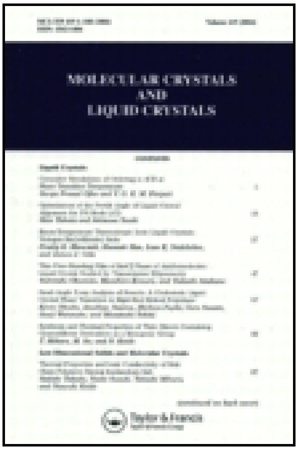

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Lattice Defects in Organic Crystals

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Lattice Defects in Organic Crystals

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Abstract—Recent studies of the physical and chemical properties of organic solids have revealed that crystalline imperfections may play a major role in determining these properties. As a result, efforts have been made to examine and characterize defects in organic crystals. The experimental techniques used for this purpose are outlined and the present state of knowledge summarized.

Introduction

The recent increasing interest in the physics and chemistry of the organic solid state has resulted in the examination of the properties of a wide variety of organic crystal types. In many cases, these properties can be ascribed to the molecules of which the crystal is comprised or to the disposition of these molecules in the crystal lattice.[1] In some cases the physical and chemical properties are found to be extremely sensitive to the methods of preparation and the subsequent physical treatment of the crystals. As for other solid systems for which similar effects have been noted, these variations have been attributed to the presence of differing concentrations of lattice imperfections in the crystals used. Thus, anomalous or variable results for dark and photo-conductance,[2] radical recombination,[3] luminescence,[4] dielectric relaxation[5] and chemical reactivity[6] have been explained in this manner. In some instances there is reliable evidence for these conclusions. In general, the lack of understanding of the nature and properties of these defects has prevented an accurate assessment of their effects.

A particular barrier to such studies has been the fact that the crystals examined have been basically imperfect. Attempts to study the effects of added defects have thus involved the measurement of a change in property superimposed upon a high background. It is essential to make initial measurements using crystals of the highest purity and perfection so that the intrinsic properties of the material can be understood; specific disorder can then be induced in the crystal and the resulting changes examined. A knowledge of the nature and properties of defects can thus help

(a) to assess the degree of imperfection of the " as grown " crystal and how it may be reduced to the intrinsic state,

(b) to determine how specific disorder can be induced in a controlled manner.

There is fundamentally no reason to assume that organic crystals should be essentially different in defect structure to other types of solid. By the time that we had commenced our studies Brandstatter,[7] Koslovskii[8] and Dawson and Vand[8] had demonstrated the presence of spiral growth patterns on organic crystal surfaces and Kochendorfer[9] had indicated that low temperature plastic deformation probably occurred by the migration of dislocations. NMR[10] and radical recombination studies[11] provided evidence for rapid translational molecular mobility in some solids. Thus it was reasonable at the outset to expect that organic crystals contained dislocations and point defects.

In order to make a reliable assessment of the properties of these defects it is essential to use a technique which involves the direct study of the defect. For most of the solid state properties[2–6] which show apparent changes with defect content this is not the case. The observed variations are either secondary effects or minor contributions to a total effect. In one case, low temperature fluorescence,[4] the defect effects have been singled out, but, as for the other techniques, the value of this for diagnosis must await more detailed studies of the effects of defects on the physical property in question.

The principal direct techniques which have been used up to the present and which provide detailed information on the properties of defects are:

Point defects: Radiotracer self-diffusion studies
High temperature creep studies
NMR line narrowing and relaxation time studies.
Dislocations: Plastic deformation studies
Etching studies.

Point Defects

The methods used for the study of the properties of point defects are, essentially, direct or indirect self-diffusion studies. Lattice self-diffusion proceeds via the point defects in the lattice and the measured self-diffusion coefficients are directly dependant on the concentration and mobility of these defects.[12] The temperature dependence of the self-diffusion coefficient reflects the energy of diffusion of the point defects in the lattice.

RADIOTRACER SELF-DIFFUSION STUDIES

Provided that crystals of good purity and perfection are available the radiotracer technique must be considered the most reliable method for studying point defect migration in organic solids. In this technique a thin layer of a radioactive form of the species to be studied is deposited on one surface of a single crystal of the material. After an annealing period at a temperature high enough to permit the radioactive species to penetrate into the bulk, the crystal is sectioned parallel to the initial face to yield a profile of diffused radioactivity. It is customary to study diffusion from an extremely thin surface layer (total activity Q) into a semi-infinite crystal. For this initial geometry, the final distribution of specific activity (A) with distance into the crystal (x) after an annealing period (t) is given by the expression[12]

$$A = Q/(\pi D_l t)^{\frac{1}{2}} \exp(-x^2/4D_l t), \qquad (1)$$

D_l is the lattice self-diffusion coefficient and varies with temperature according to the classical relationship

$$D_l = D_0 \exp(-E_d/RT) \qquad (2)$$

where E_d is the activation energy for self-diffusion. D_0 is a constant. Experimentally determined values of D_0 and E_d are given in Table 1.

together with approximate values for the self-diffusion coefficient at the melting point.

