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Abstract—The role of basal and non-basal slip in the deformation of anthracene single crystals is considered in the light of published evidence and further work to establish their relative importance is described. Compression and shear tests on suitably orientated crystals show that the critical resolved shear stress for non-basal slip is at least ten times greater than that for basal slip. It is concluded that at room temperature slip generally takes place on the (001) [010] and (001) [110] systems and that the non-basal (20$\bar{1}$) [010], (100) [010], (100) [001], (010) [100] and (010) [001] systems suggested previously are only activated to any other extent under deformation conditions which severely limit basal slip.

1. Introduction

There is current interest in the occurrence of dislocations in molecular compounds and their behavior during deformation, much of the attention being concentrated on anthracene and naphthalene.[1–16] The type and distribution of dislocations before and after deformation has been studied by etch-pitting,[1–4,12] examination of slip traces[13,14] and X-ray topography,[16] and the deformation behavior studied in bending,[11] tension,[13] shear[9,10,15] and compression.[11]

Two viewpoints have been expressed about the dislocations to be found in " as-grown " and in deformed anthracene single crystals. It has been suggested that a number of non-basal slip systems are operative during deformation[4–8] but the present authors[11–16] consider that basal slip is the dominant mode of deformation with non-basal slip playing an extremely minor role except under restricted conditions of deformation. In this paper we reconsider, in Secs. 2 and 3, some of the published evidence for basal and non-basal slip and present further confirmatory results. In section 4 we describe some new experiments designed to establish the relative importance of basal and non-basal slip during deformation and thus resolve the apparent contradiction which has arisen in the literature.

2. Etch-pitting on Basal Plane

The slip systems which have been suggested are listed in Table 1 together with the reticular area of the plane and the length of the Burgers vector. The evidence for the five non-basal slip systems is

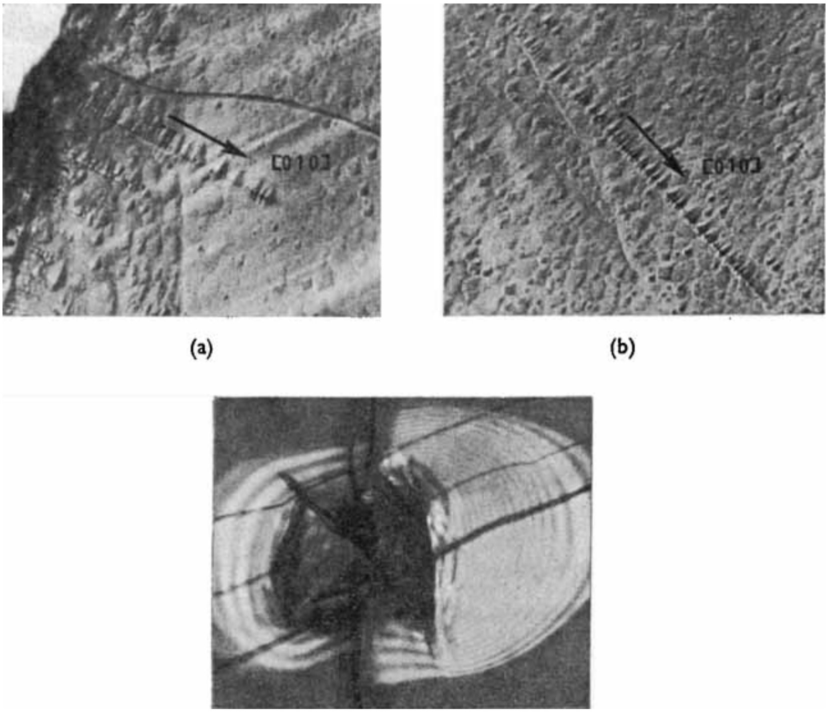
TABLE 1 Proposed Slip Systems in Anthracene (crystal structure $P2_1/a$, $a = 8.561$ Å, $b = 6.036$ Å, $c = 11.163$ Å, $\beta = 124° 42'$[18])

Slip system	Reticular area of slip plane (Å^2)	Probable "**b**" (Å)
(001) [010]	25.8	6.04
(001) [110]	25.8	5.25†
(20$\bar{1}$) [010]	56.8	6.04
(100) [010]	67.4	6.04
(100) [001]	67.4	11.16
(010) [100]	78.5	8.56
(010) [001]	78.5	11.16

† ½[110] see Ref. (14).

