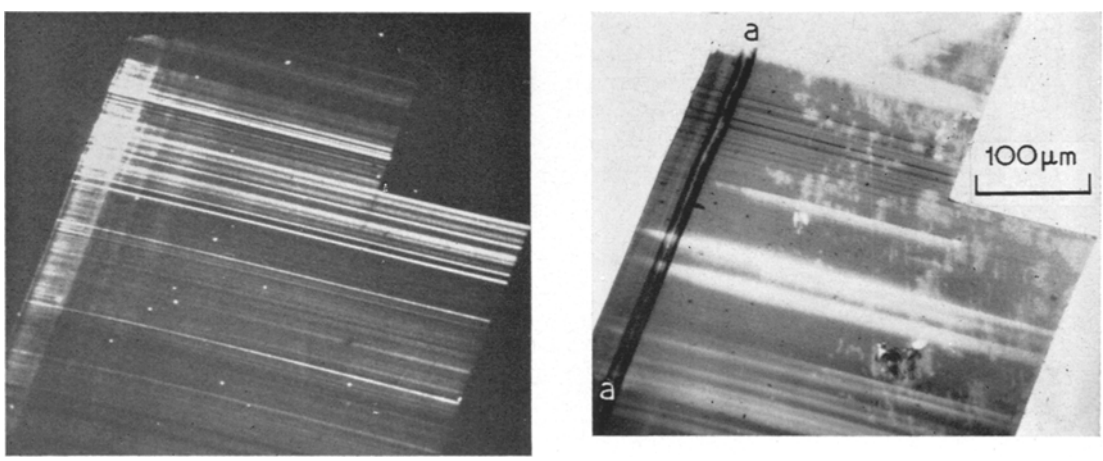
bands appear bright. Fig. 1e was obtained by using the charge collected by the two contacts as video signal. Polytype band P_1 was again the most prominent. Fig. 1f displays the variation of the intensity of the cathodoluminescence from the platelet. Polytype bands P_3 and P_4 were the two bright sources. One linear marking, l, was also visible.

The visibility of the polytype bands in the SEM charge collection micrographs was sensitive to the angle between them and the scan lines. When the scan lines were parallel to the bands the latter were not visible (fig. 2a) since an AC coupled amplifier was used. When the scan lines intersected the bands at a small angle the bands appeared discontinuous (fig. 2b). The bright line segments occur each time a scan line crosses one of the bright bands of fig. 1d.

Beautiful tartan patterns, shown in fig. 3, were obtained when another "A" platelet was examined in the scanning electron microscope. Fig. 3a is a secondary electron ("emissive mode") micrograph showing the surface topography together with any voltage contrast. Fig. 3b is a specimen current micrograph obtained with the whole lower surface of the platelet contacted by a conducting glue (Durofix). Fig. 3c is a cathodoluminescence micrograph showing the variation of emission from point to point over the platelet surface. The dust particles marked A-E provide landmarks for intercomparisons. A number of features of this platelet were markedly different from those of the platelet of fig. 1: (i) The horizontal lines were kinked where they crossed the interfaces between certain of the vertical bands. This was observed and explained by Mardix *et al* [17] as characteristic of linear markings. Therefore it is believed that the horizontal lines such as l_1 to l_5 were linear markings and the vertical bands were polytype slabs. Unfortunately the fragile platelet shattered before this could be confirmed by optical microscopy. (ii) The fact that linear sources of recom-

bination radiation were found among both the vertical and horizontal sets of lines in fig. 3c was unexpected. The literature reviewed above indicated that it was the polytype bands which had significant properties. Certain polytype interfaces were strong sources while others were not. For example the right-hand interface (which runs through dust particle A) of the band marked B_1 in fig. 3a, was a strong source (fig. 3c) but the left-hand interface was not. The cathodoluminescent properties of interfaces therefore depend on the nature of the material on both sides. Only one polytype band marked B_2, whose left-hand interface ran through dust particle, B, was a faint source of cathodoluminescence over its whole width. By contrast, the bands between the horizontal lines l_3 and l_4 as well as a band bounded along its upper edge by l_5 were strong sources of recombination radiation. These observations show that the "linear marking" structures of ZnS platelets can have significant physical properties.

