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Basal Dislocations in Single Crystals of Anthracene

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The preparation of thick, vapour-grown crystals of anthracene is described, and the characterization of basal dislocations in these crystals is discussed. It is demonstrated that the Burgers vector of dislocations (i.e. those that glide on (001) planes) cannot be exclusively in either the [100] or [010] directions, and is very likely to be [110] and/or [120]. There is some evidence for the occurrence also of a hitherto unknown slip system: $(12\bar{1})$ $[\bar{2}10]$.

INTRODUCTION

Numerous studies of the chemical and physical properties of anthracene offer convincing evidence (see Refs. 1 and 2 and refs. therein) that thin, vapour-grown single crystals display quite different behaviour from that of melt-grown crystals. It has, for example, been shown that triplet-exciton trapping, as monitored by phosphorescence and delayed-fluorescence emission, and charge-carrier localization, as manifest in space-charge-limited and thermally-stimulated currents are more pronounced in the melt-grown than in the vapour-grown samples. This behaviour has been rationalized in terms of the greater number of structural defects believed to be inherently present in melt-grown crystals, and it has been possible to show that the additional basal dislocations introduced into the crystals by mechanical deformation are partly responsible for the trapping. Hitherto, however, there has been no readily available technique that will directly reveal the concentration of such basal dislocations in these crystals. There are several reasons for this state of affairs:

a) The vapour-grown crystals employed have been so thin as to render impossible the examination of etch pits on non-basal faces.

b) Transmission electron microscopy, which is in any case applicable only to those organic materials that can survive massive doses of electron irradiation, is applicable only to the thinnest and smallest crystals, which are far too small to be used for the measurement of excitonic and charge-carrier behaviour.

c) Cleavage, cutting and polishing of non-basal faces of melt-grown crystals followed by chemical or dissolution etching has not to date proved successful.

d) X-ray topography[3] offers some promise, and has already yielded some encouraging results, but is not an unqualified success with soft organic solids, nor does it offer exceptional resolution.

This situation is quite different from that which obtains for non-basal dislocations, the concentration of which may be readily obtained by etching the well developed, basal, cleavage faces. It is, however, important that we have means of estimating the numbers of dislocations that glide in the basal plane, since these are the ones most readily introduced into the structure by mechanical deformation, and the ones most likely, if only on energetic and stereochemical grounds, to be quite different, in their influence, from the non-basal dislocations which are inclined to the (001) planes. Furthermore, a knowledge of the way dislocation networks may accommodate their total energy by forming low-angle grain boundaries, is itself desirable.

In this work we describe the preparation of thick, vapour-grown crystals, the dimensions of which are large enough to be amenable to measurement of a variety of physico-chemical properties, and the characterization of basal dislocations in them. Careful study, especially of the low-temperature luminescence behaviour, of melt-grown crystals shows that they reflect the presence of both exceedingly minute amounts of impurity and of relatively large numbers of dislocations. Accordingly, there is a tendency among molecular crystallographers to utilize rather thick crystals grown by such procedures as that developed by one of us.[4,5]

GROWTH AND MORPHOLOGY OF CRYSTALS

Figure 1a illustrates the morphology of crystals of ultra-pure anthracene[4] grown from the vapour[5] in the presence of an inert gas (such as N_2, He, Ar or Xe). Their dimensions are typically *ca* 0.5 cm × 0.5 cm × 0.2 cm.

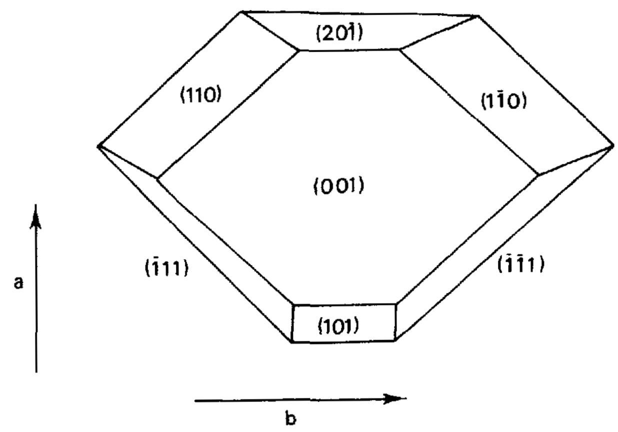


FIGURE 1a Morphology of vapour grown single crystals of anthracene showing prominent faces.