Considerable care must be taken in the selection and preparation of crystals for these studies. Self-diffusion along dislocations and sub-boundaries in the crystal proceeds more rapidly than self-diffusion through the lattice and may lead to the evaluation of enhanced diffusion coefficients.[13,14] For crystals in which the dislocation content is high this effect is obvious since curved diffusion profiles (ln A vs . x^2, Eq. (1)) are obtained. At lower concentrations the effect is less obvious since dislocation enhancement can occur without affecting the linearity of the diffusion profile.[13,14] This latter effect is particularly evident when attempts are being made to measure low diffusion coefficients ($< 10^{-11}$ cm^{2}sec^{-1}) even in good crystals.[13,14]

TABLE 1 Activation Energies and Pre-exponential Factors for Lattice Self-diffusion in Organic Solids

	D Melting point cm^2 sec^{-1}	D_0 cm^2 sec^{-1}	E_d kcal mole^{-1}	E_d/L_s	Ref.
Anthracene	10^{-11}	4×10^{14}	56.3	2.5	13
Naphthalene	10^{-11}	2×10^{15}	42.7	2.4	14
Biphenyl	10^{-11}	1×10^{14}	40.4	2.3	15
Benzene	10^{-9}	1×10^{10}	22.4	2.1	15
Cyclohexane	10^{-7}	4×10^{6}	16.3	1.9	16
Pivalic acid	10^{-8}	6×10^{6}	21.8	2.2	15
Camphene	10^{-7}	3×10^{8}	23.4	1.9	15

The degree of diffusion enhancement will depend upon two factors: the dislocation and sub-grain boundary concentration and the relative rates of diffusion in the boundary D_g and in the lattice. For the aromatic hydrocarbons $D_l < 10^{11}$ cm^2 sec^{-1} and $D_g/D_l = 10^6$ at the melting point (Table 2). Thus dislocation enhancement might be expected. We have shown however that, even under the above conditions, intrinsic self-diffusion will be observed at high temperatures ($T/T_m > 0.95$, T_m = melting temperature) in crystals containing less than 10^6 dislocations cm^{-2}.[13,14]

All the measurements on aromatic hydrocarbon crystals reported in Table 1 were made in this region using crystals of dislocation content $< 10^6\,\text{cm}^{-2}$. For the other solids in Table 1 the self-diffusion coefficients are much higher and hence, for crystals of reasonable perfection, intrinsic behaviour should be observed over a greater temperature range.

TABLE 2 Activation Energies and Pre-exponential Factor for Sub-grain Boundary Diffusion in Aromatic Solids

	D_0 $\text{cm}^2\,\text{sec}^{-1}$	E_g kcal mole^{-1}	D_g/D_l melting point	Ref.
Anthracene‡	2×10^8	31.2	10^6	13
Napththalene	9×10^7	20.8	10^6	14

‡ Data from Reucroft *et al.*[55] recalculated using self-diffusion data from reference 13.

It will be noted (Table 1) that there is a considerable variation in diffusion rates between different crystal types. Cyclohexane, pivalic acid and camphene belong to the class of materials known as plastic crystals. These crystals are the high temperature rotator phases of solids comprised of almost spherical molecules. In this form the crystals have extremely plastic properties.[17] The self-diffusion measurements on these solids were carried out on crystals in this phase. Self-diffusion rates in these plastic crystals are 10^4 times greater than in the linear aromatic hydrocarbon crystals; that for benzene, a non-linear molecule in a non-plastic phase, lies intermediate. Thus it appears that the defect mobilities are different in different crystal (or molecular) systems.

