Appl. Phys. A 57, 171–174 (1993)

Applied Physics A Solids and Surfaces

Structural Properties of Vapor-Grown C_{60} Crystals

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Received 30 October 1992/Accepted 24 March 1993

Abstract. Vapor grown crystals of C_{60} with thin flat triangular, rhombic or trapezoidal shapes of size to $1 \times 2 \times \sim 0.001$ mm as well as prismastic crystals typically $0.5 \times 0.4 \times 0.2$ mm have been grown using a high temperature vapor transport method. Room temperature X-ray precession photography shows these crystals exhibit diffraction patterns consistent with those for either (*a*) single or (*b*) twinned crystals of the previously reported face-centered cubic structure or (*c*) a more complex cell of hexagonal symmetry with $a = 10.010(2)$ Å and $c = 49.064(11)$ Å. This latter form actually is a multiple twin containing both the face-centered cubic and the close-packed hexagonal structure types. The sharp diffraction maxima for either the single or the twinned crystals demonstrate that they consist of large coherent domains and are essentially free of planar defects parallel to the twin planes.

PACS: 61.10.Jv, 61.65.+d

To date growth of C_{60} crystals from solvent has shown that significant amounts of solvent molecules may be included in lattice defects or that the solvent becomes part of the new crystal structure [1–4]. In fact, small molecules such as H_2, O_2 or N_2 have been shown to intercalate into the interstitial sites of the face-centered cubic (fcc) lattice of pure C_{60} without any lattice changes [5]. Such intercalation occurs more readily at high gas pressures or if the particle size is small. Crystals of C_{60} have also been grown from slow vaporization of solid C_{60} with sizes reported in the 1–2 mm range [6–9]. The room-temperature structure was shown to be fcc with $Fm3m$ as the space group in which the C_{60} molecules are completely orientationally disordered. This note reports room temperature X-ray results on vapor grown prisms and thin plates of C_{60}. Both single crystals and twinned crystals of the established fcc packing were studied. In addition, plates made of combinations of twins with both the fcc and hexagonal close packed (hcp) structure forms were studied.

Experimental

The starting material for crystal growth was 99.9% pure C_{60} powder obtained from Texas Fullerenes. The crystals were grown inside a quartz tube through which argon, at approximately 1 atm, flowed. The tube was heated in a zone furnace so that the C_{60} powder was at approximately 650° C. The thermal gradient in the tube was approximately 5° C/cm. The crystals formed at a 500–550° C temperature zone.

The resulting crystals included many thin plates which exhibited various habits with principal faces including equilateral triangles, rhombii, parallelograms and trapezoids. Generally, the angles formed by these faces are 60 or 120° C. Sizes of selected plates approach 2 mm on edge, but the plates are generally rather thin and, hence, fragile. Tn addition, prismatic blocks (typical dimensions of $0.5 \times 0.4 \times 0.2$ mm) and needles (typical dimensions of $1 \times 0.02 \times 0.02$ mm) were obtained.

Specimens were examined using a standard precession instrument with Cu radiation in order to obtain reasonable separation of various diffracting zones. Selected crystals were also studied on a Nicolet single crystal diffractometer, using monochromatized CuK_α radiation. Since at room temperature the data fall off rapidly with scattering angle, usually only the region less than 55° two-theta was explored over at least a complete hemisphere. Lattice constants were obtained by least-squares fit of the settings on 20–24 reflections selected to cover the entire available data range at high two-theta.

Results and Discussion

Initially it was assumed that the flat shape of the plates suggested that the (111) face had the slowest growth rate, as previously reported [81. X-ray alignment photographs perpendicular to the face readily showed three-fold symmetry. However, differences in the intensity distribution of the peaks from crystal to crystal were readily apparent. More detailed precession photography on different plates as well as

