

Low-temperature structure of solid C_{70}

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Abstract

The structure of the low-temperature phase of hexagonal close-packed (hcp) grown C_{70} is determined from single-crystal X-ray diffraction at 220 K and 100 K. An ordering of the molecules is found on the orthohexagonal supercell of a hcp structure with symmetry Pbnm. It involves alignment of the molecules with their long axis parallel to the original hexagonal axis, and a shift out of the original hcp positions. Intermolecular contacts are shown to be different from those found in C_{60} . The crystal is determined to contain stacking faults resulting in the presence of AC and BC deformed hcp arrangements in addition to the original AB stacking. The stacking disorder is shown to be independent of the phase transitions, and presumably is an intrinsic property of hexagonal C_{70} crystals.

1. Introduction

The solid states of the fullerenes C_{60} and C_{70} exhibit almost unique features related to the specific structures of these molecules. The structural changes in C_{60} crystals as a function of temperature involve an order-disorder transition of the orientations of the molecule at $T_c=260$ K [1–5]. The less symmetrical C_{70} molecule possesses a unique fivefold axis (Fig. 1), which allows in addition a phase of intermediate order with all molecules aligned, but with free rotations around this long axis.

The actual series of phases observed for C_{70} is more complicated. Both cubic close-packed (ccp) and hexagonal close-packed (hcp) structures have been

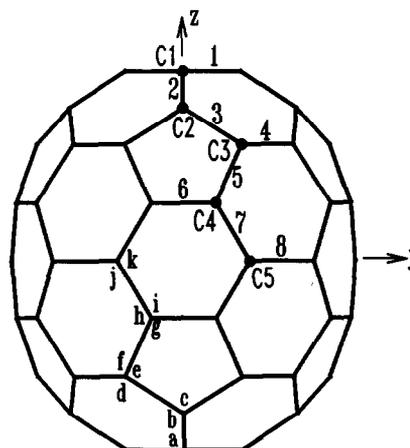


Fig. 1. Perspective view of one C_{70} molecule as obtained from the refinement. Numbers indicate bonds and letters indicate angles given in Table 2.

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found [6,7]. The phase stable at high-temperature is ccp with orientational disorder of the molecules [6,8–10]. On cooling the ccp crystals transformations to a rhombohedral and a monoclinic phase were found [8,9].

On cooling sublimation grown hcp crystals, two transitions could be identified at temperatures above (T_{c1}) and below (T_{c2}) room temperature [7]. Above T_{c1} the molecules are orientationally disordered in a hcp lattice. Below T_{c1} the molecules align along the hexagonal axis but orientational disorder around this axis remains. This alignment was identified from changes of 0.4 Å in the lattice parameters. On lowering through T_{c2} complete orientational order is obtained, which was attributed to the formation of several domains of an $a \times 2a \times c$ supercell with monoclinic symmetry [7].

In this Letter, we present the determination and refinement of the low-temperature structure of hcp C_{70} using single-crystal X-ray diffraction data. A restricted refinement was performed using the internal D_{5h} symmetry of the C_{70} molecule with only five independent atoms. In addition, rotations and shifts of the molecules were refined. The Debye–Waller factor was described in the form for rigid-body motion [11]. This formalism, as well as the possibility of using data from twinned structures were incorporated in the program REFINE from the package SDS [12].

2. Experimental

Synthesis and X-ray diffraction experiments have already been reported (wavelength, $\lambda=0.71$ Å) [7]. Below T_{c2} an apparent unit cell was found as a fourfold hexagonal supercell of the room-temperature phase, with $a=b=20.033$ (12) Å and $c=18.53$ (5) Å at 220 K. Intensity data at 220 K comprise 4483 reflections measured up to $\sin(\vartheta)/\lambda=0.34$. They were averaged in Laue group 2/m, resulting in 2259 unique reflections of which 933 were observed ones ($I > 3\sigma(I)$). At 100 K 2502 reflections were measured up to $\sin(\vartheta)/\lambda=0.28$, resulting in 1265 unique reflections and 612 observed ones. For both measurements, the hexagonal symmetry was not fulfilled well. The only systematic extinction condition found corresponded to a twofold screw axis along c . This led us previously to interpret the diffraction pattern

