Comment

Comment on "Coexistence of fcc and hcp phases of C_{60} "

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The unusual features observed in TEM images of solution-grown fcc C_{60} crystallites (Z.G. Li and P.J. Fagan, *Chem. Phys. Letters* 194 (1992) 461) can be explained either by assuming the presence of a bct (body centered tetragonal) phase, or by identifying the bright spots with extremes of the projected charge density, suggesting a hcp phase.

In a recent Letter [1], Li and Fagan reported the observation of an unusual defect in solid C_{60} in its room temperature fcc phase. The authors attribute the appearance of extended arrays of spots on an approximately square grid (marked "(A)" in their fig. 3 of a high-resolution TEM image in [110] projection) to BCCCBAC... stacking in the [111] direction. It is the purpose of this Letter to point out that the observed image can be explained in a different way. We will first propose an alternative stacking of close-packed layers that can allow for the observed image, assuming (following Li and Fagan in their suggested explanation of their fig. 3) that the pattern of bright dots reflects the pattern of molecular centers as seen in a [110] projection of the packing. Subsequently, we will propose a different model that allows for a more direct association of the observed bright dot pattern with the projected charge density.

In a hard-sphere model of fcc ...ABCABC... stacking the layer distance is $\sqrt{\frac{2}{3}}$ (in units of the sphere diameter); the layer distance between *identical* layers in the BCCCBAC...sequence would be 1, i.e. more than 1.2 times the regular spacing, a conspicuous modification that is not apparent in the picture, however. Since twinning is frequent in the sample (marked "(T)"), the unusual pattern could be associated with the twinning plane $\bar{T}$ in the sequence ...ABCATACBA..., where $\bar{T}$ can be either B or C. A Shockley partial, which is a common defect in close-packed lattices, has associated with it a layer, that is only *partly* B, and *partly* C, with the two regions sep-

arated by a more or less extended transition region where the atoms or molecules "hesitate" between B and C positions. This is illustrated schematically in fig. 1 where the atomic positions in an fcc twin are drawn in a [110] projection (in this projection, which is the same as that of fig. 3 in ref. [1], all *non-visible* atoms are in close-packed columns perpendicular to the plane of the drawing, behind the atoms shown). As indicated, the left-hand side of the twinning plane (marked by arrows) is in B registry, and

Fig. 1. [110] view of fcc twin of close-packed spheres. The indications of the stacking order to the left and to the right of the figure are identical, except where indicated by arrows. The central part of the picture models the feature (A) in fig. 3 of ref. [1]. The local arrangement is body centered tetragonal (bct), rather than fcc or hcp.

the right-hand side is in C registry, with atoms in tetrahedral positions over triangular trimers in the supporting A layer. In the transition region, on the other hand, the atoms sit on top of the Peierls barriers between two nearest neighbours in the supporting A layer, i.e. they appear right above the atoms of the A layer in this projection. It is clear that the central area of fig. 1 closely resembles the (A) area of fig. 3, ref. [1], albeit that there is no evidence in fig. 3 [1] in support of the proposed origin of the arrangement, i.e. a transition from B to C stacking in the same layer. Also, fig. 3 [1] suggests that the arrangement is not restricted to three successive layers but may contain any number of AtAt... stacked layers ("t" for *transition* layer). The layer distance is $\frac{1}{2}\sqrt{3}$, i.e. 1.06 times the regular spacing, a difference too small to be detected in fig. 3 [1]. However, this figure exactly equals 8.7/8.2, the ratio between the longest distances observed in powder diffraction profiles.

Apparently, an extended region of ordered AtAt... stacking embodies a new phase of solid C_{60} . The unit cell may be chosen to be bch (body centered hexagonal), with $a=b=1$, $c=\sqrt{3}$ (hcp: $c=2\sqrt{\frac{2}{3}}$, all in units of the molecular center-to-center distance in fcc C_{60} , ≈ 10.04 Å), and with molecular centers at (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ($(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$ in hcp). However, in view of the high symmetry, a bct (body centered tetragonal) unit cell is more appropriate, with $a=b=\frac{1}{2}\sqrt{6}$, $c=1$. (This unit cell is easily recognized in the central region of fig. 1: a sphere in the t layer has four close neighbours, two in a row and two in a column; the centers of these neighbours form a 45° tilted square, the *ab* face of the unit cell; the fourfold *c* axis is perpendicular to the plane of the drawing.) The spacegroup is $I4/mmm$ (No. 139), with molecular centers at special positions (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, provided the molecules are freely rotating or orientationally disordered, and no solvent molecules are included. The coordination number is 10 (as compared to 12 in fcc or hcp), with four next-nearest neighbours at distances $\frac{1}{2}\sqrt{6}$; the hard-sphere packing density is 0.70 (0.74 in close packings). The same coordination number is found in the monoclinic phase of pentane-solvated C_{60} [2], however with a smaller packing density, 0.66, owing to a larger distance ($\sqrt{2}$) to the 8 next-nearest neighbours. This suggests that the bct structure is likewise stabilized

by the inclusion of solvent molecules (as was already proposed by Li and Fagan [1] to explain the origin of the unusual stacking). The stacking of a t layer on a A layer can be affected by a threefold degeneracy, to the effect that the fourfold axis of the bct unit cell may be aligned with either of the three close-packed rows in A planes. In fig. 1 the bct fourfold axis is perpendicular to the plane of the drawing, aligned with the $[110]_F$ rows; if it were aligned with $[101]_F$ or $[011]_F$, the appearance of the central region would be hardly distinguishable from ordinary ABA or ACA stacking, suggesting that other regions in fig. 3 [1] may have the same structure as that marked (A).