CREEP STUDIES

For other solid systems it has been shown that plastic deformation at high temperatures (creep) takes place by mechanisms which are controlled by the self-diffusion of point defects. The empirical relationship between applied stress σ, strain rate $\dot{\epsilon}$ and temperature can be written [18]

$$\dot{\epsilon} = A\sigma^n \exp(-E_c/RT)$$

A and n are constants and E_c is the activation energy for creep. At temperatures close to the melting point, in solids in which the grain size is small, creep can take place solely by the diffusion of point defects (Nabarro-Herring Creep)[19]; under these circumstances $n = 1$. At lower temperatures or in specimens of large grain size this mechanism gives way to a dislocation climb mechanism. Dislocations of a particular sign are generated at sources in the lattice and climb through the lattice until they reach a sink or alternatively they meet a dislocation of opposite sign. In the latter case the two dislocations are mutually annihilated. The dislocation can only climb via point defects in the lattice and the rate of climb and hence creep, is again controlled by the rate of diffusion of point defects to the dislocation. For this mechanism the theoretical value of $n = 4.5$.[18] For both mechanisms $E_c \simeq E_d$. If it can be shown that either of these mechanisms hold for organic crystals then creep studies could provide an unambiguous method for verifying E_d. Since $\dot{\epsilon}$ and D_l are inter-related, the self-diffusion coefficient can also be determined.[18] An examination of the spread of the experimental values for n and E_c determined for dislocation climb creep in metals shows that in fact n varies from 4 to 6 and that in general $E_c \leqslant E_d$[20]. The results of several creep studies carried out under constant stress conditions are presented in Table 3. The values of n vary from 4.4 to 6 and are well within the spread of values obtained for metals. Thus it can be concluded that creep is taking place by a dislocation climb mechanism. The equivalence between E_c and E_d for the plastic crystals confirms the validity of the radiotracer data. The values of E_c for the aromatic hydrocarbons are lower than the radiotracer values but, analogous to metals, $E_c < E_d$ can also be accepted as confirmation of E_d

TABLE 3 Creep Data for Organic Crystals[15]

	n	E_c kcal mole^{-1}	E_c/E_d
Pivalic Acid	5.3	22	1
Camphene	5.0	24	1
Adamantane	4.4	35	1
Naphthalene	6	34	0.8
Biphenyl	5	31	0.8

The stresses required to produce measurable creep rates for aromatic hydrocarbon crystals (ca. 100 g cm^{-2}) are much greater than for the plastic crystals (ca. 2 g cm^{-2}). This reflects the considerable differences in self-diffusion rates between the two crystal types.

Nuclear Magnetic Resonance Studies

Up to the present time this technique has proved to be of limited application. Diffusional motions have only been detected in plastic crystalline phases.[10] The first evidence for this type of motion was obtained using broad line techniques.[21] In normal crystals and in the low temperature non-rotator phases of most plastic solids the NMR line widths are broad and correspond to the interactions between protons in virtually stationary molecules. As the temperature is increased to the crystallographic transition point a considerable decrease in line width occurs due to the onset of molecular rotation in the crystal lattice. At still higher temperatures there is a further gradual decrease in line width to a value similar to those observed in the liquid state. Because of the similarity to well proven effects for metals[22] and ionic crystals[23] this latter decrease has been attributed to the onset of self-diffusion in the lattice. Attempts to evaluate activation energies for self-diffusion from the temperature dependance of the line width in this region have yielded values which are not in agreement with those obtained from radiotracer studies.[24] The values of E_d obtained using this technique are approximately half those obtained from radiotracer experiments (e.g. Table 4). This explanation for the cause of the line narrowing is therefore open to some doubt as far as organic solids are concerned. Several possible reasons have been proposed to account for this anomaly.[24] Experiments devised to test these have so far failed.[25]

More recently, new NMR techniques have been developed for the study of ultra slow motions in solids.[26] These involve the measurement of the spin lattice relaxation time in the local field which is very sensitive to diffusional motions. From this relaxation time the mean jump frequency and hence D_t can be evaluated.[27] Preliminary studies by Resing[28] have yielded activation energies for self-diffusion which are in good agreement with those obtained by radiotracer and creep studies (Table 4). This technique has the advantage that it is non-destructive. If it can be extended to non-plastic organic solids then it may prove to be an excellent technique for studies of point defects. Attempts to observe this effect in non-plastic crystals have so far failed, presumably because of the considerable differences in self-diffusion rates.[28]

TABLE 4 Comparison of NMR and Tracer/Creep Data[21, 28]
E kcal mole^{-1}

	NMR line narrowing	NMR relaxation time	Tracer/ Creep
Cyclohexane	8.5	—	16.3
Adamantane	—	36.3	35

