Comment

Comment on “Atomic force microscopy characterization of stable faces in cubic C_{60} single crystals”: Possible evidence for growth-promoting cross-twinning

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Abstract

An explanation is given for a molecular arrangement on a face of a C_{60} fcc single crystal as observed recently with atomic force microscopy (B. Keita et al., Chem. Phys. 179 (1994) 595). The explanation relies on a cross-twinning model of fcc crystal growth, and involves local fivefold symmetry.

In a recent paper [1] Keita et al. report on the first observation of resolved molecular positions on all stable faces of fcc C_{60} single crystals with atomic force microscopy. Although most patterns of molecular arrangements are consistent with expected patterns on (111) and (100) faces, a single pattern (Fig. 7 of Ref. [1]), consisting of an array of rhombs, could not be explained satisfactorily. The rhomb-diagonals are reported to have lengths $BD = 11.3 \text{ \AA}$ and $AC = 14.0 \text{ \AA}$, respectively (implying $AD = 9.0 \text{ \AA}$, and $\angle DAB = 77.8^\circ$ for an ideal rhomb), whereas $AD = 8.0 \text{ \AA}$ and $\angle DAB = 72^\circ$. Since the shortest intermolecular distance in fcc C_{60} is $10.04 \text{ \AA}$, the four molecules A, B, C and D cannot be in the same plane. Indeed, the authors state, that the molecules are not always at the same level, and may overlap. A tentative explanation is given by observing that the diagonals in the rhomboidal unit cell of the (311) plane are in the ratio $\sqrt{5/3} = 1.29$, close to the observed ratio 1.24, albeit that the diagonals themselves are some 60% too long. The planar arrangement in the (311) plane excludes an explanation of the short distance $8.0 \text{ \AA}$.

It is the purpose of this Comment to propose an alternative explanation, and at the same time to demonstrate that this explanation emerges in a natural way from an assumed model of fcc crystal growth.

A number of fcc materials have been observed to crystallize frequently in the shape of thin hexagonal or equilateral triangular platelets, with slow-growing (and, consequently, large) (111) faces [2–5]. The triangular platelets are single reflection twins, with a single twinning plane parallel to the (111) faces. They have grown from similarly singly twinned hexagonal platelets by accretion of atoms to only three of the six sides of the hexagons, these being the sides where the twinning produces reentrant angles between $(\bar{1}11)$, $(1\bar{1}1)$, and $(11\bar{1})$ faces of one twin individual with their mirror images on the other twin individual. Thus, the triangular platelets are evidence for the essential role of reentrant angles for growth in lateral directions. A doubly twinned hexagonal platelet (i.e. with *two* twinning planes parallel to (111)) exhibits reentrant angles on all six sides, and will grow in all lateral directions into a larger (but equally thin) hexagon. The

growth promoting effect of the reentrant angles is not affected by the distance between the two twinning planes; reducing this distance to the smallest possible value, i.e. with the twin planes in adjacent layers, is equivalent to a stacking fault, ABCBCA. Detailed quantitative analyses of the growth promoting properties of reentrant angles connected with stacking faults can be found in a series of papers by Ming [6].

As explained, parallel stacking faults will stimulate growth in only two dimensions, producing only thin crystals. Anisotropic growth of C_{60} crystals has already been explained in this way [7,8]. Isotropic growth requires reentrant angles on *all* close-packed faces, which can be accomplished by introducing stacking faults in other directions as well, as has been proposed previously [9].