as being due to a twin of an $a \times 2a \times c$ monoclinic superstructure [7]. Alternatively, the observed diffraction pattern can be assigned to the presence of three orientational twins of an orthorhombic superstructure described on the orthohexagonal $a_0 \times \sqrt{3} a_0 \times c$ supercell [13]. Any reasonable form of order then only allows the space group Pbnm. The extinctions which remain in the diffraction pattern of a twin of this structure were indeed observed, although a few low-order reflections were found with small intensities violating these conditions ($\vartheta < 5^\circ$). Refinements using monoclinic symmetries indeed converged to a structure model compatible with Pbnm symmetry, showing the latter to be the true space group.

The hcp structure has two molecules in each hexagonal unit cell, with their centers on a twofold special position. In the low-temperature structure the orthohexagonal supercell contains one independent molecule on the fourfold position $(x, y, \frac{1}{4})$, $(0.5+x, 0.5-y, \frac{3}{4})$, $(-x, -y, \frac{3}{4})$, and $(0.5-x, 0.5+y, \frac{1}{4})$, where $x=x_0=\frac{1}{2}$ and $y=y_0=\frac{1}{6}$ correspond to the special positions in hexagonal symmetry. The molecules are aligned with the horizontal mirror plane of D_{5h} coinciding with the crystallographic mirror plane of Pbnm. The position of the single independent molecule can then be specified by a shift parallel to the mirror plane, out of the initial position $(\frac{1}{2}, \frac{1}{6}, \frac{1}{4})$. Crystallographic symmetry prevents tilting of the molecule, and only one angle, φ , representing clockwise rotation around the c axis was refined. As the initial orientation the center-to-atom vector in the top pentagon was aligned to the $-a$ axis.

The initial refinement of the 220 K data included the structural parameters according to D_{5h} symmetry, the twin ratios, as well as a fixed isotropic overall temperature parameter ($B=0.014$ Å²). Convergence was obtained at $R_F=18.4\%$, with almost equal occupations for the three twin domains (0.308, 0.335(2) and 0.357(2)). Refinement of the temperature parameters immediately led to negative values for them, and seemed unfeasible. Despite the poor fit, a well defined minimum with respect to φ was found.

A difference Fourier map showed additional electron density in the molecular planes perpendicular to c , with a shape resembling C_{70} molecules, and at positions representing the C layer, if the pseudohexagonal structure is considered to be an AB-type stacking and ccp would be ABC stacking. One additional

independent C_{70} molecule was included in the refinement at the fourfold position ($\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$). The molecular structure was restricted on the primary molecule, while the shift vector and the rotation angle were varied independently. The R -factor dropped to 11.1% with an occupancy fraction of about 0.12 for the second independent molecule. Refinement of the temperature factors now lead to reasonable values. Using the T, L, S formalism [11] the best fit was obtained with $R_F=9.6\%$. The poor crystal quality at low temperature, probably caused by the large deformations of the crystal going through the phase transition T_{c1} , and the diffuse scattering due to stacking faults, hampered further improvement of the fit. Especially low-order reflections were affected by the diffuse scattering. Assuming that two molecules in different orientations occupy the same site did not improve the fit any further. To be able to refine the temperature parameters it was necessary to delete 26 low-order reflections from the refinement.

The data measured at 100 K showed similar features as those measured at 220 K. With the same independent parameters, the best fit converged to $R_F=9.1\%$ with the same volume fractions for the twin domains, and with the same occupation fraction of the C-type molecule (0.124(4)) as found at 220 K. These similarities show that below T_{c2} no further structural changes proceed.