NATURE OF THE POINT DEFECT

Organic molecules form close packed solids. The manner in which the molecules pack together is often the major factor in deciding the crystallographic structure of the solid.[29] In such systems interstitial molecules are unlikely and the most probable point defect is a vacant lattice site. No calculation or measurements of the energy required to form a vacancy E_f have been made for an organic solid. Jost[30] has suggested that, for molecular solids as a whole, this energy should be approximately equal to the lattice energy, W_l. Calculations and measurements of this factor for argon[31] lend some credibility to this statement. The activation energy for diffusion will be the sum of two terms, the energy for formation and the energy for migration E_m of the diffusing defect. For most solids the energy of migration of a lattice vacancy is of the same order of magnitude but less than that for formation. Thus for vacancy diffusion

$$E_d = E_f + E_m < 2W_l$$

W_l is approximately equal to the latent heat of sublimation L_s so that within the error of the analysis $E_d \simeq 2L_s$.

The values of the fraction E_d/L_s are given in Table 1. These values cover the range from 1.9 – 2.5. Thus it is not unreasonable to assume that the predominant point defect is a vacant lattice site.

For other solid systems in which vacancy self-diffusion is well established the pre-exponential factor $D_0 = 0.1 - 10\ \text{cm}^2\,\text{sec}^{-1}$,[32] which is much lower than the values obtained for organic solids. The pre-exponential factor can be expressed as

$$D_0 = \gamma a^2 \nu \exp(\Delta S_d/R)$$

where γ is a geometric factor and a and ν can be equated to the lattice spacing and the lattice vibrational frequency respectively. The product $\gamma a^2 \nu$ will not vary markedly from one solid to another and the entropy term ΔS_d will be the main factor in deciding the magnitude of D_0. ΔS_d is comprised of terms related to the formation and migration of the defect. It can only be assumed that either or both of these terms are large compared to those for other solids and that the diffusion process includes a high degree of disordering. This may reflect the state of the defect in that it may not be a discrete vacancy.[33] Alternatively it may simply be that high pre-exponential factors are characteristic of the vacancy self-diffusion of bulky polyatomic molecules in organic solids. There is certainly a marked increase of D_0 with increasing molecular complexity from argon (simple sphere)[34] $D_0 = 4\,\text{cm}^2\,\text{sec}^{-1}$ via plastic crystals (polyatomic sphere) $D_0 \simeq 10^7\,\text{cm}^2\,\text{sec}^{-1}$ and benzene (small non spherical) $D_0 \simeq 10^{10}\,\text{cm}^2\,\text{sec}^{-1}$ to the aromatic hydrocarbons (linear) $D_0 \simeq 10^{15}\,\text{cm}^2\,\text{sec}^{-1}$. Obviously further work must be carried out to decide the true nature of the point defect but in the light of present knowledge it would appear that the predominant point defect may be a lattice vacancy, the mobility of which varies considerably in different types of crystal.

Dislocations

Two of the techniques described above also yield evidence for the existence of dislocations. The creep experiments show that deformation at high temperatures proceeds by dislocation migration and the radiotracer technique indicates the presence of rapid diffusion paths in the solid which can be explained, with some confidence,[13,14] in terms of dislocations and sub-grain boundaries. In those extreme cases where measurable quantities of radioactive material diffuse down these defects this latter method can be used as a decoration technique for the determination of the relative concentrations of dislocations and sub-grain boundaries in the crystal.[35] These techniques do not however provide any detailed information on the nature, orientation and concentration of dislocations or their behaviour under normal handling conditions. More information on these points can be obtained from low temperature plastic deformation and etching studies.

LOW TEMPERATURE PLASTIC DEFORMATION

At low temperatures (*ca.* 0.5–0.8T_m depending on the rate of diffusion in the solid) the mobility of the vacancies in the lattice becomes too low to allow deformation by dislocation climb. Below these temperatures the deformation occurs predominantly by dislocation glide. This is achieved by the slipping of adjacent crystal planes neighboring a dislocation.[36] This slip will always take place in the direction of the Burgers vector of the dislocation and thus the determination of the plane and direction of slip gives the orientation of the dislocation. Studies of the stress-strain relationships for certain orientations of the crystal using tensile, compression, shear or bending tests coupled with microscopic examination of the deformed crystal surface can thus provide information on the preferred slip systems and the crystallographic distribution of dislocations in the crystal lattice.