In order to explain the observations of Keita et al. a crossing of single stacking faults seems inappropriate, since no extended area with a deviating pattern is produced. Rather the crossing of two twin-bands has to be considered, cf. Fig. 1 (a twin-band is the region between two closely spaced – six layers apart in the drawing – parallel twin planes). In this model five domains share a $[110]$ edge (perpendicular to the plane of the drawing), resulting in an axis of approximate (local) fivefold symmetry; two such axes are visible in the drawing, piercing the page in the centres of the highlighted pentagons. Since four of these five domains have an undistorted fcc structure (at least in the drawing), the fifth domain must be distorted, to make the angular spacings of the five domain walls, that meet at the axis, add up to 360° . Two such domains, each being connected with one or the other axis, are easily recognized by the two rhombs that have been outlined, one in the interior of its domain, the other at a grain-boundary. The distortion causes these rhombs to be different from comparable rhombs in the undistorted domains, but quite similar to the rhombs that have been observed. The dimensions are: $BD = 10.9 \text{ \AA}$, $AC = 13.5 \text{ \AA}$ (both 4% below the observed values, i.e. faithfully reproducing the observed ratio 1.24, which is significantly below the value that would be expected from an undistorted (110) face, $\sqrt{2} = 1.41$), $AD = 8.7 \text{ \AA}$, $\angle DAB = 77.9^\circ$ ($360^\circ/4 \times 70.53^\circ$). However, it is likely that the strain will be evenly distributed over all five domains surrounding the common edge, especially when they are of comparable size, resulting in a more or less extended region with exact (local) fivefold rota-

Fig. 1. Schematic representation of molecular centers of C_{60} molecules in the crossing region. The view is down the $[110]$ direction of the macroscopic single crystal (to which the domains marked "C" belong). Bold arrows mark two crossing slabs of material, that run throughout the crystal, and that are mirror twins of the C matrix, either on $(\bar{1}11)$ or $(1\bar{1}1)$. Open circles are in the plane of the drawing ($z=0$), and at $z = \pm 1, \pm 2$, etc. (in units of $\frac{1}{2}a\sqrt{2} \approx 10 \text{ \AA}$), black dots are at $z = \pm \frac{1}{2}, \pm \frac{3}{2}$, etc.; shaded circles mark guessed positions near incoherent grain boundaries. Pentagons mark the sites where the arrangement has approximate fivefold symmetry. The two rhombs are in regions where the arrangement is slightly different from fcc. Thin arrows mark reentrant angles.

tion symmetry. Although this would make $\angle DAB = 72^\circ$, as observed, this would also affect the ratio of rhomb-diagonals, to an extent that can only be estimated after a simulation of the relaxation process. It should be understood that Fig. 1 is only a schematic representation of one of many possible arrangements. Thus, the crossing twin bands may be much broader (increasing the distance between the two fivefold axes, and the fcc area between the two distorted domains), or may consist of widely different numbers of close-packed layers. However, in all cases, the fivefold axes should exist in *pairs*, for the macroscopic crystal to be qualified as a *single* crystal (a single fivefold axis would result in a macroscopic twin).

As is well known, fivefold symmetry is a common feature in *small* particles (multiply twinned particles, MTPs) and clusters, but cannot be incorporated in three-dimensional crystals, as it is incompatible with

three-dimensional lattice translations. However, if twinning (and especially cross-twinning) is introduced, local fivefold symmetry obviously *can* be accommodated in an otherwise perfect crystal, and may even be essential to its growth.

Reentrant angles between close-packed planes that are perpendicular to the plane of the drawing of Fig. 1, are indicated by thin arrows. The surface facing the viewer will not be flat, but will contain upward and downward folds (ridges and grooves, respectively) at the domain boundaries. Fig. 7b of Ref. [1] is suggestive of such folds, running mainly in two directions, possibly corresponding to that of the two (crossing) twin bands, e.g. $[2\bar{1}\bar{1}]$ directions; apparently there are many twin crossings. The fair agreement of the model parameters with the observed values suggest that the face of Fig. 7c is parallel to a (110) net in the macroscopic crystal, as originally also considered as a possibility by the authors, that was subsequently rejected for other reasons, however.

Finally we note that the construction of crossing stacking faults or crossing twin layers, that is thought to be essential to isotropic crystal growth [9], is only

possible in fcc crystals. Moreover, as has been shown previously [9], a new layer that has been nucleated in the reentrant angle, is always in correct fcc registry (e.g. “B”), thus explaining the fcc stacking order ABCABC. This is believed to be the reason for solid C_{60} to be fcc, rather than hcp.

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