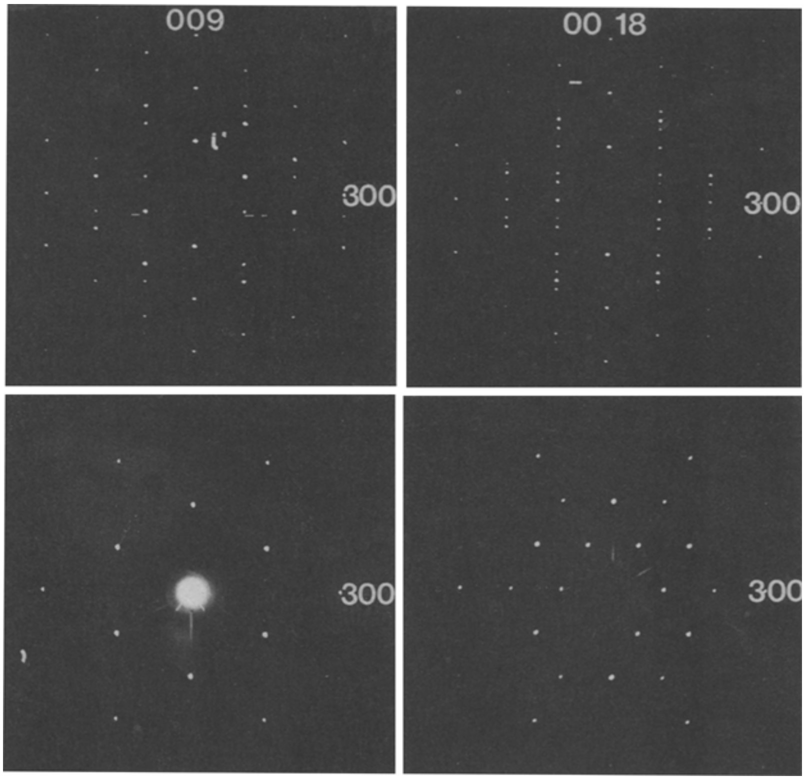

Fig. 1. *(top)* Precession photographs taken along the [$\bar{1}$10] on a hexagonal basis to compare a twinned fcc crystal *(left)* with the twinned multiphased syntactic crystal giving an apparent hexagonal ($c = 49$ Å) cell *(right)*. Both crystals are mounted on the [100] as indicated by the 300 peak on the horizontal while the [001] direction is vertical. As the crystal was mounted, note on the left that for peaks with $l = 3n$, the stronger peaks belong to the obverse ($-h+k+l=3n$) indexed cell while the weaker to the reverse cell ($h-k+l=3n$). On the right, these same reflections show the stronger peaks correspond to the reverse cell as the crystal was arbitrarily mounted. Note on the right that the 100 and 200 peaks are present. The simple hcp reflections occur also for hkl, where $l = 3n$ using the indexing of the more complex ($c = 49$ Å) cell. Thus the 00 18 peak really corresponds to the superposition of the fcc-type 009 peaks (indexed on its hexagonal cell) with that for the 006 for the simple hcp cell. *(bottom)* Precession photographs along [001] on a hexagonal basis. All diffraction spots shown for the fcc crystal *(left)* are superpositions of the two twin members since $l = 0$, thus $h-k$ or $-h+k$ (for reverse and obverse rhombohedral, respectively) must equal $3n$; the 300 peak is shown. For the ($c = 49$ Å) crystal *(right)*, these same spots also have contributions from the simple hcp member while the other $hk0$ peaks with $h+k \neq 3n$ are also present and correspond to those for the simple hcp member only; again the 300 peak is shown. (If the bottom left had been indexed on the fcc cell, the inner six spots correspond to ±(20$\bar{2}$), ±(2$\bar{2}$0), and (0$\bar{2}$2) or the type {220} while the outer six to the type {422}. Based on this indexing, note that in addition to the identical two sets of six spots, the remaining strongest spots on the bottom right are of the type 1/3 {422} and 2/3 {422}.)

on the prismatic crystals were necessary to fully understand the twinning behavior.