The first application of this technique to organic crystals was by Kochendorfer[9] in 1937. As a result of his study he concluded that low temperature plastic deformation in organic crystals did occur by dislocation migration. He indicated that the principal slip system in naphthalene was (001) [010] (slip in the (001) plane in [010] direction) with the possibility of slip in the (010) plane.

Following this publication there was a lapse of interest in organic crystals until recently when papers have appeared on the plastic deformation of metaldehyde[39,37] naphthalene,[38,39] and anthracene.[40] In all cases it is confirmed that plastic deformation is dislocation controlled. Gordon[38] and Robinson and Scott[40] support the proposal that the principle slip system for naphthalene is (001) [010] but also propose other possible slip systems. In particular they note that one slip system (001) [110], which is possible in pure crystals, is inhibited in impure crystals. This suggests a relationship between impurity segregation and dislocation pinning. Anthracene is crystallographically similar to naphthalene and hence might be expected to contain similar slip systems. Robinson and Scott[40] suggest that there are differences however and that, although (001) [010] slip is possible, (001) $\frac{1}{2}\langle 110\rangle$ is favoured.

ETCHING STUDIES

The results obtained from the above technique become more substantial when taken in conjunction with one of the techniques for the direct observation of dislocations.[43] These latter techniques enable the orientations of dislocations to be determined and also show their disposition and concentration in the lattice. Of the various techniques available[41] the only one so far applied to organic solids is the etching technique.

The emergent ends of dislocations form high energy sites at the crystal surface. As such they are regions of enhanced reactivity and are available for preferential attack by solvents or chemical reagents. The overall result is to yield a pit at the head of the dislocation which can be detected by microscopic examination. The ideal etchant should contain, or produce during etching, a poison to inhibit the dissolution or reaction of the surface around the pit. When this is the case, a well defined pit is produced which is often crystallographically orientated. A list of the etchants which have been successfully used for organic crystals are presented in Table 5. This table also indicates the principal features of the etch pits produced.

The reliability of the etchant can be proved by etching two adjacent cleaved faces of a crystal and also by the continued etching of a particular face.[42] Since dislocations should surely cross the cleavage boundary a reliable etchant should yield similar patterns on each face. The continued etching proves that this process is not a surface effect. The results of such a test on a benzoic acid crystal are depicted in Fig. 1. The excellent correspondence between the two halves shows the reliability of the etchant.

Detailed studies of etch patterns on crystal surfaces have been carried out for anthracene[43] and sucrose[44]. These all show the familiar arrangements of dislocation etch pits that have been noted for other solids types i.e. single dislocations, pairs representing dislocation loops and arrays of dislocations. Examples can be detected in Figs. 2 and 3 in which the crystallographic orientation of the pits is shown. These photomicrographs represent dislocations which emerge on the (001) plane of the crystal and lie in directions at angles to this. In addition to these features (i.e. sharp pits) there are often a large number of background pits and flat bottomed pits. Examples

TABLE 5 Dislocation Etchants for Organic Crystals

Etchant	Crystal	Nature of etch pits	Ref.
Thermal			
Hot air	Naphthalene	Structureless pits on (001) faces	45
	Plastic crystals	Conical pits with varying degrees of structure	15
Solvent			
Water	Naphthalene	Conical pits, structureless on (001) faces	46
	Benzoic acid	Pyramidal pits, crystallographically aligned on (001) faces	15
Benzene	Anthracene		43
50/50 Ethanol –water	Sucrose	Structured pits on (100) faces	44
Chemical			
Fuming H_2SO_4 –conc. H_2SO_4	Naphthalene Anthracene Biphenyl Tetracene Pyrene	Pyramidal pits, crystallographically aligned on (001) faces	43, 46, 47
Conc. HNO_3–acetic acid–water saturated with $AgNO_3$	Anthracene	Crystallographically aligned pits on (001) faces	48
Methanol-Iodine	Anthracene	Specific for dislocations in impure crystals	48

of the former can be seen in the background to Fig. 1 and the latter in Fig. 3. When a dislocation has moved from its original position, for example by plastic flow, subsequent etching no longer continues to develope the etch pit in depth but simply etches laterally. The result is that the pit loses its sharpness and developes a flat bottom. In the particular example shown (Fig. 3) the crystal was etched, squeezed lightly with tweezers and re-etched to show this effect. The crystal depicted in Fig. 1 was unstrained and hence it is unlikely that dislocation migration has occurred. The background pits probably represent the sites of vacancy clusters. Similar pits have been noted in anthracene.[43]