The possibility had to be considered that the cathodoluminescence observations were misleading [25, 26]. ZnS has a dielectric constant of 5.13 [47]; therefore its refractive index is 2.265 and the critical angle, for total internal reflection is 26° 20′. That is, light generated in the interior of the platelet by the incident electron beam can only get out if it is incident on the surface in a direction making an angle of 26° 20′ or less to the surface normal. Thus it is conceivable that surface facets which were nearly normal to the direction to the photomultiplier used to detect the cathodoluminescence, by allowing a higher than average fraction of the radiation out to the photomultiplier, might be responsible for the observed bright lines and bands. It was established that this effect was not playing any significant role by tilting the platelet from the orientation normal to the electron beam to one nearly perpendicular to this and parallel to the face of the photomultiplier. None of the lines and bands of high emission in the cathodoluminescence micrograph (fig. 3c) altered noticeably in relative intensity at any tilt. The fact that surface tilts had no effect, means that direct emission of light was relatively unimportant. Most of the light must have been emitted after multiple internal reflections so that the original direction of emission of the photon and the orientation of any local portion of the surface was of little importance. Moreover any time delay between the generation of the photon and its escape through the surface could not be significant. The minimum time interval between adjacent picture points assuming 10^3 per line and taking the minimum line scan time available on the SEM, was then not less than 4×10^{-6} sec. In this time light would travel 5.3×10^4 cm in ZnS. The greatest dimension of any platelet was about 5 mm and the thicknesses were a few tens of microns. Thus the light would have to undergo not less than 10^5 total internal reflections to be delayed long enough before emission to contribute, spuriously, to the brightness of even the next picture point on the fastest line scan speed. So many reflections without emission or absorption are improbable and the possibility of light from one point contributing to the brightness of



(a) (b)

Figure 4 Platelets of ZnS sublimated in a stream of argon. (a) SEM cathodoluminescence micrograph. (b) Charge collection micrograph. a – a was an axis along which two platelets joined.

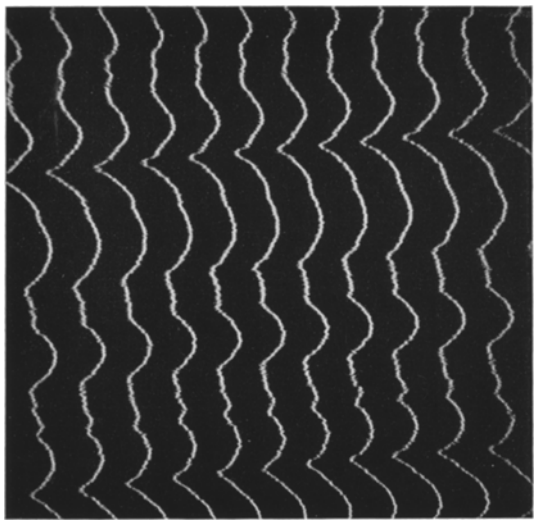


Figure 5 Graphical display of the cathodoluminescence intensity along a number of vertical scans of the platelet of fig. 4.

the image of the next point can be discounted. This was confirmed by the fact that no streaking or tailing on the later side of the bright points of SEBERR micrographs was observed. This fact also showed that no other causes of delayed emission, such as trapping or recombination mechanisms with emission times long compared with 4×10^{-6} sec, were operative either.

Fig. 4 is a pair of micrographs of an A′ platelet. This was actually a complex specimen with a second, smaller platelet sticking up from the axis of intersection, marked a in fig. 4b. Fig. 4a shows the many sources of cathodoluminescence in the platelet. Polarised light microscopy showed many narrow polytype slabs to run parallel to these roughly horizontal sources. Fig. 4b is a charge collection micrograph in which certain lines of the polytype set appear dark and others appear as bright bands. In secondary electron microscopy the irregular areas that appeared light in fig. 4b appeared dark. They were therefore contaminated surface areas from which the number of secondary electrons emitted was reduced.

