



Hexagonal close-packed C_{60}

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Abstract

C_{60} crystals were grown from purified powder material with a multiple sublimation technique. In addition to crystals with a cubic close-packed (ccp) arrangement, crystals were found with a hexagonal close-packed (hcp) structure. Detailed crystallographic evidence is given, including complete refinements, of the room-temperature structures of both polytypes. The radius of the C_{60} molecule was determined as 3.541(1) Å, and was found to be equal for both ccp and hcp crystals.

1. Introduction

The synthesis of macroscopic quantities of buckminsterfullerene, C_{60} , allowed the study of its solid state properties [1,2]. The first reports on the crystal structure of C_{60} were concerned with crystals grown from solution, and stated it to be a hexagonal close-packed (hcp) arrangement of nearly spherical molecules [2,3]. Subsequent work was concerned with significantly purer material, and C_{60} crystals, grown by sublimation, were always found to be cubic close-packed (ccp) [1,4–13]. More recently, the hcp arrangement of C_{60} was reported to occur in powders or thin films [14–16]. However, the purity of these samples is not clear in all cases, and solvent molecules might be the origin of the hcp stacking. The only quantitative study [16] failed to obtain a good agreement between measured and calculated structure factors, which can be due to a large degree of stacking disorder [17], or the presence of solvent molecules, both effects which were not accounted for in the structure model [16]. In the present Letter, we re-

port the structure determination of a single crystal of sublimation grown hcp C_{60} , using single-crystal X-ray diffraction.

2. Experimental

As described elsewhere [12], C_{60} was isolated using liquid column chromatography and subsequent drying of the material. The purity of C_{60} is among the best reported. Contamination by C_{70} and C_{60} oxide was less than 0.05%, while the concentration of the solvent toluene was less than 1%. Further purification was done by repeated sublimation of the powder, which should have reduced the toluene content by several orders of magnitude [18]. Single crystals were grown by sublimation in an evacuated tube containing the pure C_{60} in a temperature gradient from 620 to 600°C [18].

According to this procedure, several batches of crystals were prepared. Most of the crystals had a morphology compatible with F-centered cubic sym-

metry [12]. Several of these crystals were analyzed using single-crystal X-ray diffraction, and indeed gave reflections at room temperature corresponding to the $Fm\bar{3}m$ space group. A low-temperature ($T=100$ K) data collection was done for one such cubic crystal, resulting in 2176 unique reflections measured up to $\sin(\theta)/\lambda=0.91$. Refinement lead to $R_F=0.052$, using the structure model proposed by David et al. [9] and Bürgi et al. [10], thus showing the good quality of the crystals obtained. Out of several hundred crystals examined, two crystals were found (one each in two different batches) which did show facets corresponding to hexagonal symmetry. Analysis on the diffractometer of one of these crystals indicated a mixture of hexagonal and cubic phases. The hexagonal part was cut off from the sample, and was mounted again for X-ray diffraction. Prolonged random search for reflections only gave reflections which could be indexed on a hexagonal unit cell. In particular, no reflections were found at positions corresponding to the cubic lattice. The morphology of the second crystal also indicated both hcp and ccp to be present.

A room temperature single-crystal X-ray diffraction experiment was performed on the hexagonal crystal of dimensions $0.17\text{ mm} \times 0.33\text{ mm} \times 0.58\text{ mm}$. Lattice parameters for the hexagonal crystal were determined from the setting angles of 20 reflections in the range $15.6^\circ < \theta < 16.5^\circ$ (Table 1). All reflections in one hemisphere were measured up to $\theta=26^\circ$. Averaging in Laue symmetry $6/mmm$ reduced 5923

measured reflections to 629 unique reflections, with internal consistency $R_I = \sum |I_0 - I_{ave}| / \sum I_0 = 0.045$. Extinction conditions were found to be compatible with the space group $P6_3/mmc$. The unit cell leaves room for only two molecules, with their centers at the hcp special positions $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$. Refinements were performed using the formalism for free rotating molecules (or rather molecules with a random distribution of their orientation) [7]. The C_{60} molecule then is represented by a spherically symmetric electron density, obtained as the convolution of a spherical shell of radius R and the electron density of a single carbon molecule. The only structural parameter to be refined is the radius R . In addition an isotropic temperature factor and the scale factor were refined. An analogous measurement and analysis was done for a cubic crystal at room temperature (Table 1). The different amounts of unique reflections for ccp and hcp is in accordance with the latter having a primitive unit cell which is twice as large, the different orders of the point groups, and that for ccp intensities were measured up to larger angles.