based entirely on etch-pitting studies on the basal plane of high-purity single crystals grown from the melt or from the vapour.[1–8] In most cases the crystals grown were examined in the "as-grown" condition or after cleaving on the basal plane; the etch-pits corresponding to the points of emergence of dislocations introduced during growth, by the complex stress fields set up on cooling from the growth temperature or by the complex stresses during cleaving.[1–7] In one case, deformation was carried out by compressing the crystal in a stainless steel vice on opposite (010) faces, the dislocations introduced being identified as mainly those that glide on (100) or (20$\bar{1}$) planes in the [010] direction.[6] However, as the stress axis is parallel to the slip planes the shear stress on these slip systems would be zero and some misalignment or movement must have taken place, resulting in a complex stress system, for any deformation to have occurred at all. Thus in all reported cases the stress systems which have given rise to the non-basal dislocations observed on etch-pitting the basal plane are ill-defined.(1–8)

Our results confirm that crystals grown from the melt or from the vapour contain non-basal dislocations, see for example Ref. (12), and that additional non-basal dislocations may be produced during cleaving (Fig. 1a), although this also produces extensive slip on the



(a) (b) (c)

Figure 1. (a) Melt-grown single crystal cleaved on basal plane and etched immediately with mixed acid etch (Ref. 12) showing rows of deep etch-pits parallel to [010] associated with dislocations introduced during cleaving, together with the shallower, flat bottomed etch-pits associated with the " grown-in " dislocations. ×80.

(b) Melt-grown single crystal cleaved on basal plane and then indented on that plane using a Leitz micro-hardness tester and load of 50 g, showing freshly introduced row of etch-pits parallel to [010]. Hardness impression off plate to bottom right, etching conditions as for (a). ×80.

(c) Hardness impression in basal plane of cleaved crystal, load 50 g, showing extensive cleavage cracking and interference fringes due to separation of layers of the crystal parallel to the basal plane. ×120.

basal plane.[11] A few non-basal dislocations have also been produced by indentation of the basal plane using a Leitz micro-hardness tester (Fig. 1b), but the general appearance of the hardness impression indicates that the crystal is brittle when deformed in this manner (Fig. 1c), and that plastic deformation is limited. After both cleaving and hardness testing the increase in the density of etch-pits associated with non-basal dislocations was small (Fig. 1a and b).

A disadvantage of etch-pitting as a method of investigating the deformation behavior is that it has not been possible, to date, to produce etch-pits on surfaces other than the basal plane so that no estimate can be obtained of the increase in the basal dislocations after any given deformation. Etch-pitting studies undoubtedly establish that non-basal slip does occur, but statements such as " there is strong evidence that, on deformation two kinds of non-basal dislocation are readily introduced into the lattice "[6] are misleading, and the claim that " the most widely occurring type of dislocation is that in which slip takes place on (010) planes in the [001] direction "[5] is incorrect, in view of the great preponderance of basal dislocations introduced by most modes of deformation. However, a recent paper on etch-pitting in related compounds has given greater emphasis to the occurrence of basal dislocations in anthracene.[17]

3. Mechanical Deformation

The relative importance of the various slip systems which have been reported (Table 1) is best determined by carrying out controlled deformation tests on crystals with a wide range of orientations with respect to the stress axis and measuring the critical resolved shear stress for slip on each system. The results of tensile, shear and compression tests on anthracene, and on the isomorphous compound naphthalene, have been reported previously.[9–11,13–15] Kochendorfer[9] found that slip in naphthalene occurred on the system (001) [010] and also on the (010) plane in a direction normal to the (001) plane, while Gordon[10] found that the only operative slip system was (001) [010]. Our results[11,13–15] showed that slip in high-purity anthracene and naphthalene occurred on the two basal systems (001) [010] and (001) [110], although the latter in naphthalene was rendered inactive by small amounts of impurities.[13]

Let us reconsider the evidence that deformation of high-purity single crystals occurs at room temperature predominantly by basal slip. The orientations of anthracene single crystals which have been deformed in tension are shown in Fig. 2, which contains the orientations of 15 crystals which have been tested since the original publication.[14] The stress-strain curves, which of course were dependent on orientation,[14] were determined for all crystals. The stress for the