Fig. 5 is a higher magnification "X-modulation" micrograph of an area of the A′ platelet of fig. 4a showing the localised bands of high cathodoluminescence emission. It consists of a set of vertical line scans showing the quantitative variation of cathodoluminescence intensity (in arbitrary units of amplified photomultiplier signal) as horizontal deflection. It can be seen that the shape of the curves at each of the horizontally displaced scanned lines was approximately the same. That is, the form of the cathodoluminescence sources was constant along their lengths. It also appears that there were two kinds of maxima. There were relatively sharp peaks which were recorded as narrow lines in fig. 4a and there were broad maxima which appeared as broad bands in fig. 4a. Comparison with a secondary electron micrograph of the same area indicated that some but not all the bright cathodoluminescent emitters corresponded to features giving rise to contrast in the secondary electron picture.

3.2. Transmission Electron Microscopy

Fig. 6 is a micrograph and transmission electron diffraction pattern obtained from a thinned striated ZnS R platelet. X-ray analysis of the platelet as a whole showed it to have the wurtzite structure and $(11\bar{2}0)$ orientation. However, the strongest, paired spots in fig. 6b showed that the basic structure of this local area of the platelet could be interpreted as twinned sphalerite (or 6H) as indexed in fig. 6c. In addition there are spots at positions marked X between the twinned spots. These could be interpreted as indicative of the simultaneous presence of a structure with a repeat distance in the crystal lattice which is greater than that of the twinned sphalerite (or 6H) since the X spots are more closely spaced in the reciprocal lattice of the diffraction pattern. Thus the additional X spots would indicate the presence of a polytype structure with a unit cell more than six double atom planes high (as for 6H) and having its *c*-axis parallel to the streaks in the diffraction pattern. The streaks then would arise from defects on the crystal planes perpendicular to the streaks. These defects seen edge-on in the micrograph as lines in fig. 6a were stacking-faults. Thus the diffraction pattern can be interpreted as showing that in an area of a square micron there were simultaneously present twinned sphalerite (or 6H), a longer repeat sequence (higher number) polytype and irregularly spaced (random) stacking-faulting. An alternative interpretation in terms of a particular distribution of faults in wurtzite (2H) is also possible (S. Mardix*, private communication).

Fig. 7 shows two other specimens giving diffraction patterns similar to fig. 6b. The fault arrangements are clearly different from one

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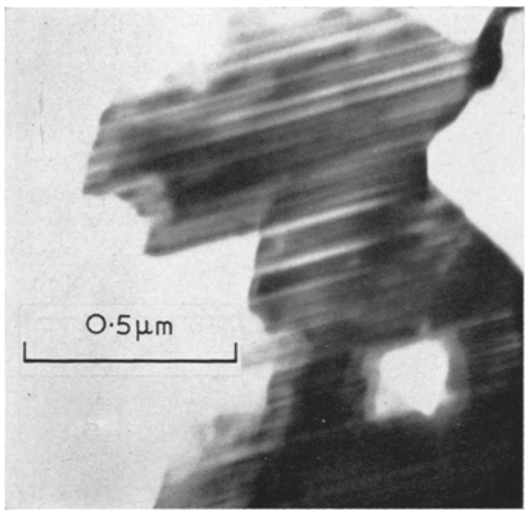
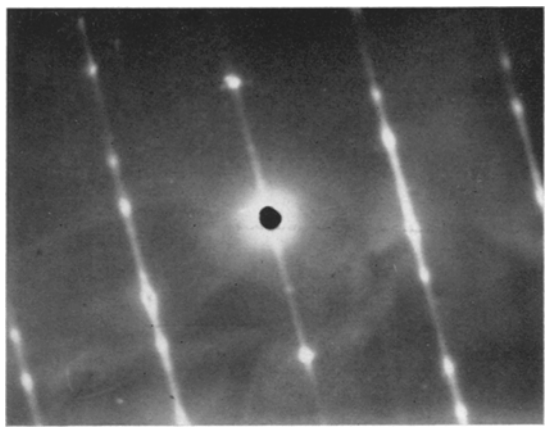


