

The structure and growth of C₆₀ platelets

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Crystals of C₆₀ grown from solution or by vapour deposition often exhibit platelike morphologies, and electron diffraction patterns of these crystals show forbidden reflections whose origin has not been fully explained. We suggest that the anomalous reflections arise from the presence of twins in the crystallites, and that this provides an explanation for their rapid platelike growth.

1. Introduction

The structure of crystalline C₆₀ has been the focus of intense interest since the discovery by Krätschmer et al. of a technique for preparing bulk quantities of this new allotrope of carbon [1]. Some studies have suggested that the structure can be described as hexagonal close-packed (hcp) with stacking disorders [1,2], while others have indicated that there is a mixture of hexagonal and face-centred cubic (fcc) crystals [3,4]. The consensus now appears to be that the room temperature form of C₆₀ can be satisfactorily described as fcc [5], but uncertainties remain concerning certain aspects of the X-ray and electron diffraction patterns. In particular, [111] electron diffraction patterns from platelike crystals often show reflections in positions which would be forbidden in a perfect fcc structure. Here, we describe the nature of these anomalous diffraction patterns and put forward a suggestion for their origin which, if correct, would also explain the growth mechanism which leads to the platelike morphology.

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2. Experiment

Solid C₆₀ was prepared in the following way. Electrolytic grade graphite rods were arc evaporated in ≈ 150 Torr helium using a dc voltage of 32 V and a current of 180–200 Å. The resulting soot was collected and extracted with toluene for three days in a Soxhlet apparatus, after which the solvent was removed under reduced pressure. The dark solid isolated was dissolved in carbon disulphide and activated neutral alumina was added until the mixture had the consistency of damp sand. The solvent was then removed under reduced pressure in order to mount the fullerenes on the alumina without crystallisation [6], and the mounted fullerenes were transferred to a column of alumina packed in hexane. Elution was started with a mixture of 10% toluene in hexane to wash the fullerenes onto the column and then continued with 5% toluene in hexane. The purple C₆₀ band was collected until almost all of it had been removed; collection was discontinued with a small amount of C₆₀ still on the column to avoid contamination with C₇₀. The solvent was removed from the C₆₀ under reduced pressure and the solid was dissolved in a minimum of carbon disulphide and filtered. After removing the carbon disulphide under reduced pressure, the residue was washed with diethyl ether to remove any hydrocarbon impurities. The brown-black product was then

heated under a dynamic vacuum ($\approx 6 \times 10^{-2}$ Torr) at 150°C for 5 h to yield pure C_{60} as a light tan brown solid.

Specimens for electron microscopy were prepared by lightly grinding the solid and depositing it directly onto carbon film support grids. The specimens were examined in a JEOL 2000FX transmission electron microscope operated at 200 kV. Care was taken to minimise exposure of the crystals to the electron beam in order to avoid beam damage.

3. Results and discussion

The general appearance of the crystalline C_{60} is shown in fig. 1. Many of the particles were irregular in shape, but a high proportion could be classified as either rods or plates. In the present study we were interested only in the platelike crystals, an example of which is arrowed in fig. 1. These crystals invariably produced hexagonal diffraction patterns, suggestive of the fcc $[111]$ zone axis, but with spacings and intensities which could not be explained by

a simple fcc structure. A typical example is shown in fig. 2a. Here there is an inner ring of relatively weak reflections in positions which would be forbidden in a perfect fcc crystal, surrounded by a brighter ring whose positions correspond to the fcc $\{220\}$ spacings. The forbidden reflections can be indexed as $1/3\{422\}$ in the fcc notation, and further forbidden spots occur at $2/3\{422\}$, $4/3\{422\}$ and so on, as shown in fig. 2b. Previous authors have observed similar diffraction patterns [1,2,3,7,8], although some of these have indexed the patterns in the hexagonal notation. The most detailed study published to date was carried out by Luzzi and co-workers [7] who have used specimen tilting to investigate the nature of the forbidden reflections. They report two important observations. Firstly, the $1/3\{422\}$ spots do not appear to be discrete reflections, but rather represent rods of intensity in reciprocal space. Secondly, the anomalous reflections are not observed in all four $\{111\}$ directions, but only occur in patterns recorded with the beam perpendicular to the plates' large faces. These observations lead them to conclude that the forbidden reflections are due to planar