As has been indicated already, it was assumed in the foregoing discussion that the bright spots on the HREM images could be identified with the (projections of) molecular centers. However, as has been pointed out by Van Tendeloo et al. [3], the HREM image of C_{60} crystals is not simply the projection of atoms aligned in columns in the viewing direction, but rather the projection of the charge density. Whether it is the maxima or the minima of the projected density that are imaged as bright spots depends on sample thickness and defocus. Thus, in general, image simulation, accounting for the experimental conditions and for the charge distribution in the C_{60} molecule, will be indispensable to provide a basis for the interpretation. However, in favourable cases (e.g. projections along close-packed rows), the HREM image can be directly compared with a pattern of equivalent features that may be recognized on a projection of the assumed structure. This is illustrated schematically in fig. 2, where a set of equivalent (with respect to projected charge density) sites in a $[110]$ projection of a fcc twin is highlighted by shading (note that the twin-plane layer is in stacking-fault position). Apparently, in the lower and upper part, the pattern of the marked areas is the same as that of the molecular centers. In the central region, however, where the stacking is locally hcp, the markings become situated on a nearly square (8.7×8.2 Å) grid, i.e. a pattern that is different from the zig-zag pattern of molecular centers in the hcp region, but quite similar to the pattern of bright spots in the (A) region of fig. 3 or ref. [1], suggesting that identifying these spots with high projected charge density (rather than with the molecular centers) could give an alternative explanation of the unusual

analysis of the direction of diffuse streaking in reciprocal space [5]), the reciprocal lattice points $(100)_H$, $(010)_H$, $(1\bar{1}0)_H$, etc., are on the vertices of a hexagon, centered at the origin, and *perpendicular* to the $[111]_F$ direction. On the other hand, the reciprocal lattice points $(110)_B$ and $(\bar{1}\bar{1}0)_B$ are on the $[111]_F$ axis, close to the coinciding $(111)_F$ and $(002)_H$ points, which should be visible on a $[10\bar{1}]_F$ zone-axis pattern. The special position of $(110)_B$ in reciprocal space may have a small (if not unobservable) effect on the leading edge of the "saw-tooth" peak [5]. All reciprocal lattice points, connected with $d=8.7$ Å, lie on the same sphere centered at the origin. Since these lattice points are actually diffuse streaks in the $[111]_F$ direction, the streaks are tangential to the sphere for the hcp points, but radial for the bct points. A small shrinking of the sphere will make it lose "contact" with the hcp streaks (responsible for the leading edge of the saw-tooth), but not with the bct streaks. This could result in a softening of the leading edge.

A final remark concerns the possible origin of the uni-directional stacking disorder that is apparent from fig. 3 [1]. It has been observed that C_{60} crystallites are frequently in the shape of plate-like grains, with well developed (111) faces [5], suggesting relatively high growth rates in lateral directions (e.g. $[\bar{1}\bar{1}1]$, $[1\bar{1}\bar{1}]$, etc.), and slow growth in the $[111]$ direction. The slow growth direction has been identified with the direction of diffuse streaking in reciprocal space, i.e. with the direction in which stacking faults are frequent. Apparently, there is no structural information present on the (111) face that could prevent a new layer from settling in a stacking fault position. However, the stacking faults already present in the crystal (parallel to and below the (111) surface), have associated with them non-integral

surface steps on the $(\bar{1}\bar{1}1)$, $(1\bar{1}\bar{1})$, etc., faces, that act as growth centers *which prevent wrong stacking* on these faces. This could explain why stacking faults do not occur in *all* symmetry-equivalent directions, which, in turn, is responsible for the *absence* of non-integral steps on the (111) face and slow growth in the $[111]$ direction. Apparently, nearly perfect, isotropic fcc growth requires the presence of (a few) *crossing* stacking faults, providing *all* close-packed faces with growth promoting, stacking-fault resisting, non-vanishing steps; the existence of such crossings in C_{60} crystals has been demonstrated recently [7]. This growth mechanism has been proposed previously [8] to explain the preference for fcc over hcp crystallization for atoms or molecules that are effectively spherical, with isotropic van der Waals interactions. It could be the solution of the crystal structure problem, not only for the rare gases, but also for C_{60} .

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