3. Discussion

The diffracted intensities obtained above T_{c1} on the same crystal obey $P6_3/mmc$ symmetry [7], while the refinements show a fractional occupancy of the C position as well. This, and the absence of additional Bragg reflections, e.g. those corresponding to a ccp arrangement, give strong evidence that the C_{70} crystals contain randomly distributed regions of identical hcp arrangements denoted by AB, CA and BC stackings. These regions are connected through stacking faults, which can be characterized by the non-integer translations $(0, \frac{1}{3}, 0)$ and $(0, \frac{2}{3}, 0)$ with respect to the orthohexagonal unit cell. From the relative occupancies of the A- and C-type positions (0.880(3) and 0.120, respectively) one derives that the stacking sequences involving the C-type layer occupy a volume fraction 0.24. The stacking disorder can be related to

the small differences in energy for ccp and hcp stackings [14], evidenced by the fact that both hcp and fcc crystals have been found experimentally. Stacking disorder seems to be an intrinsic growth feature of these crystals.

The molecular geometry obtained from the refinement is close to that obtained by theoretical calculations on a free molecule (Table 1, refs. [15–18]), and to that obtained by electron diffraction on thin films [19]. Differences up to 0.03 Å are found for the bond lengths, which is always less than four times the standard deviation (Table 2). The bond angles do not differ by more than 0.5° from the theoretical values, which is less than one standard deviation. In electron diffraction [19] quite different values were obtained for the lengths of bonds 6 and 8, than were found in the calculations. For bond 6, our refinements are in

Table 1
Geometry of the refined C_{70} molecule. Numbers (bonds) and letters (angles) refer to Fig. 1

Bonds		Angles	
number	length (Å)	number	(deg)
1	1.434(8)	a	119.9(4)
2	1.377(10)	b	120.3(5)
3	1.443(9)	c	106.6(6)
4	1.369(10)	d	119.9(5)
5	1.442(7)	e	108.1(6)
6	1.394(11)	f	120.5(5)
7	1.418(7)	g	108.6(5)
8	1.457(12)	h	120.3(7)
		i	121.7(5)
		j	119.0(4)
		k	115.3(8)

Table 2
Atomic coordinates of the independent atoms of C_{70} . The complete list of coordinates follows by application of D_{5h} symmetry, with the fivefold axis along z . The coordinates refer to the orthorhombic cell, with the center of the molecule in the origin of the coordinate system. The crystallographic position of this center and the orientation of the molecule are defined in the text

Atom	x	y	z
C1	-0.1218(6)	0.0	0.2122(3)
C2	-0.2382(7)	0.0	0.1727(4)
C3	-0.2752(4)	-0.0666(4)	0.1306(2)
C4	-0.3364(5)	-0.0401(4)	0.0647(2)
C5	-0.3219(6)	-0.0830(5)	0.0

good agreement with the theoretical structures, while for bond 8 the refined structure is in between the electron diffraction and theoretical results. The dumb-bell shape of C_{70} found in ref. [19] is not confirmed by the present refinements.

The parameters describing the orientations and positions of the molecules in the best fitted model are $\varphi = -5.24(6)^\circ$ and $t = (0.0013(4), -0.0066(2), 0)$ for the primary molecule with an occupational fraction of 0.880(3), and $\varphi = -7.3(6)^\circ$ and $t = (-0.001(3), 0.003(1), 0)$ for the molecule at the C position with occupation 0.120. These values agree well with a lattice dynamics optimization of the crystal structure [20]. Those calculations were inter-

preted as leading to monoclinic symmetry, but actually correspond to the orthorhombic model presented here [13]. Their values were $\varphi = -6.5^\circ$ and $t = (0.0, -0.006, 0)$ [20]. The rotation angle depends on the chosen molecular geometry, and one can expect an even better agreement between experiment and simulations, when the latter are done with the molecular geometry obtained here.

The orientational ordering of C_{70} as presented here, agrees with calculations that use van der Waals interactions only [20], while for C_{60} additional, Coulombic terms are required in the lattice energy expression, to be in agreement with the experimentally determined crystal structure [1–5]. This discrep-