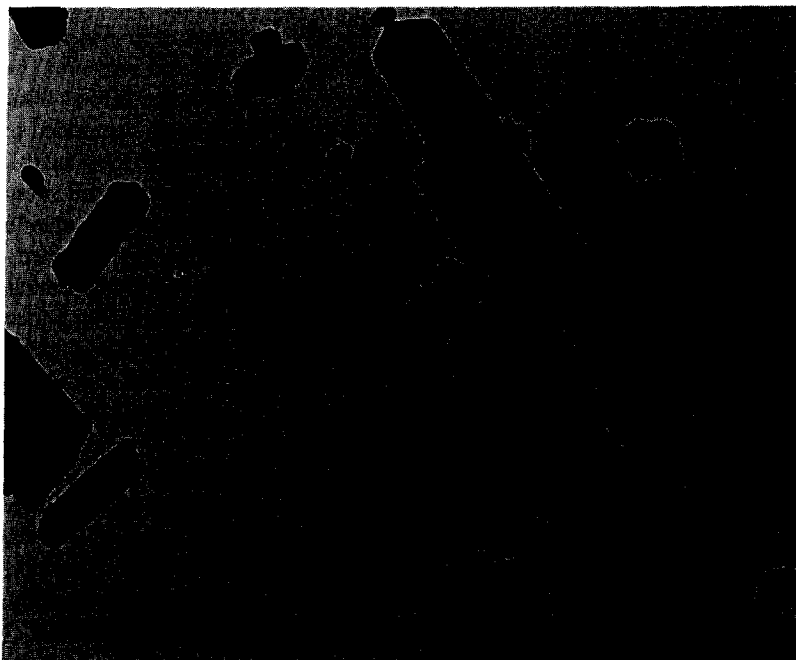


Fig. 1. Low magnification bright field micrograph showing morphology of C_{60} particles. Typical platelike crystallite arrowed.

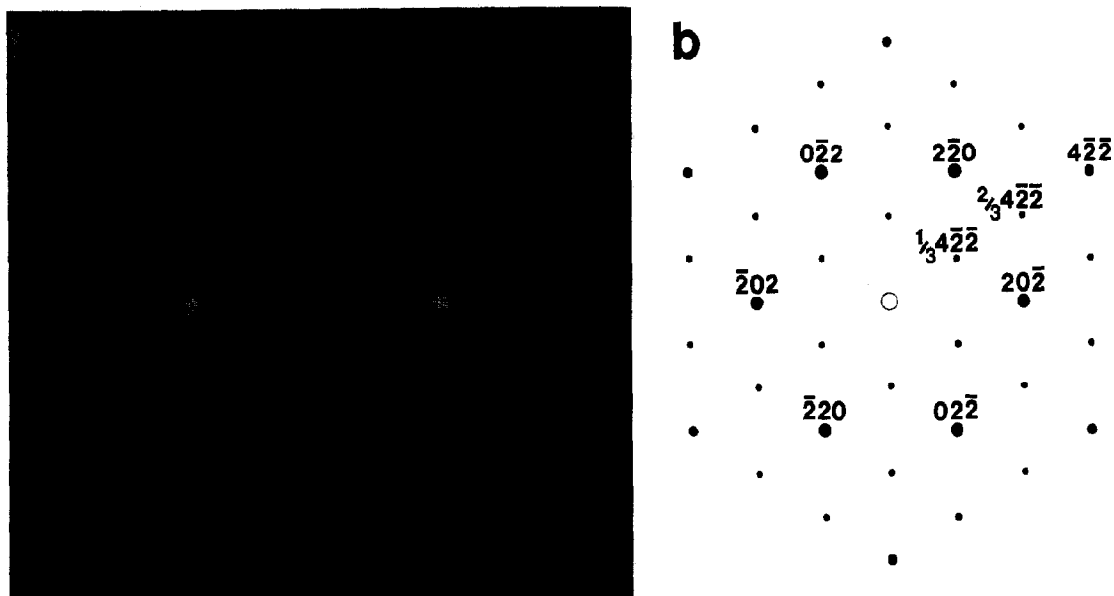


Fig. 2. (a) Selected-area diffraction pattern from platelike C₆₀ crystal. (b) Indexing of pattern in the fcc notation, with extra spots of the type 1/3{422}.

faulting on a single set of (111) close-packed planes which occurs during the growth by sublimation. However, they do not specify the precise nature of the faulting, neither do they propose a detailed mechanism for the rapid platelike growth.

