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Interferometric Studies of the Slip Phenomena in the Growth of Palmitic Acid Crystals

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Palmitic acid crystals grown from solution have been studied by the application of multiple-beam interferometry and phase-contrast microscopy. Joining with one another of crystal monolayers and other crystal plates having a series of growth steps have been illustrated. Of special interest are the patterns which show that the internal slip of molecular layers which has been reported by Anderson & Dawson for only monomolecular layers can take place over distances ~ 1000 Å. The dislocations taking part in this slip would be those with multiple Burgers vector and thus these observations are evidence of the movement of large dislocation groups.

Introduction

In a series of papers Dawson & Vand (1951), Dawson (1952) and Anderson & Dawson (1953) have studied, by the electron-microscopic techniques, the spiral growth of long-chain organic molecules, in accordance with the dislocation theory (Burton, Cabrera & Frank, 1951). Some micrographs of *n*-nonatriacontane, $C_{39}H_{80}$, showed a striking feature that an internal slip of paraffin layers had taken place when the crystal settled on the surface of the microscope specimen mount. As a result, when a thin crystal monolayer settled on another crystal plate having a series of growth steps the underlying growth steps were found to be imprinted on the monolayer. However, this transmission of the lower growth pattern through the crystal was observed to occur only for unimolecular layers and not for any thick layers. The spiral growth steps were also found to be equal to the molecular units of the substance in solution, and no multimolecular growth steps were encountered. Using interferometric techniques Verma & Reynolds (1953) reported the existence of spiral growth steps which are integral multiple (including unity) of the X-ray unit cell. This therefore suggested that by using optical techniques the multimolecular internal slip of layers could possibly be observed for substances exhibiting multimolecular growth steps. For this purpose palmitic acid, $CH_3(CH_2)_{14}COOH$, was chosen. This optical study of the growth of palmitic acid, with evidence of the slip over large distances, is reported here.

Experimental

The interferometric methods formerly employed for the study of stearic acid (Verma & Reynolds, 1953) have been used identically in the present study. Crystals of pure palmitic acid were grown from benzene, ethyl alcohol and carbon disulphide solutions on glass substrates.

Observations and discussion of results

On the basal planes (*a b* face), which develop predominantly, growth spirals could be observed. Of particular interest were the patterns which arise when two crystals are in contact with one another. For these observations the crystals may be divided into two types: (1) 'crystal layers' with uniform thickness showing no visible growth structure; (2) 'crystal plates' with a series of growth steps. The different possibilities for the joining of the crystals are (*a*) a crystal layer meeting or touching another layer, (*b*) a crystal layer settling on another layer, (*c*) a crystal layer settling on a crystal plate and vice versa, and finally (*d*) a thick crystal plate falling on another, a case which is trivial since one merely obstructs the view of the other. The following figures illustrate these possibilities.

The simplest case of crystal layers meeting one another is exemplified in Fig. 1. As growth edges advancing on the glass substrate touch each other, they fuse with one another, leaving an unbroken crystal level without any steps. This is possible only if all the layers are monolayers. Hence it may be concluded that nucleation of palmitic acid crystals takes place as monolayers which take up crystallographic shapes. At the time when growth ceased, advancing growth fronts enclose figures, e.g. a triangle. Observations of 'growth trigons' on octahedral diamond faces have been explained similarly by Tolansky & Wilcock (1946).

The next case (*b*) is illustrated in Fig. 2, which shows a phase-contrast micrograph of two partly superimposed crystal layers (doubly silvered). The crystal layers coincide exactly in orientation when settling on one another; such parallel orientations should be favoured on energy considerations.

The cases of a crystal layer falling on a crystal plate and vice versa are to a very large extent equivalent, and are shown in Figs. 3 and 4. Fig. 3 shows the