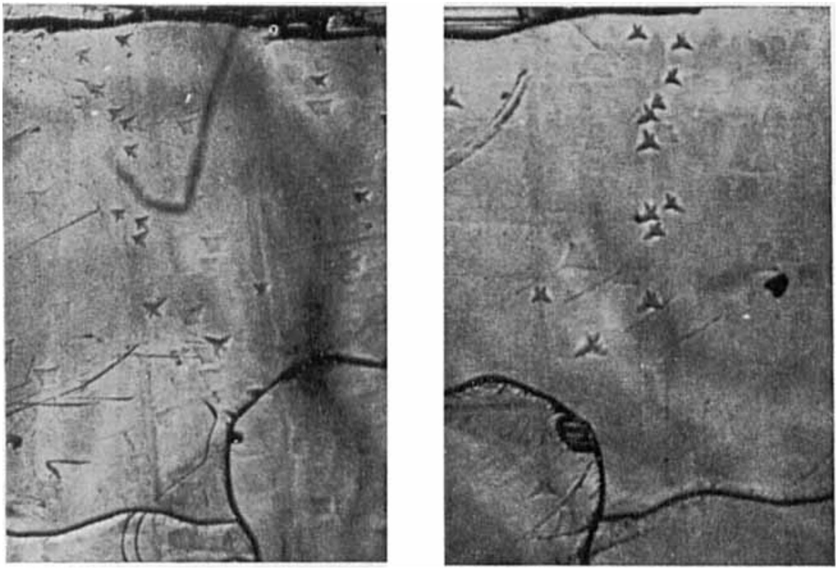

Figure (1a) Figure (1b)

Figure 1. Mirror image relationship for a cleaved crystal of benzoic acid etched for (a) 1 min. (b) 5 min. in water (200 ×).

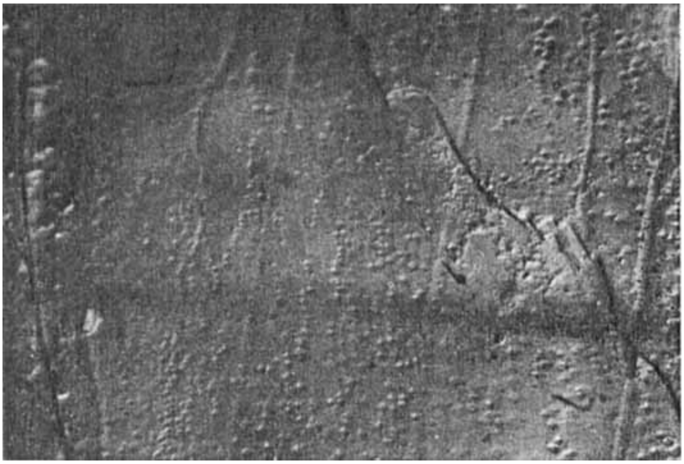

Figure 2. Arrays of dislocations in the (001) surface of an anthracene crystal-Sulphuric acid etch (50 ×). The long axis of the pits lie along the ⟨100⟩ direction.

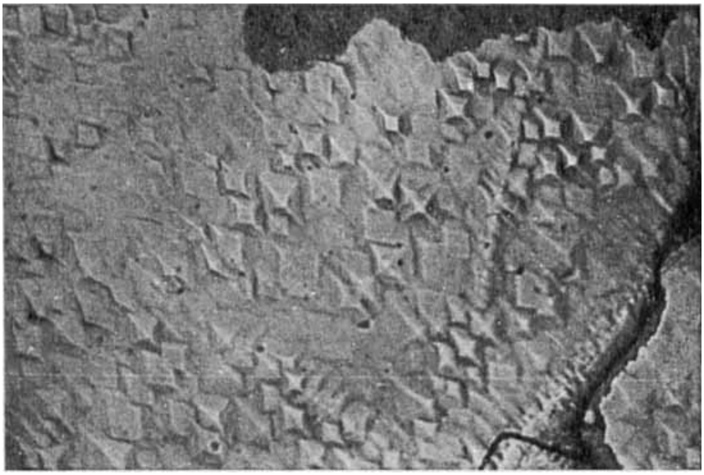

Figure 3. The effect of small stresses on dislocation patterns in Anthracene-Sulphuric acid etch (50 ×).