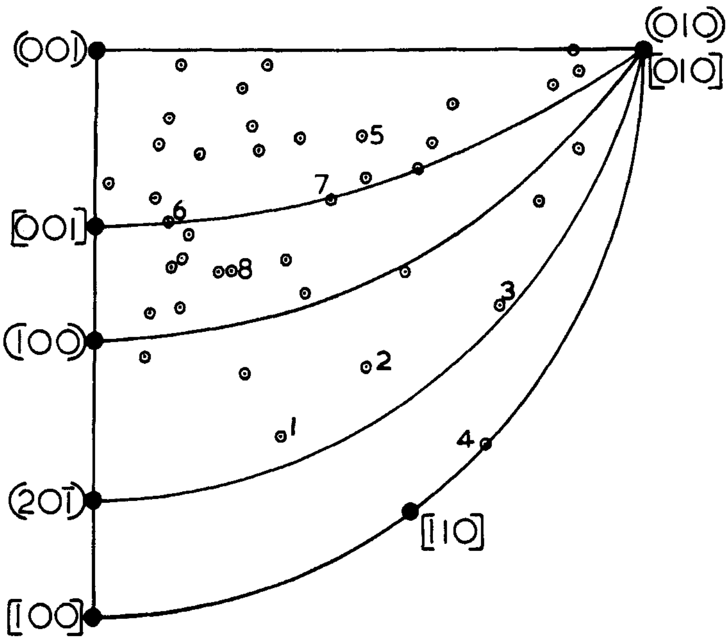


Figure 2. The orientations of single crystals used in tensile tests at 298 K.

onset of plastic deformation is plotted in Fig. 3 as a function of $\cos\phi\cos\lambda$[19] where ϕ is the angle between the normal to the basal plane and the tensile axis and λ is the angle between the slip direction and the tensile axis. The close agreement between the experimental points and the curve calculated by assuming that slip occurred on either (001) [010] or (001) [110] indicates that these are the major slip systems in unconstrained deformation in tension (Fig. 3). If slip had occurred predominantly on non-basal systems during these tensile tests the experimental points would lie not on a single curve with a minimum at 0.5 but would be scattered about some curve

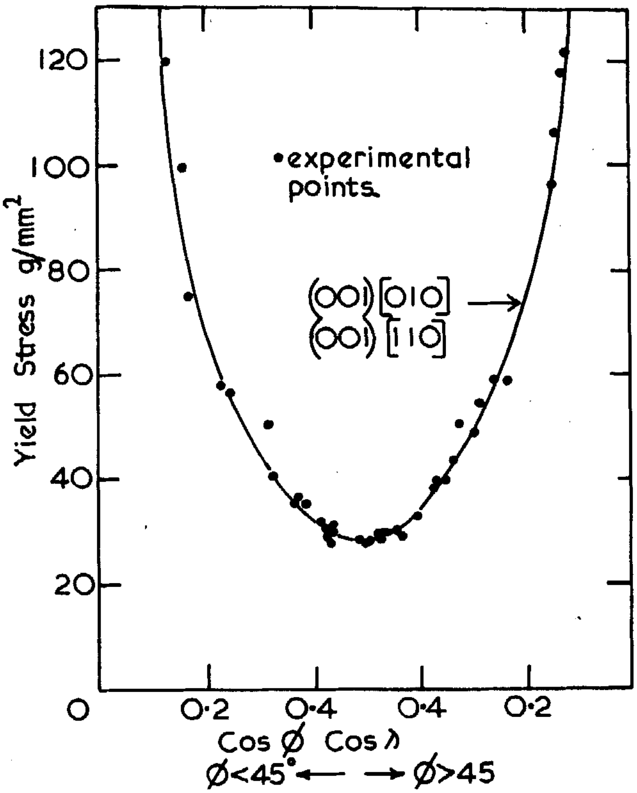


Figure 3. The yield stress for plastic deformation at 298 K as a function of orientation, together with the curves calculated assuming slip on the (001) [010] and (001) [110] systems.

with a minimum at a different value of cos ϕ cos λ depending on the operative slip system.

The yield stresses (Fig. 3) of the crystals of all orientations (Fig. 2) gave a constant value of 13–15 g/mm^2 for the critical resolved shear stress in the slip plane and in the slip direction assuming slip to be on either (001) [010] or (001) [110] whereas varying values are obtained, depending on orientation, if non-basal slip is assumed (Table 2). As described in Ref. (14), examination of slip traces on the surface of the deformed crystals confirmed that basal slip was always predominant. In addition, X-ray examination of crystals before and after deformation showed no splitting of the diffraction spots even after extensive deformation (Fig. 4), indicating that slip occurred

TABLE 2 The Yield Stress of Crystals Deformed in Tension Together with the Orientation of the Stress Axis with Respect to One of the Basal and Two of the Non-Basal Slip Systems ($\cos\phi \cos\lambda = k$) and the Critical Resolved Shear Stress on These Systems