In addition to the vapour-growth technique described in Ref. 5, a simple device was used for the preparation of some of the crystals used in this work. An ampoule containing anthracene and an inert gas at about 1 torr was placed in the glass apparatus shown in Figure 1b. It consists of a central tube *a*, surrounded by jackets *b* and *c*, which are separated from one another by a septum. Flasks containing solvents with different boiling points are attached to joints *d* and condensers are fitted to joints *e*. Nucleation can be effected with acetic acid/toluene azeotrope and water (105°C and 100°C, respectively). Continued growth without additional nucleation can be provided by replacing the azeotrope with pentanone-3, bp 101°C. The gradient between the two zones is best defined when the sample ampoule is supported in a thermally insulating ring, *f*.

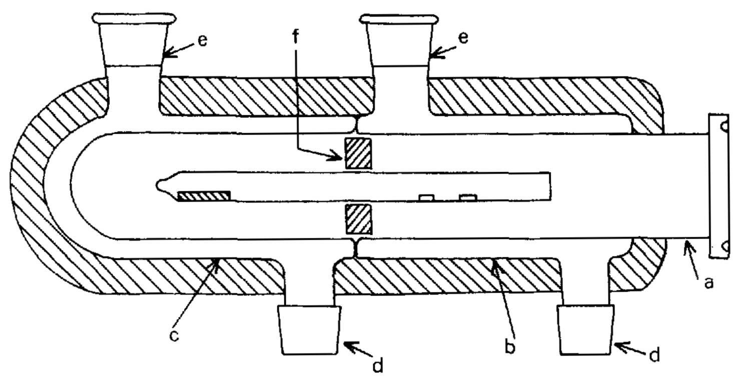


FIGURE 1b Glass apparatus for the vapour growth of anthracene crystals.

The morphology is almost identical to that of vapour-grown crystals prepared under vacuum, and described by Robinson and Scott[6]; (001), (201) and (110) faces are the most prominent.

SLIP TRACES AND DISLOCATION ETCHING

Examination of both (20$\bar{1}$) and (110) as-grown faces reveals prominent slip traces running, respectively, along [010] and [$\bar{1}$10] (Figures 2a and 2b). The fact that slip traces are observed on (20$\bar{1}$) indicates that there is a component of the Burgers vector of the responsible dislocations in [100]. (This is in agreement with Robinson and Scott's conclusions that slip preferentially occurs on (001) planes by means of dislocations with Burgers vector in [010] or 1/2[110]). Consequently, it could be that in these vapour-grown crystals some of the dislocations may have Burgers vector 1/2[110] or 1/2[120]†. Near the edges of the crystals there is marked curvature of the slip traces (seen clearly in Figure 2a). This may be explained if there is a component of the Burgers vector in [010] and so further supports the occurrence of 1/2[110] and/or 1/2[120] as favoured slip vectors for basal dislocations in these crystals.

We have also been successful in etching some of the prismatic and pyramidal as-grown faces using 20% oleum. Figure 3 shows etch patterns on (20$\bar{1}$) and (110) as-grown faces. An approximate value for the density of emergent basal dislocations at both faces is 1×10^5 cm^{-2}. It is noticeable that there are pronounced alignments of etch pits in [010] on (20$\bar{1}$) and i [$\bar{1}$10] on (110), and that the concentration of dislocation etch-pits increases in regions close to the edges where slip traces show pronounced curvature. Etching the basal, cleaved surfaces of these crystals (also with 20% oleum) reveals a concentration of *ca* 1×10^3 cm^{-2}, typical of the density of non-basal dislocations in vapour-grown crystals.

It is evident, therefore, that, even though the concentration of non-basa dislocations is not increased when anthracene is grown from the vapour, rather than from the melt, the concentration of basal dislocations is rather large. Repeated attempts to cut, polish and etch non-basal surfaces of massive melt-grown crystals have failed, so that a direct comparison between the thick vapour-grown and melt-grown crystals is not at present feasible. However, Figure 4, which shows a (100) cut surface exposed to tetrahydrofuran for 5 seconds, indicates that in melt-grown samples polygonization

† Since this work was completed we have obtained independent evidence, by diffraction contrast transmission electron microscopy[7] of the occurrence of basal dislocations of the type (001) [12ω] where ω is probably zero.