In attempting to understand the growth and structure of the platelike C₆₀ crystallites, it is helpful to refer to earlier work on fcc metals. Extra 1/3{422}-type reflections are in fact quite commonly observed in diffraction patterns from thin films or small particles of fcc materials. These can arise in two different ways, namely surface effects and twinning. The surface effects arise as follows. An fcc crystal in the [111] direction can be thought of as a stack of close-packed planes with layering of the type ABCABC so that the fourth layer lies directly under the first and so on. If the crystal has an incomplete number of layers in this direction, say an extra A plane, this has the effect of introducing new periodicities with the spacing 1/3{422}, which would not be present in a perfect structure. This phenomenon was first demonstrated by Cherns using evaporated (111) gold films [9]. It is possible that the extra reflections observed in C₆₀ arise in this way, but this would not explain why the platelike morphology occurs in the

first place. Neither would it explain why extra reflections appear to be always observed in [111] patterns from platelike C₆₀ crystals. A more probable explanation is that the particles contain two or more twins parallel to the large faces, since in this case the systematic absences are always broken, irrespective of the number of layers in the crystal [10,11]. Moreover, parallel twinning would account for the rapid platelike growth, since the "twin plane re-entrant edge" mechanism could operate. This growth mechanism has been observed in a wide variety of fcc metals, including gold particles grown from solution [10,12], silver particles grown by evaporation [13] and supported platinum particles in heat-treated catalysts [14]. The mechanism was first described by Wagner [15], who showed that the presence of two parallel twins in a cubic crystal produces a system of surface grooves which provide preferential nucleation sites for incoming atoms. Thus accelerated growth occurs in directions parallel to the twins, while the large (111) faces grow relatively slowly. The grooves form as a result of {111} faceting at the crystal's edge, driven by the reduction of surface energy. Fig. 3 shows a schematic cross section of a platelet according to Wagner's model.

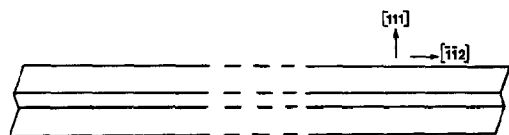


Fig. 3. Cross section through platelike particle containing two parallel twin boundaries, showing re-entrant edge structure.

It is possible that a similar growth mechanism may operate for the rod-shaped particles, since these were often observed to be notched at one end, but the structure of these crystallites has not yet been examined in detail.

4. Conclusions

Numerous studies of crystalline C_{60} , including the original paper of Krätschmer et al. [1], have reported electron diffraction patterns from platelike crystals which cannot be explained in terms of the simple fcc structure. This has led to a certain amount of confusion in the literature, with some authors suggesting that there may be two forms of solid C_{60} , one with the fcc structure and one with the hcp structure. However, as we have explained in this Letter, it is quite possible that the anomalous diffraction patterns are due to twinning and there may therefore be no need to invoke a hexagonal phase. The presence of lamellar twins in the thin platelets would explain not only the form of their electron diffraction patterns, but also the rapid anisotropic growth of these crystallites, which would occur by Wagner's twin-plane re-entrant edge mechanism. The question arises as to the origin of the twin boundaries themselves. One possibility is that they occur in the early stages of growth as the result of coalescence between very small single crystal particles, a process which is known to occur in fcc metals.

Finally, it is worth pointing out that twin-accelerated growth may also occur in other fullerene or fulleride crystals which crystallise with the fcc structure. Indeed, platelike crystals of C_{70} exhibiting diffraction patterns similar to the one shown in fig. 2a have already been reported [16]. In the case of the superconducting alkali-metal doped C_{60} fullerides, some of which are known to be fcc [17], twin-ac-

celerated growth may facilitate the preparation of superconducting thin films.

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