3. Discussion

The refinements of both ccp and hcp C_{60} give a good convergence to low reliability factors (R_F). Noteworthy is that they lead to the same radius for the C_{60} molecule within two times the standard deviation of 0.001 \AA . The value $R=3.541(1)\text{ \AA}$ is in excellent agreement with previous studies of the ccp modification [7,11]. Together with the absence of any reflections outside the hexagonal lattice, this proves that a good quality hcp C_{60} crystal has been grown of macroscopic sizes. The high-purity material and the good fit to the diffraction data using C_{60} only, exclude the possibility that the hcp phase is stabilized by the presence of other molecules. Impurities may play a role in forcing growth of a metastable hcp phase. This and the possibility that hcp is stable at high temperatures are presently under investigation.

In the disordered phase, deviations from complete orientational disorder have been determined for the ccp phase [11]. Such deviations are expressed in the Bragg reflections through intensities being (slightly) different from the intensities of a crystal with free rotating molecules. Most pronounced differences will

Table 1
Structural parameters and experimental data for C_{60} . The ratio c/a for a hcp sphere packing is $\sqrt{8/3}=1.633$

	Cubic	Hexagonal
space group	$Fm\bar{3}m$	$P6_3/mmc$
a	14.156 Å	10.009(1) Å
c		16.338(1) Å
	$a/\sqrt{2}=10.010\text{ \AA}$	$c/a=1.6323$
radius	3.5397(13) Å	3.5413(8) Å
B_{iso}	1.38(7) Å ²	1.46(5) Å ²
R_F	0.059	0.062
$[\sin(\theta)/\lambda]_{max}$	28°	26°
No. reflections	8078 (twinned)	5923
No. unique	216	629
No. observed	159	443
R_I	0.029	0.045

be found for the higher-order reflections. Comparing partial R_F factors for reflections in intervals of $\sin(\theta)/\lambda$ shows that the higher-order reflections in hcp are fitted less well than in ccp. This is an indication that at room temperature the deviations from complete orientational disorder will be larger in hcp than in ccp crystals.

On lowering the temperature, the ccp C_{60} undergoes a transition at T_c : 255 K to an ordered phase with symmetry $Pa\bar{3}$. The site symmetry of the molecules reduces to $\bar{3}$, and the ordering involves finding a optimum orientation of the molecules for rotation around the three-fold axis [7,8]. The best fit to the low-temperature diffraction data is obtained with a disordered occupation of each molecule site with two molecules differing 60° in rotation angles [9,10]. The occupation of the major orientation is about 80% below 100 K, as was also reproduced in our refinement. With only one orientation, there is only one type of intermolecular contact for any value of the rotation angle. The optimum orientation can be characterized by the inter-pentagon bond of one molecule facing a five-fold ring in the other molecule, the latter of which is composed of all single bonds [7,8]. When the minor orientation is taken into account, a double bond facing a six-fold ring is also found.

A similar type of ordering can be envisaged for the hcp crystals, albeit with a yet to be determined transition temperature. Maximal subgroups of $P6_3/mmc$ which allow an ordered structure are $P6_3mc$, $P6_322$, $P\bar{3}m1$, $P\bar{3}1c$, and $Cmcm$. In all these groups the site symmetry fixes the orientation of the molecules, leading to unfavourable intermolecular contacts. Requiring at least one rotation angle to be a free parameter, the highest-symmetrical candidates for the low-temperature space group can be divided into two sets. The first gives an ordering analogous to the cubic phase, and might have space group $P6_3$, $P31c$, $P321$, or $P\bar{3}$. All of them give 3 as molecular symmetry and lead to one independent molecule in the unit cell. The second class are orthorhombic space groups like $Pbnm$, and describe an ordering analogous to that in hcp C_{70} [17]. The molecular symmetry as imposed by the space group is m and there is only one independent molecule in the unit cell. $P3m1$ and $P312$ lead to internal symmetries $3m$ and 32 , respectively, which again allow only one orientation of C_{60} .

The four possible hexagonal/trigonal space groups

for the ordered phase have in common the molecular symmetry, which is different from the molecular symmetry $\bar{3}$ as found for the cubic phase [8]. The differences between these four groups is how the rotation of the molecule in one close-packed layer is transferred to the molecule in the other close-packed layer. A major difference with the ordered ccp crystals is, however, that there is more than one independent, crystallographic crystallographic contact, and that optimizing the rotation angle requires optimizing at least two different types of contact between the molecules. The origins of this obviously are the differences between hcp and ccp structures. With such a big difference between ordered $Pa\bar{3}$ ccp crystals and any possible way of order in hcp C_{60} , it is not clear whether the ordered phase will adopt one of the cubic-like phases (molecular symmetry 3), or that the ordering will follow that of hcp C_{70} on an orthorhombic lattice [17]. Further studies concerning the low-temperature structure of hcp C_{60} are in progress.

In conclusion, hexagonal close-packed C_{60} has been synthesized, as shown by a complete single-crystal X-ray diffraction study. The crystallographic data (Table 1) indicate that the quality of the hcp crystal is comparable to the quality of ccp crystals.

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