Some plates showed patterns for particular zones which could be indexed on the fcc lattice expected for a truly single crystal. Such a crystal is consistent with an 123123123... close packed stacking along the three-fold axis normal to the face of the plate. Other plates required twinning of the crystal normal to the plate. This becomes evident because unequal volumes for the two twin members (or components) were present in the particular specimen under observation. Such twins may be most easily understood as a reversal of the stacking ...12312321321... which abruptly occurs and introduces a mirror at that boundary. Both members of the twin correspond to the ~24.5 Å repeat along the three-fold axis which would require three layers of molecules (of thickness ~8.18 Å) for the 14.17 Å of the fcc structure. However, the results of the twinning is more easily understood when the observed X-ray reflections in the photographs are placed on a hexagonal (rhombohedral) basis rather than the true cubic basis. (Such hexagonal indexing also helps to understand both the relationship of the stacking sequence mentioned above and the relation of the cubic components (or members) to that of the hcp form for the more complex twin described below.) In Fig. 1, the top left photograph are of such a twinned fcc crystal; note that the indexing is shown on the hexagonal basis. One member of the twinned crystal appears as obverse rhombohedral while the other as reverse rhombohedral; thus for reflections with $l \neq 3n$, comparisons of $+h, +k$ with $-h, +k$ allows one to determine the relative volume of the two members. (When $l = 3n$, the reflections superimpose on each other.) Many such twinned crystals with varying size of the two members were observed.

Interestingly, on different specimens diffraction patterns were obtained for what appeared to be a "single" crystal with a stacking requiring six layers; such a close packed stacking requires a hexagonal cell of $a = {\sim}10.0$ Å and $c = {\sim}49.1$ Å (Fig. 1, right). If this packing represented a unique structure arrangement, such a cell would require an intriguing long-range ordering. Two stacking sequences can be envisioned, one involving a repeat for two cells along *c* of 1231321231321... while the other a repeat of 1212131212131.... (As described below, this crystal really is a complex twin.)

In the diffraction patterns of all the plates examined to date, the diffraction spots are sharp and not streaked. This observation is consistent with the individual twin members consisting of a single or large coherent domain(s) and containing no random stacking faults separated by less than ~1500 Å to 2000 Å the upper limit of detection by X-ray profile methods. Random stacking faults occurring more frequently reduce the size of the coherent domains, lead to broadened diffraction peaks, and eventually, if sufficient numbers are present, may lead towards streaks or rods in certain directions. (An example of such broadening is given in Fig. 3 of VanTendeloo et al. election diffraction study [9]; their figure can be compared directly with our Fig. 1 top left.) Several of the plates and prisms were examined on a single crystal diffractometer. Room-temperature cell parameters for single crystals of the fcc form were 14.165(2) Å; twinned crystals of the fcc form gave essentially identical values as one might expect [10]. One of the above mentioned hexagonal specimens yielded $a=10.010(2)$ Å and $c=49.064(11)$ Å with a volume of 4260.08 $Å^3$, corresponding to a cell containing 6 C_{60} molecules.

Intensity data on untwinned crystals of the fcc form were averaged over symmetry equivalent *hkl*'s (*R*-index over such equivalent reflections is 0.019) and the resulting observed structure factors were refined with the known, completely constrained structure. The model consists of completely disordered C_{60} molecules located at 4*a* sites in space group $Fm3m$. The scattering factors for the C_{60} molecule were calculated using the mean diameter of 7.065 Å, as determined from the low temperature structure [11]. A single isotropic thermal parameter was used; the least-squares determined value is $U=0.0025(2)$ $Å^2$. The final R value of 0.072, though acceptable, is somewhat higher than expected, but similar to results reported by Chow et. al. [12]. These authors have shown that the nature of the orientational order of the C_{60} molecules in the $Fm3m$ lattice is important.

On the other hand, when intensity data collected on the above-mentioned hexagonal ($c=49$ Å) crystal were subjected to models based on the stacking sequences given above, poor fits with large R-values were obtained. However, careful reconsideration of the photographic data as well as the intensity data set suggested the correct solution.