(a)



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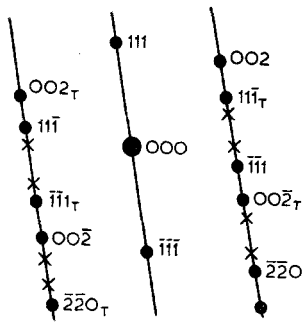

(c)

Figure 6 Transmission electron microscope observations of a thinned area of a striated ZnS platelet grown by a chemical reaction technique. (a) Micrograph. (b) Diffraction pattern. (c) Indexed plot of (b). Twinning, by a rotation of 180° about the streaked [111] direction, doubled the main spots as indicated by the subscript T in the indices. Polytype 6H is a regularly twinned sphalerite structure and would produce the same set of main diffraction spots.

another and from that in fig. 6a. This observation makes the interpretation in terms of a particular distribution of faults appear inapplicable in the present case. Thus figs. 6 and 7 indicate that the basic twinned sphalerite plus higher polytypes could co-exist with genuinely random fault sequences. Other specimens were observed in which only the doubled spots and the continuous streaks of fig. 6b occurred. That is, twinned sphalerite (or 6H) and random faulting sometimes co-existed without higher polytype structures.

These striated platelets were weakly cathodoluminescent and the electron microscope specimen chamber was seen to be filled with a dim green light. Specimens of this kind sometimes caused the electron beam to jump erratically due to electrostatic charging. The thicker platelets often disintegrated in strips under the electron beam [42]. On occasion large areas, or, in two cases, entire specimens totally disappeared without warning. This form of disruption sometimes occurred immediately on first viewing and sometimes after several minutes viewing. It only occurred with striated specimens.

4. Discussion

It is not possible at present to make detailed or quantitative interpretations of the observations reported above. They constituted an initial survey of the sort of information that could be obtained by applying a range of techniques to a complex and variable group of structures. However, certain conclusions follow immediately and these are outlined below.

The polytype bands are a form of macroscopic structural defect and it has long been known that they can have significant physical effects. The linear markings, however, do not correspond to any form of structural defect visible in any of the techniques used nor to any defects reported in any of the structural studies listed in section 1. Therefore, none of the mechanisms of piezo- or pyro-electric effects [20], changing the width of the forbidden energy gap [21], or of permanent polarisation [22], that have been proposed for bands of alternating crystal structure (in order to explain anomalous photovoltages), are applicable to linear markings.

The fact that linear markings can be cathodoluminescent sources (fig. 3) thus shows that

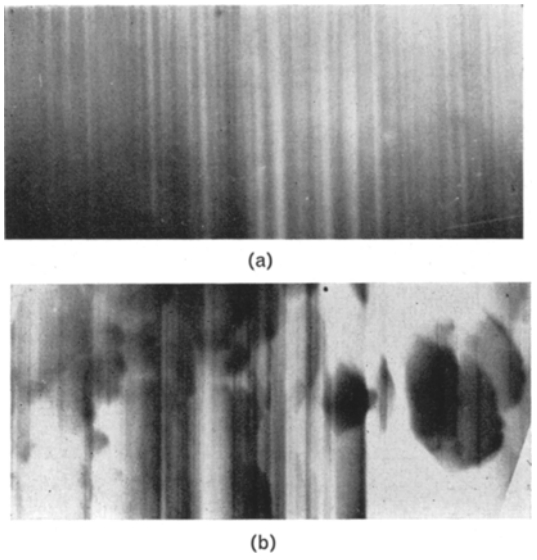

Figure 7 Transmission electron micrographs of thinned areas of two other striated ZnS platelets grown by the chemical reaction process.

