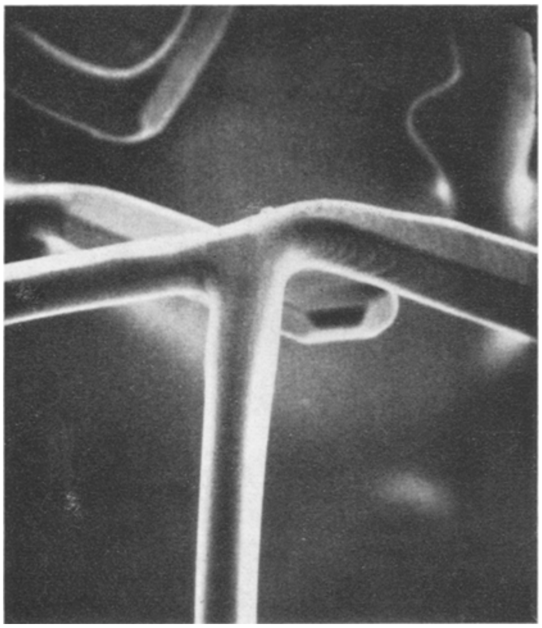

Figure 3 Part of field of fig. 1 (×800).

whiskers have joined smoothly and continued to grow in a new direction.

We believe that the whiskers formed by condensation from the vapour phase. Their composition is unknown; they may be pure iron or a concentrated alloy. The observation that metal whiskers formed on the alumina block which separated the alloy strip from its "gettering box" could only be interpreted in terms of deposition from the vapour. The supersaturation $(P_M - P_T)/P_T$, where P_T, P_M are equilibrium vapour pressures of pure iron at the growth temperature, T, and at the maximum temperature, 1250° C, varied from 0 to 2500; over this range, whisker diameters increase from ~ 1 to ~ 50 μm, and lengths decrease from ~ 1000 to ~ 5 μm. The micrographs refer to a supersaturation of 10 to 200, whisker diameter ~ 10 μm and length ~ 150 μm. These dimensions are similar to those of whiskers grown on pure iron at a similar temperature and vacuum [3].

There is no direct evidence as to the role of impurities in the growth of these whiskers. The fact that they mostly develop near (but not *at*) grain boundaries, where impurities are apt to segregate, suggests that impurities may play a part, and certainly the extreme sensitivity of the metal surface to contamination (as shown by the difficulty of securing reproducible surface-controlled secondary recrystallisation) supports the view that the same contamination may help whisker growth. A recent study of whisker growth on pure iron during high temperature oxidation [4] established clearly that surface impurities determined where whiskers grow, which may be a pointer to interpreting the present results. In that study, it was found that whisker growth varied from one grain to another, which was interpreted in terms of orientation-dependent impurity adsorption. Figs. 1 and 2 show a similar variation of whisker density in the present experiment.

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Formation of Zinc Sulphide Polytypes by Spiral Growth around Dislocation Clusters

Crystals of the ZnS type have two basic modifications, namely the cubic sphalerite structure and the hexagonal wurtzite structure (3C and 2H, respectively, in Ramsdell's notation [1]). However, ZnS crystals rarely appear in these extreme forms, but usually display a large variety of polytypes, which are intermediate between the basic cubic and the hexagonal structures. Although a large amount of work on polytypism has already been done, especially concerning SiC [2] and ZnS [3], a satisfactory explanation of this phenomenon has not yet been given. The growth mechanisms in SiC and ZnS seem to be different. SiC usually develops bulk crystals from the beginning, whereas ZnS crystals start to grow as whiskers.

At present, the generally accepted view is that the polytypes of ZnS grow spirally around large dislocations [4]. In order to account for some polytypes, dislocations with Burgers vectors of tens and hundreds of lattice constants must be assumed. The existence of such large dislocations is, however, very improbable, since their strain energy must be very high and they should dissociate into small dislocations. Moreover, it is difficult to conceive how such large dislocations come into being. Because of the high strain energy at the centre of a large dislocation, one expects that the dislocation core will be hollow. Such hollow channels have often been observed [4], and this is accepted as experimental evidence for the existence of large dislocations. It will be seen, however, that the mechanism suggested here also accounts for this observation.

When ZnS crystals are grown from the vapour in a quartz vessel, the crystals begin to grow as thin islets on the wall of the vessel and grow laterally until the islets meet. At this instant numerous whiskers shoot off and grow rapidly from the substrate. At a certain stage the growth of the whiskers stops and they begin to grow laterally, usually forming platelets [5].

Here we shall essentially deal with the second stage. We assume that the islets of the substrate are cubic and nearly perfect. The $\langle 111 \rangle$ direction of the islets, which is their growth direction, is always perpendicular to the walls of the vessel. However, within the respective $\{111\}$ plane the islets have random orientations with respect to each other, so that when they meet the crystals must become heavily dislocated. Some of the dislocations will be suitable as growth centres and will eventually form clusters around which diverse polytypes can grow in spirals.