In reality the hexagonal ($c=49$ Å) crystal consists of a multiphased syntactic crystal, a multiple twin which changes structure-type along the stacking direction. Such crystals, also referred to as intergrowth phases, are well known in the Tl-based high-temperature superconductors and can be best thought of as a stack of different colored poker chips, each color representing a different phase, which have in common essentially identical planes of atoms as boundaries [13]. In the case of the Tl-based materials, compositional variation in the immediate vicinity during crystal growth is believed to be the driving force of their formation [13]. In our hexagonal ($c=49$ Å) specimen, one has components of both the fcc form (twinned as described above) and the simple hexagonal close pack (hcp) arrangement. The *c*-axis of the simple hcp cell consists of 1/3 the more complex c-axis and equals 16.355 Å. Thus, the precession photograph is a superposition of the patterns of the different members of this multiple twin (such photographs may be used to distinguish the different phases present in the Tl-based materials [13]). This particular specimen contains nearly as much of the fcc structure phase as of the simple hcp phase. To show that this specimen is made of three twins, one may sort the observed *hkl* intensity data indexed on the hexagonal ($c=49$ Å) cell into five data groups or sets: (a) one consisting of peaks which superimpose and contain contributions from both fcc and the hcp domains, (b) one consisting of peaks which are due to only the simple hcp domain ($c=16$ Å), (c and d) two different but related groups containing peaks due to the separate fcc domains and, finally, (e) one group of *hkl*'s for which none of the three domains contribute. The (c) and (d) sets correspond to the contribution of the two members of the fcc form; i.e., using hexagonal indices, the obverse and reverse rhombohedral *hkl*'s with $l \neq 3n$. For the (c) and (d) sets, the appropriate comparison of *hkl* reflections showed that these two members are in the ratio of a three to one volume. These data sets also scale with data on the truly single crystals of the fcc type.

The simple hcp data set, (b), was refined with the known structure. This consists of C_{60} molecules at 1/3, 2/3, 1/4 and at symmetry equivalent positions (2/3, 1/3, 3/4). A single isotropic thermal parameter was used. A value for $U=0.0027(2)$ $Å^2$ was obtained with $R=0.071$. Similar R-index values have been obtained on other twinned fcc crystals in which the appropriate twin separation (obverse, reverse) have been made.

We wish to emphasize that the domains forming the hcp component must be large and coherent (greater than the 1500C Å to 2000 Å detectable limit by X-ray profile methods) since their diffraction spots are as sharp as those for the cubic domain (see Fig. 1). Comparison of the diffraction profiles taken on our diffractometer show that, at similar values of two-theta, the peak widths corresponding to the hcp member are the same as those for the fcc members in the same plate; these peak widths are the same as those obtained on other single or twinned crystals exhibiting only the fcc structure. Thus our crystals are relatively defect free, contain no or few stacking faults, and consist of large coherent domains. Optical microscopy of the edges of the plates (normal to the direction twinning occurs) reveals no or at most an occasional re-entrant edge structure in most of the crystals grown. Hence, we believe some of the twinned crystals may contain only one mirror plane and consist of only two single domains. We believe that the low thermal gradient in the growth tube contributes towards the formation of crystals with large coherent domains and no or few stacking faults.

To date, we have not isolated a pure single crystal of the simple hcp form. Nevertheless, we clearly have demonstrated the existence of large hcp domains in twinned crystals. In the particular plate examined using diffractometer data, the volume of the hcp component was almost as large as that for the fcc component. The similar value of the R-index for that data compared to those for our cubic crystals suggests that the level of structure fit is similar; the hcp form for C_{60} is, therefore, established. Further refinements would require modeling of the orientation nature of the molecules in the same manner as Chow et. al. [12], but this requires the use of a single-domain hcp crystal.

Further, the complex twinning which may occur suggest that when employing either X-ray or electron diffraction, care needs to be taken to examine a particular specimen along various orientations in order to determine the nature of the twinning. After the initial submission of this paper, Harris et al. [14] appear to have examined a similar twinned crystal, but one in which the hcp component was very much smaller than the fcc domain(s) or twin components (compare their Fig. 2a with our Fig. 1, lower right).

It is not clear what might lead to such multiphase crystal growth in the pure material. Perhaps tiny strains introduced by temperature gradients during growth or from wall attachment might induce a small compression along one of the [111] of the fcc stacking and this then favors the hcp stacking. Further, the presence of the different structure packing may be contributing to the small differences of the transition temperatures observed by various groups for the reversible phase transition from the high-temperature $Fm3m$ phase to the low-temperature simple cubic $Pa3$ phase [15].

Acknowledgements. It is a pleasure to gratefully acknowledge discussions with Don T. Cromer on spherically averaged scattering factors. The authors thank the reviewer for pointing out work of [9] and [14]. Work at Sandia was supported by U. S. DOE and funded in part by its Office of Basic Energy Sciences, Division of Material Science under contract #DE-AC-04-76DP00789.

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