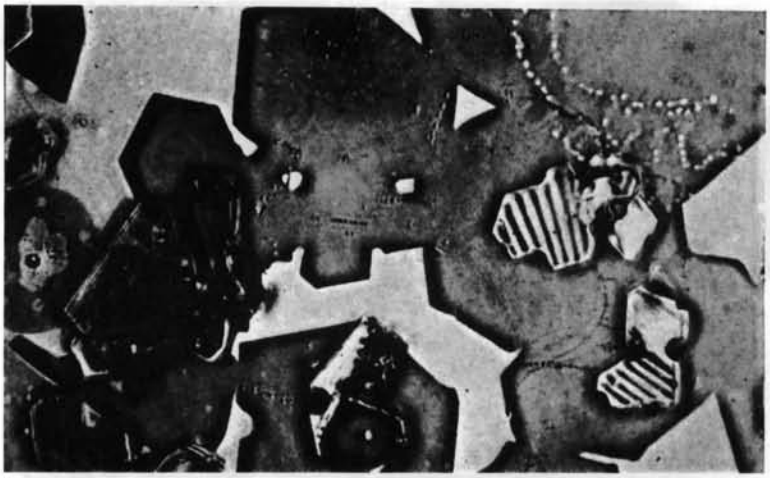

Fig. 1. Phase-contrast micrograph of doubly silvered crystals showing the fusing of the advancing monolayers. ×340.

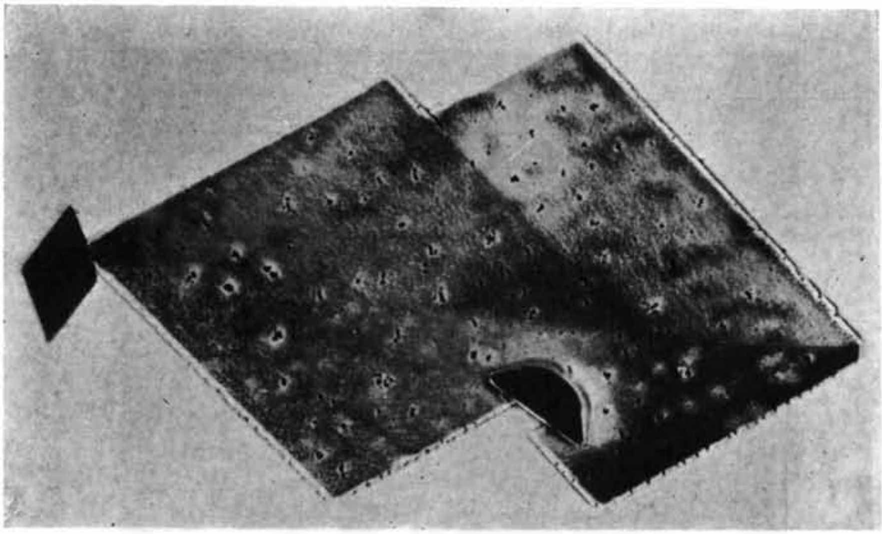

Fig. 2. Phase-contrast micrograph of doubly silvered crystals in which one crystal layer has settled on another. ×230.

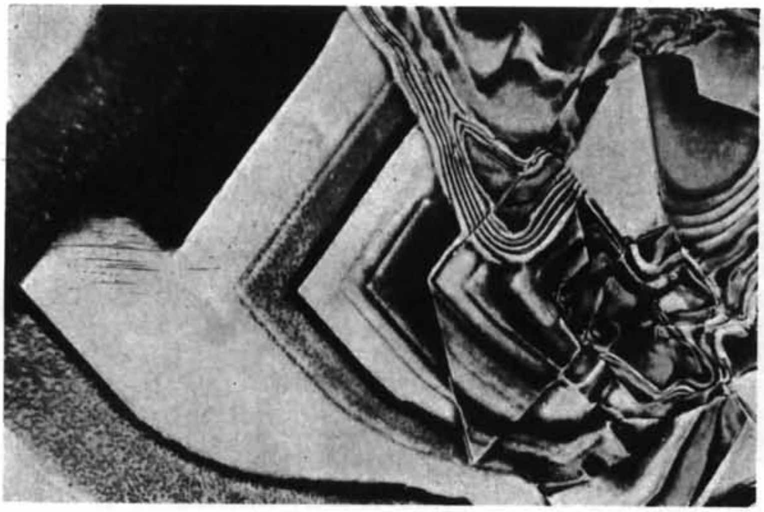

Fig. 3. Multiple-beam Fizeau fringes for $\lambda = 5461$ Å, where a crystal layer ~ 1000 Å thick, after settling on a crystal plate, has taken the contours of the underlying growth steps. ×150.