The dislocations considered as the basic growth type have elementary Burgers vectors of the $a\langle \frac{1}{2}\frac{1}{2}0 \rangle$ type, and axes in the $\langle 111 \rangle$ direction perpendicular to the wall of the vessel, which actually is the growth direction of the whiskers. Such dislocations are composed of alternate segments of two 60° dislocations and one pure screw. Assuming, for instance, the pure screw to be in the [110] direction, this can be represented by the vector equation

$$a[\tfrac{1}{2}\tfrac{1}{2}0] + a[\tfrac{1}{2}0\tfrac{1}{2}] + a[0\tfrac{1}{2}\tfrac{1}{2}] = a[111]$$

which describes a dislocation in the [111] direction with the Burgers vector $a[\frac{1}{2}\frac{1}{2}0]$. The existence of such dislocations has been suggested by Hornstra [6]. Of course, one cannot assume that the segments alternate in a strictly regular way, so that the dislocation line may slightly deviate from its $\langle 111 \rangle$ direction or may be curved. However, this fact does not refute the proposed growth mechanism, and even gives it some additional support, since it accounts for some observed effects.

The proposed model is as follows. To fix ideas, we shall assume the substrate, i.e. the primary islets, to grow as perfect cubic crystals showing (111) faces. However, the structure of the substrate is really irrelevant for our model. Now suppose that a growth dislocation in the [111] direction, with a Burgers vector $\mathbf{b} = a[\frac{1}{2}\frac{1}{2}0]$, is formed in the substrate. The dislocation creates a step on the surface, which will easily capture the atoms from the vapour. This will make the crystal grow rapidly by spiral growth around the dislocation, and will slow down the primary growth which will become insignificant. Let us denote the three types of close-packed (111) planes of the cubic crystal by A, B, C, as usual, and let us call the free face of the primary crystal A. After a full turn of the growth step the original A layer will come back as B, then as C, then again as A, etc. Thus an endless spiral layer will grow, forming an almost perfect cubic (3C) crystal.

Two near-by growth dislocations with identical screw components and opposite edge components will give rise to a wurtzite (2H) crystal. In this case the growth will proceed by a double layer. One should, of course, bear in mind that a partial dislocation must appear in the (111) somewhere between the two growth dislocations. This partial is likely to be smeared out over a large area and its presence is irrelevant to the growth mechanism.

Two dislocations with like edge components and a third dislocation with an unlike one will give rise to the 9R polytype; the layer will be threefold. With three identical dislocations the layer will be threefold and the crystal will grow as 3C. This, however, will be more strained than the basic one-layer growth type. In general, several different combinations of dislocations may produce the same polytype.

Four dislocations, two of which have like and two of which unlike edge components, will cause the crystal to grow as 4H; the layer being fourfold. The polytype 15R will grow around a cluster of five dislocations with one net edge component.

Not only may different combinations of dislocations produce the same polytype, but also a given combination of dislocations may give rise to different polytypes, depending on the details of the mutual arrangement of the dislocation lines.

From a macroscopic point of view, such a cluster will, of course, behave like a large dislocation.

Clearly, more complicated clusters will be relatively rare, and this accounts for the fact that the simple polytypes are the most frequent ones. On the other hand, the probability of a given polytype will also depend on the stability of its dislocation cluster. In general, it has to be shown that such dislocation clusters are sufficiently stable to ensure the growth of a reasonably large crystal. One can, however, easily see that at least grain boundary arrangements of dislocations will have a fairly high stability. The stability of clusters of growth dislocations is now being calculated.

It is clear that the centre of the growth spiral, i.e. the region of the dislocation cluster, must be heavily strained and thus have a high free energy. This explains why, in etching experiments, the centre may be eventually etched out and appear hollow. Because of the high free energy of the centre, the crystal may also preferentially grow in the outermost regions of the growth step, so that a crater will be formed at the centre during the growth. However, once the step is there, the crystal may keep growing even around a hollow channel. The vapour pressure inside the channel will be lowered and this will further decrease the growth rate at the centre. This will result in a whisker with a conical hollow channel. Such crystals are actually very frequent [5].

The change of polytype in the same crystal can be explained by the disappearance or introduction of one or several dislocations.

As has been mentioned already, it is improbable that the dislocations will be strictly parallel. According to current calculations, it seems that the dislocations will tend to diverge. A diverging cluster will eventually lose its identity as a cluster. This will lead first to changes in the polytypes and then to a breakdown of the growth step, and finally at a certain stage the growth will stop altogether.

Thus, it is concluded that the proposed mechanism accounts for the observed phenomena of polytypism. Alternatively, the present considerations can serve as a reinterpretation of the structure of large dislocations. A detailed and systematic account on the structure of growth clusters and the respective polytypes, as well as on the results of the calculations of their stability and other effects, will be given in a forthcoming paper.

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