The effect of stress shown in Fig. 3 indicates the ready motion and, presumably, generation of dislocations by normal handling. Further evidence for this is depicted in Fig. 4. In this case a crystal was cleaved in the usual fashion using a razor blade. The cleavage usually occurs in two stages, initially the crystal cleaves slowly and then suddenly splits apart. During the first part of the cleavage considerable plastic flow occurs. This will generate a high concentration of dislocations in this region. The more rapid splitting is accomplished without much flow. The results are well shown in Fig. 4. Similar excessive dislocation contents have been found on polished crystal surfaces. Thus, although the etching method is reliable, care must be taken when evaluating dislocation contents from cleaved and polished crystals. On the other hand, when considered in conjunction with the crystallographic orientation of the molecules in the lattice, the examination of such patterns can lead to the determination of the possible slip planes and hence to the orientation of dislocations in the solid.

In two excellent papers Thomas and Williams have made a detailed analysis of the possible orientations and geometries of dislocations in anthracene[43] and sucrose.[44] For anthracene they show that the most widely occurring dislocations are those which glide in the (010) [110] directions. Less widely occuring are dislocations in

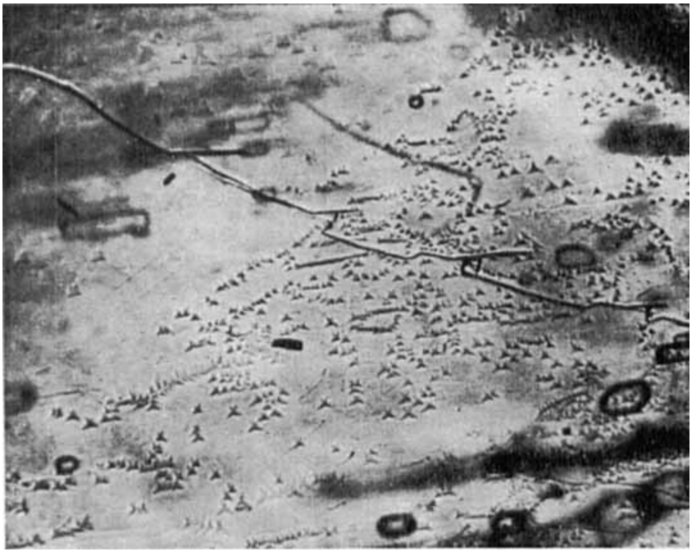

Figure 4. The effect of cleavage on the dislocation content of benzoic acid crystals-water etch (100 ×) (cf. Fig. 1).

the (100) plane which glide in [010] directions. This information complements that obtained from the deformation studies.

Up to the present time these two techniques have been applied to very few systems. It is obvious however that when used together and when applied to more diverse solids they will provide a valuable tool for the determination of the properties of dislocations in organic solids.

Other Defects

Mention has been made above of studies by Lipsett and co-workers[4] of the low temperature fluorescence of naphthalene and anthracene. In these studies it was shown that particular emission bands could be assigned to defect fluoroscence. A point defect fluorescence was identified and also a fluorescence which was said to be associated with disordered regions in the solid. This latter defect may arise from the trapping of misoriented molecules in the lattice during growth and could well be a feature of organic crystal lattices.

The Defect Content of 'As Grown' Crystals

From the above data we can safely say that the organic crystals contain point defects and dislocations. Our knowledge of their nature and their properties is limited to a few particular examples. At least something is known of their mobilities and concentrations. We can therefore speculate on the nature of the inherent defect structure of an " as grown " crystal and how it might be reduced to an intrinsic state.

The most generally used method for the preparation of organic crystals is from the melt by the Bridgman technique.[49] This involves the growth of the crystal by lowering the melt, enclosed in a sealed tube, through a temperature gradient. As the melt crystallizes, it forms a solid containing the equilibrium number of point defects corresponding to the melting temperature. On cooling, the equilibrium will be maintained by the diffusion of excess defects to sinks in the lattice. How efficiently this will occur will depend upon the rates of self-diffusion and the rate of crystal growth. In general, all " as grown " crystals contain some excess point defects. In addition to the presence of excess point defects the crystal may contain excessive numbers of dislocations. Organic crystals have high expansivities and thus considerable strain will be developed in the crystal during growth in a steep temperature gradient. This will result in plastic flow and hence in the introduction of dislocations. These factors which produce excess defects should be considerably reduced by growing crystals in strain free conditions at low temperatures viz. from solution or the vapour phase. In this way a lower concentration of point defects and dislocations will be induced during growth. Table 6 shows the measured dislocation contents of several types of crystals grown by different methods. As suggested, the concentration of these defects is greatest in the melt grown crystals and is much lower in the small vapour and solution grown crystals. The large vapour grown crystals grown by the Sloan technique[51] contain more dislocations than the smaller crystals. This is presumably the result of the thermal stresses set up in the bulk during growth on a glass substrate.