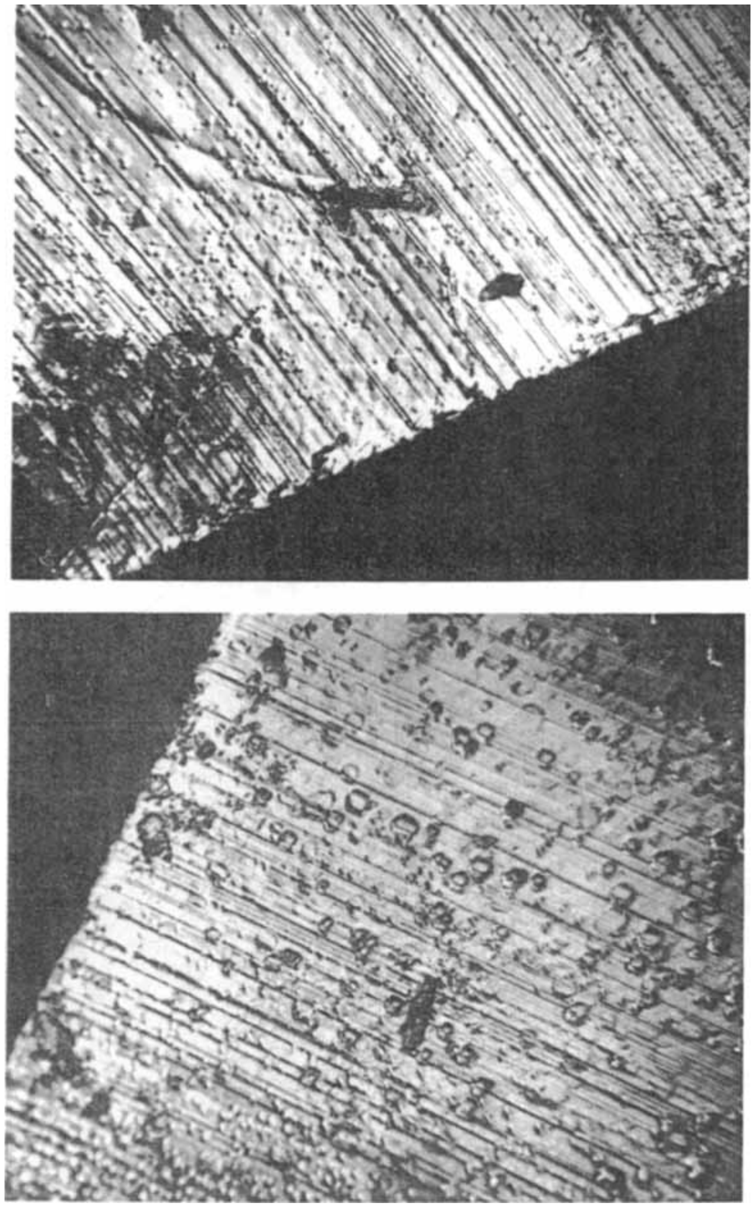
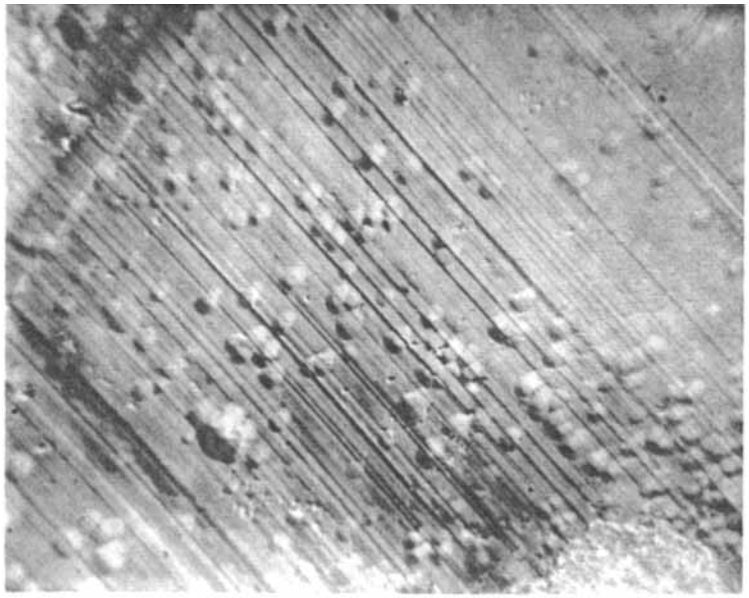


FIGURE 2 Nomarski interference contrast optical micrographs of (*a*) (20$\bar{1}$) and (*b*) (110) as-grown faces of a vapour grown anthracene crystal showing prominent slip traces in [010] and [$\bar{1}$10] respectively. Note the curvature of the slip traces at the crystal edge.
(*a*) × 320.
(*b*) × 320.