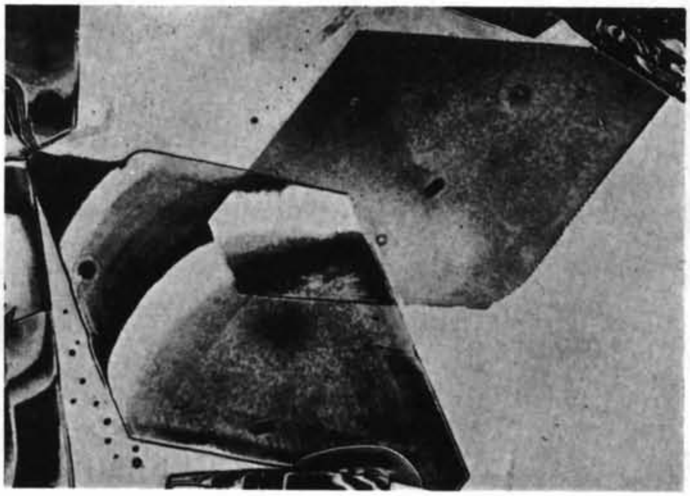

Fig. 4. Fizeau fringes for $\lambda = 5461$ Å, illustrating the joining of a crystal layer showing uniform tint and a crystal plate with a series of growth edges each 250 Å high. ×180.

multiple-beam Fizeau fringes formed by internal interference for the crystal which has been silvered on both sides. Here a small crystal layer has settled down on a crystal plate having a series of growth steps several hundred Ångström units high. The fringes are contouring the growth steps which shows that the crystal plate is sitting flat on the glass substrate. The step structure of the underlying crystal plate has been imprinted on to the layer, showing that it has taken the contours of the growth steps. From the shift of the series of fine Fizeau fringes running across the boundary of the crystal layer, it is seen that its thickness is about 1000 Å. Another very clear example of this is shown in Fig. 4. Here one crystal has fallen partly covering another. The crystal in the right half of the figure is a crystal layer of uniform thickness, since it shows uniform tint, and its thickness is about 800 Å, as deduced from the shift of the fringes across the boundary of the crystal layer. The growth steps on the crystal plate are about 250 Å high, as shown by the fringes for $\lambda = 5461$ Å. Assuming that the crystal layer has fallen on the crystal plate, then it has acquired the step structure of the underlying crystal surface.

Consider now the alternative that in Fig. 4 the crystal plate with the step structure has fallen on the crystal layer. Since the interference fringes are contouring the growth edges, that part of the crystal plate not superimposed on the crystal layer is lying flat on the glass substrate. This could have happened only if the crystal plate has slipped down the thickness of the crystal layer (~ 800 Å) over the superimposed part along the three edges of the underlying crystal layer. Thus in both the cases, whether the crystal layer is on top of the crystal plate or vice versa, owing to the internal slip of the molecular layers, the same configuration of the compound crystal is left behind. Since the density of the crystal is less than that of the solution, either alternative is permissible, since the crystal monolayer will not sink down as soon as it is formed.

A similar transmission of growth layers through a monomolecular layer of *n*-nonatriacontane was reported by Anderson & Dawson (1953). This transmission of growth layers arises owing to the internal slip of the molecular layers. These authors, however, found that the process of slipping was confined only to monomolecular layers, but the above interferometric observations show that slip of molecular layers can be transmitted through fairly thick (~ 1000 Å) crystal layers.

The model used to explain the slip in real crystals is the movement of dislocations. The dislocations that take part in the unit slip are those with the unit Burgers vector, and only unit dislocations were observed in the electron-microscopic studies. Examples of unit slip on silver crystals have been explained similarly (Forty & Frank, 1953). Obviously the slip through these comparatively large distances observed on palmitic acid crystals is due to the dislocations with multiple Burgers vector. A study of the spiral growth pattern and the measurement of step heights by the multiple-beam interference fringes has shown the step heights to be integral multiple of the X-ray unit cell, so that the dislocations of multiple Burgers vector are actually formed on palmitic acid crystals. Thus these observations afford the evidence of the movement of large dislocation groups. The stresses under which this movement occurs are not well understood but it appears that the movement of even large dislocation groups can take place comparatively easily for long chain organic molecules.

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