		Slip system					
		(001) [110]		(20$\bar{1}$) [010]		(010) [001]	
Specimen	Yield stress g/mm^2	k_1	τ_R (g/mm^2)	k_2	τ_R (g/mm^2)	k_3	τ_R (g/mm^2)
1	59.0	0.246	14.5	0.383	22.6	0.315	18.6
2	56.5	0.264	14.9	0.483	27.3	0.421	23.8
3	118.0	0.127	15.0	0.418	49.3	0.346	40.9
6	30.0	0.469	14.1	0.174	5.2	0.235	7.0
7	32.0	0.436	14.0	0.392	12.6	0.500	16.0
8	29.0	0.489	14.2	0.343	9.9	0.388	11.3

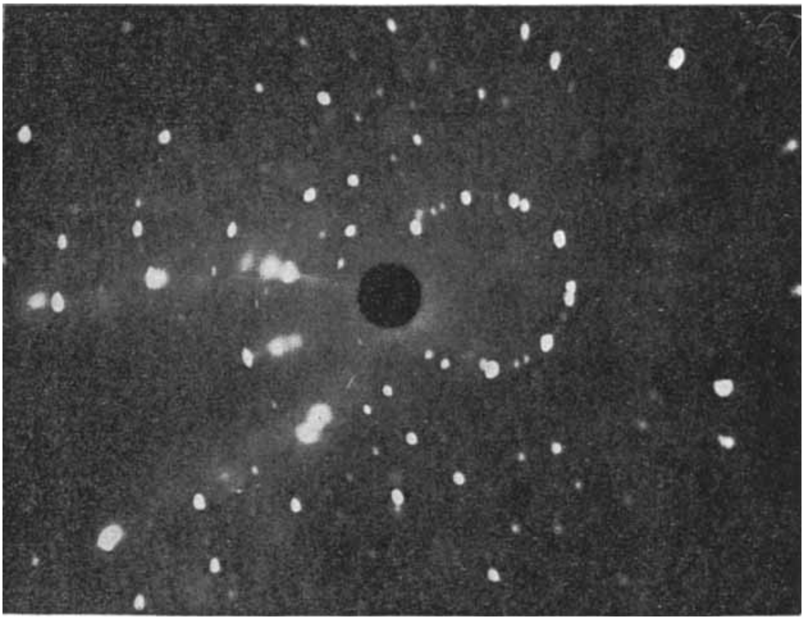


Figure 4. X-ray diffraction Laue pattern from single crystal of anthracene showing sharp diffraction spots after 30% elongation. Orientation of crystal marked 5 in Fig. 2.

predominantly on one crystallographic plane. Finally, etch-pitting on the basal plane showed no significant increase in non-basal dislocations after tensile deformation.

4. Yield Stress for Basal and Non-Basal Slip

The available evidence indicates that in unconstrained deformation in tension, slip takes place only on the basal plane, even when other possible slip systems are favourably oriented. This is presumably because the critical resolved shear stress for deformation on the basal slip systems is much lower than that for non-basal slip. The latter can only be measured directly, therefore, if the mode of deformation is such that basal slip is precluded. This is possible for some of the non-basal slip systems which have been suggested.

Stress-strain curves have been recorded for single crystals of anthracene compressed in an Instron testing machine with the basal plane perpendicular to the compression axis. It can be seen from Fig. 2 that under these conditions the (100) [001] slip system is the most favourably orientated for slip to take place. The crystals were brittle when deformed in this manner and only slight plastic deformation occurred, the maximum plastic strain recorded being 0.014 (Fig. 4). The critical resolved shear stress for slip on the (100) [001] system was 564 g/mm^2, or approximately 40 times that for slip on the basal systems (001) [010] and (001) [110] (Fig. 5).

The critical resolved shear stress for slip on the (010) [100] system can be determined by constrained deformation in shear with the plane of shear parallel to the slip plane, as described previously for shear testing on the basal plane.[15] In this mode of deformation only slight plastic deformation was observed, the maximum plastic strain being 0.005. The critical resolved shear stress for slip on the (010) [100] system was 490 g/mm^2 (Fig. 5) compared with 13–15 g/mm^2 for slip on the (001) [010] or (001) [110] systems.[14,15]

It is difficult to determine a value of the critical resolved shear stress in shear on (010) [001] because of buckling of the crystal by bending perpendicular to the basal plane, caused by slip on the basal plane, and suitable orientations with respect to the stress axis cannot be obtained to ensure that slip is confined solely to the $(20\bar{1})$ [010] or