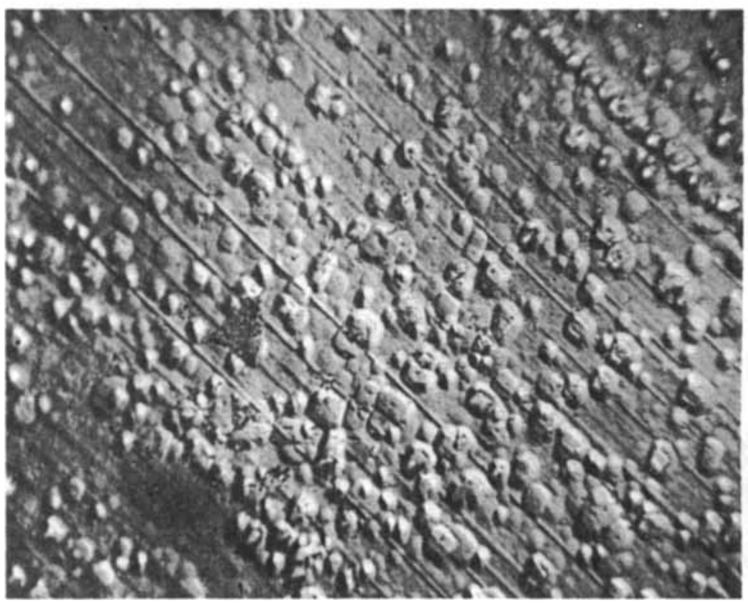


FIGURE 3 Nomarski interference contrast optical micrographs of etch patterns on (*a*) (20$\bar{1}$) and (*b*) (110) as-grown faces of a vapour grown anthracene crystal following exposure to 20% oleum. Note pronounced alignments in [010] and [$\bar{1}$10] respectively.
(*a*) × 800.
(*b*) × 320.

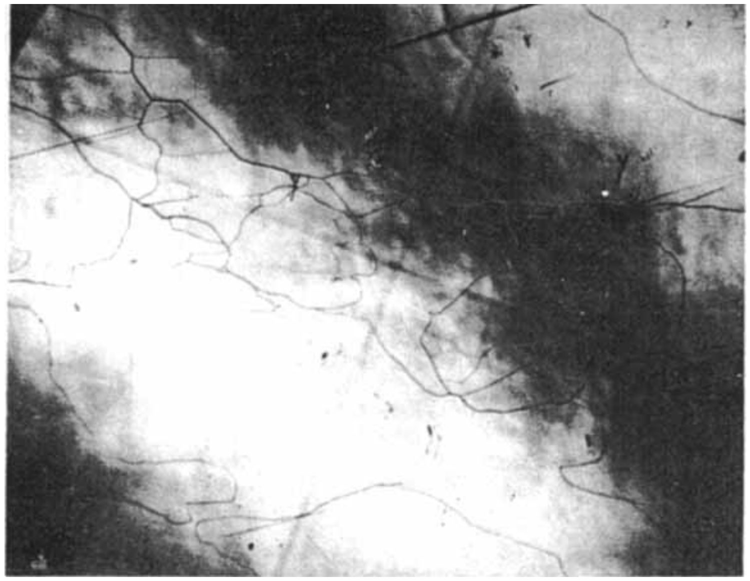


FIGURE 4 Optical micrograph of a cut (100) face exposed to tetrahydrofuran showing evidence of low-angle grain boundaries.
× 50

of dislocations (both basal and non-basal) into low angle boundaries is quite extensive.

From Figure 3a, it is to be noted that there are alignments of etch pits along [418] on the (20$\bar{1}$) face. We can interpret such an alignment in terms of a slip system symbolized by (12$\bar{1}$) [$\bar{2}$10], which has not hitherto been detected for anthracene or for any other related aromatic hydrocarbon crystallizing in the space-group $P2_{1/a}$.

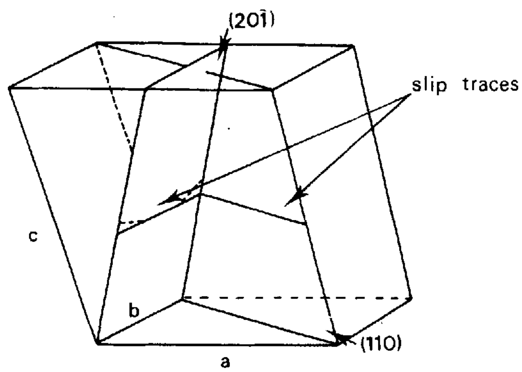


FIGURE 5 Schematic illustration of the interpretation of slip traces observed in vapour grown anthracene crystals.

Summarizing, therefore, we see from Figure 5, which schematically illustrates the topographical features and their interpretation in terms of feasible slip systems, that the so-called basal dislocation (i.e. gliding in {001} planes) has a Burgers vector which cannot be exclusively in either the [100] or [010] direction and is very likely to be [110] and/or [120].

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