changes of structure are not a necessary condition for the appearance of localised luminescent properties in ZnS. Moreover not all polytype band structures had charge collecting or radiative recombination properties. This shows that changes of structure are not a sufficient condition for localised electrical or luminescent properties. The fact that polytypic or polymorphic structure changes are not essential for the appearance of the anomalous photovoltaic effect either, is shown by the fact that very large photovoltages have been obtained with films of Ge [48], Si [48] and GaAs [49], none of which is polymorphic.

The present observations, as well as those of Mardix *et al* [5-12] and of Daniels [38, 39] using polarised light microscopy and X-ray techniques, show that the striated structure is much more complex and random than a simple alternation of cubic and hexagonal phases. Over distances of the order of a micron striated structures may exhibit (i) twinning as shown in figs. 6 and 7, (ii) martensitic phase transformations between cubic and hexagonal material, i.e. *regular* arrays of stacking-faults [13-15], (iii) complex polytypic stacking sequences [5-12] of which some possible evidence was presented in fig. 6, and (iv) irregular arrays of stacking-faults (figs. 6 and 7) corresponding to the "stacking disorder" or "one-dimensional disorder" that was found by X-ray methods [4]. Moreover, several of these structures can simultaneously occur in a distance of the order of a micron. This variable and complex structure of the striations may be the explanation of the fact that the anomalous photovoltages generated by striated platelets are extremely irreproducible from one platelet to another. As shown above, the cathodoluminescent and charge collecting properties of the polytypic bands also varied greatly from platelet to platelet.

The observation of localised sources of cathodoluminescence in striated platelets (figs. 1f, 3c, 4c and 5) lends credence to early reports of localised electroluminescence in striated ZnS [2]. Such sources and the cathodoluminescent source observed here are quite different from the double-comet-like sources found in luminescent powder particles [25, 26] and rod crystals [52].

Williams and Yoffe [30] observed localised cathodoluminescence effects associated with faults or polytype bands in ZnS cooled to 100° K by using an ultraviolet sensitive detection system. They showed the emission to contain exciton lines corresponding to energies only slightly less than the forbidden gap energies. When suitable beam currents were used and appropriate wavelengths were selected for detection they observed the whole area occupied by hexagonal (wurtzite) material to emit uniformly. The detector used to produce figs. 1f, 3c, 4a and 5 above, however, was sensitive to visible radiation. Wavelengths in the visible region correspond to energies much less than the forbidden gap width and the transitions concerned therefore necessarily involve levels deep in the forbidden gap. These might conceivably be associated with structural defects such as vacancies or dislocations or with "activator" impurities. Both the localised charge collection effects and the localised cathodoluminescence observed in figs. 1 to 5 could be due either to physical defects or to chemical inhomogeneities (segregation), possibly due to the presence of the physical defects.

There are a number of other observations in the literature indicating that fault or polytype striations [2, 24, 51] or dislocations [50, 52-54] play a role in luminescence. Similarly it is known that striations are associated with the anomalous photovoltaic effect [1, 18, 19] and there is evidence for electrical effects at striations [23]. However, none of these observations indicating that electrical or optical effects in ZnS or CdS may be associated with physical defects, are conclusive. This is because the best II-VI materials

are of low purity by semiconductor standards and the deformation or growth processes employed to introduce defects generally occur at sufficiently high temperatures to make diffusion and segregation possible.

Striated platelets have been extensively studied, as indicated in the Introduction, because they were one of the best of the poor forms in which ZnS was available and because of their interesting properties. However, striated platelets are too complex and variable in structure and properties to be useful for quantitative studies of the intrinsic properties of ZnS or for device applications. For these purposes it will be necessary to develop improved growth techniques such as epitaxy [55-57].

Acknowledgement

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