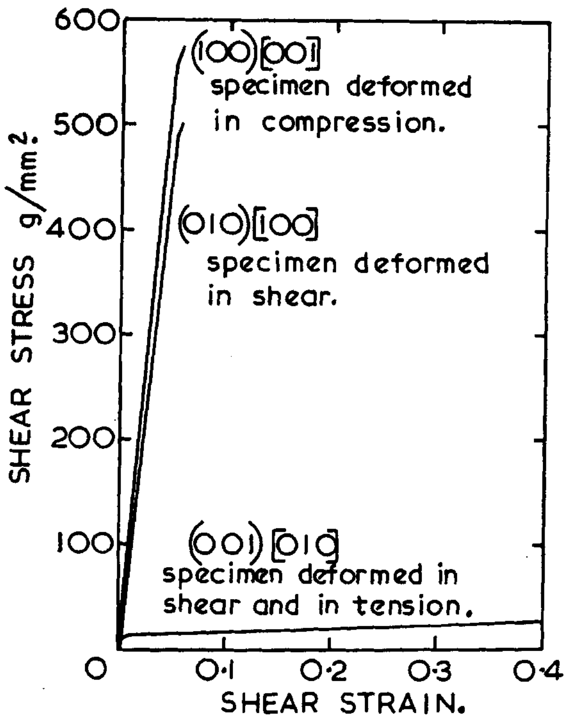


Figure 5. Shear stress–shear strain curves for anthracene single crystals deformed on the (001) [010], (010) [100] and (100) [001] slip systems.

(100) [010] systems. However, some measure of a minimum value for these three systems can be obtained indirectly.

Crystals were cut and polished so that the orientation of a compression axis across two parallel faces was that marked 4 in Fig. 2. This orientation gives the maximum shear stress on the (010) [100] system ($\cos\phi \cos\lambda = 0.5$) followed by, in order of decreasing $\cos\phi \cos\lambda$, (20$\bar{1}$) [010], (100) [010] and (010) [001] (Fig. 2, Table 3). Under these conditions slip on the basal plane is precluded as it is parallel to the stress axis ($\cos\phi \cos\lambda = 0$). The stress–strain curves in compression of crystals of this orientation gave an average yield stress of 637 g/mm^2, which gives a resolved shear stress on the four non-basal slip systems ranging from 319 g/mm^2 for (010) [100] to 184 g/mm^2 for (010) [001] (Table 3). Although the amount of plastic deformation obtained was too small to determine the active slip system, the results allow lower limits to be placed on the critical

TABLE 3 Minimum Values of Critical Resolved Shear Stress, τ_R, for Slip on Non-Basal Systems (obtained from compression tests on crystals of orientation 4 in Fig. 2)

Slip system	$\cos\phi\cos\lambda$	τ_R (minimum) g/mm²
(010) [100]	0.500	319
(20$\bar{1}$) [010]	0.483	308
(100) [010]	0.405	259
(010) [001]	0.288	184

resolved shear stress for slip on the non-basal systems (Table 3). It is unlikely that in these tests slip occurred on (010) [100] as the shear stress on this system did not reach the critical resolved shear stress of 490 g/mm² determined directly (Fig. 5).

Figure 5 and Table 3 show that the lowest value of the critical resolved shear stress for slip on a non-basal system is at least 10 times larger than that for basal slip. This means that unless the crystals are accurately aligned with respect to the stress axis in an orientation which specifically inhibits slip on the basal plane, basal slip will always predominate over non-basal slip. In fact, taking into consideration the low rates of work-hardening during easy glide on the basal plane,[14,15] the shear stress will rarely reach the critical value for slip on a non-basal system before extensive basal glide has taken place and the crystal fractures by cleavage on the basal plane. The ease of generation of basal as opposed to non-basal dislocations is substantiated by the observations of basal dislocations alone in X-ray topographs from crystals with a high degree of structural perfection.[16]

The discussion above refers to the deformation of high-purity single crystals at room temperature. The relative importance of the various slip systems may possibly be altered by the temperature of deformation or by the impurity content. However, our previous results[14] indicate that basal slip is the dominant mode of deformation over the temperature range 200–410 K and that although, in naphthalene at least,[13] increasing impurity content eventually blocks the (001) [110] slip system, there is no evidence that non-basal slip then takes place.

5. Conclusions

The critical resolved shear stress for slip on basal and non-basal systems in anthracene indicates that deformation will occur predominantly by slip on (001) [010] and (001) [110] for all orientations except those which specifically preclude basal slip. The non-basal slip systems suggested on the basis of etch-pitting on the basal plane can only be activated under restricted deformation conditions and are of minor importance in the deformation of anthracene, though they may be much more significant in determining other physical and chemical properties.

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