There are similar variations in point defect content. For the plastic crystals the self diffusion coefficients are relatively high and the " as grown " crystals are virtually intrinsic. This ease of equilibration

TABLE 6 Dislocation Content of Organic Crystals Grown by Various Methods[15,43]

Nature of crystal	Approximate number of dislocation etch pits (cm^{-2})
Melt grown	
aromatic	10^5–10^7
plastic	10^3–10^4
Solution grown	
aromatic	10^3
Vapour grown	
aromatic (flake)	10^2
aromatic (large crystal)	10^4–10^5
plastic (large crystal)	10^2–10^3

is paralleled by the fact that these crystals can be grown at much higher rates than other organic crystals.[50] This rapid self-diffusion probably also accounts for the lower dislocation contents that are found in melt grown plastic crystals. On the other hand, the mobility of point defects in aromatic crystals is extremely low and hence the possibility of point defects being trapped in the lattice is high. These may be trapped as single defects or, where excessive numbers are trapped, they may cluster together during cooling. This clustering could account for the background etch pits depicted in Fig. 1. The total degree of disorder is well shown by the data in Table 7 which shows the variation of diffusion coefficient (and hence point defect content) with annealing for naphthalene crystals. The value obtained for the as grown crystal is several times higher than for the well annealed crystal. If the speculation that this is due to the quenching in of defects is correct then more rapid growth rates should produce an even more marked difference. This is found to be the case (Table 7).

The vapour and solution grown crystals are usually too small for self-diffusion studies and hence it is difficult to assess their non-equilibrium point defect content. The crystals grown from the vapour phase by the Sloan method can be used for this purpose. These prove to be more perfect than the melt grown crystals.

Where there are excessive concentrations of defects resulting from growth or from subsequent handling these can be removed by

TABLE 7 Effect of Growth Rate and Annealing on Imperfections in Naphthalene Crystals[50]

Growth Rate mm hr^{-1}	Annealing period at 79°C (hr)	D(65°C)‡ cm^{2}sec^{-1} × 10^{13}
2	0	27.4
	72	19.1
	100	8.1
	250	8.1
4	0	950
	250	450

‡ Diffusion Period 400 hr.

annealing at high temperatures. The annealing characteristics of dislocations and point defects have been studied for melt and vapour grown crystals of aromatic hydrocarbons.[15,50] As might be expected, long annealing periods are required but these do result in a significant reduction in defect content (Tables 7 and 8).

TABLE 8 Effect of Annealing on Dislocation Content[35]

	Annealing period hrs	Approx. no. dislocation etch pits cm^{-2}
Biphenyl	0	10^6–10^7
	240	10^5–10^6
	480	10^4–10^5
Naphthalene	0	10^5–10^6
	280	10^3–10^4
Anthracene	0	10^6–10^7
	100	10^5–10^6

One other source of possible imperfections is the inclusion of impurities; either residual impurities or those generated during growth. In recent years a considerable amount of effort has been expended in the development of techniques for the purification and analysis of organic crystals.[52] The limit of detectability for most impurities is *ca.* 1 ppm. The question therefore arises as to how these residual impurities may affect the defect structure. We have examined this problem for several systems and conclude that when impurity molecules of different size to the host are trapped in the lattice they tend to generate dislocations.[14,35,46]

Conclusions

From the results of the experimental studies that have been carried out it can be concluded that organic solids contain dislocations and vacancies. The orientation and glide planes of the dislocations depend on the crystallography of the solid and the shape of the molecule. The mobility of the vacancy is similarly dependant.

The techniques used permit the characterization of the defect structure of "as grown" crystals and indicate how these may be reduced to a more perfect state. This opens the way for studies of the introduction of defects into the solid and the definitive examination of the effects of particular defects on the physical and chemical properties of the solid.

Preliminary studies of the effects of defects have commenced. Thomas and Williams have examined the chemical effects of defects in their studies of the role played by dislocations in photochemical transformations in anthracene[43,53] and in the carbonization of sucrose. Sherwood and Jarnigan[54] have studied the effects of impurity induced defects on space charge limited photocurrents in anthracene and Kawada and Sherwood[13] the influence of dislocations on self-diffusion in anthracene. The extension of these investigations may lead to the development of more accurate diagnostic techniques for the evaluation of the defect structure of organic crystals.

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