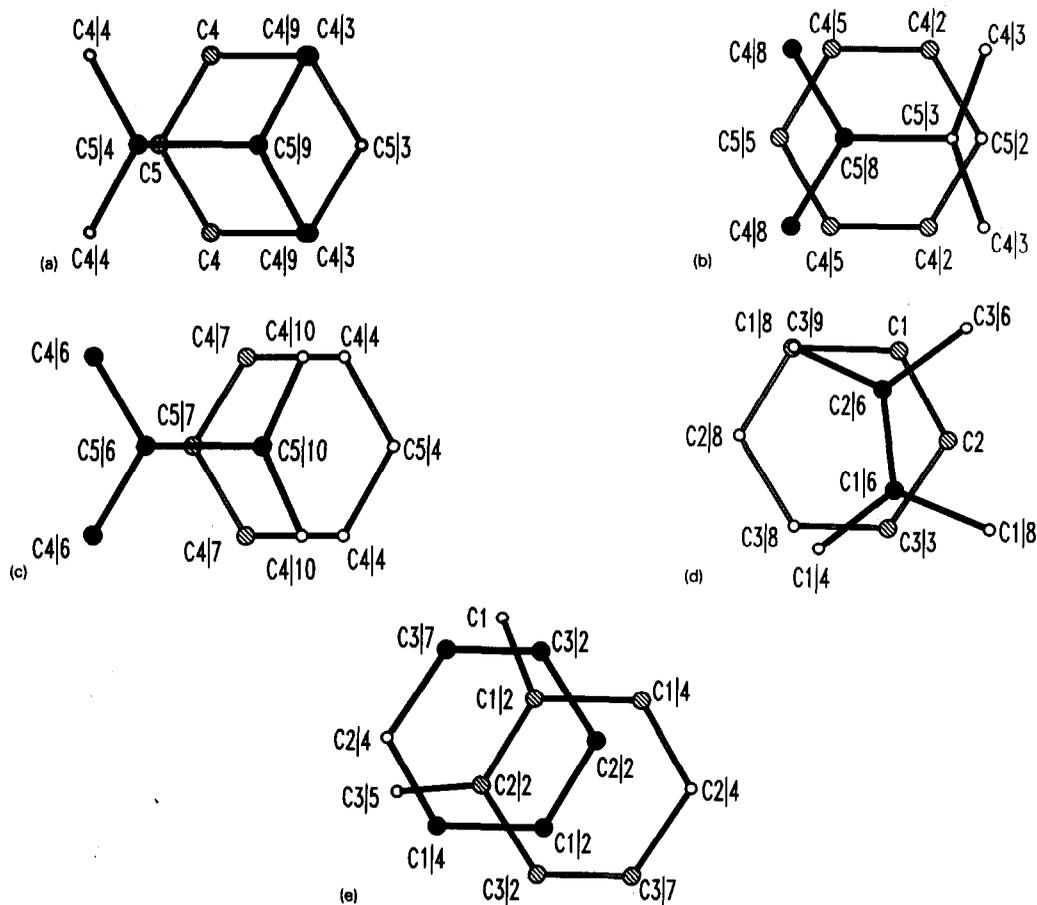


Fig. 2. Intermolecular contacts viewed perpendicular to a sixfold ring of the molecule at $(\frac{1}{2}, \frac{1}{6}, \frac{1}{4})$. The second molecule is at: (a) $(\frac{2}{3}, \frac{1}{6}, \frac{1}{4})$, (b) $(1, \frac{2}{3}, \frac{1}{4})$, (c) $(0, \frac{2}{3}, \frac{1}{4})$, (d) $(0, \frac{1}{3}, \frac{3}{4})$, (e) $(\frac{1}{2}, -\frac{1}{6}, \frac{3}{4})$. Filled and hatched circles represent atoms at closest approach of the two molecules. Open circles represent atoms beyond 3.5 Å. The numbering corresponds to Fig. 1, with the second number indicating the symmetry operator.

Table 3

Shortest interatomic distances (Å) for the intermolecular contacts. Contact types a through e correspond to Figs. 2a through 2e

Contact type a	Contact type b	Contact type c	Contact type d	Contact type e
C4–C5 4 3.500(9)	C5 5–C4 8 3.529(9)	C5 7–C5 6 2.978(12)	C1–C2 6 3.286(9)	C1 2–C2 2 3.402(9)
C4–C5 9 3.408(9)	C5 5–C5 8 3.481(11)	C5 7–C4 6 3.510(10)	C1 8–C2 6 3.506(9)	C1 2–C3 2 3.292(7)
C5–C5 4 3.300(11)	C4 5–C4 8 3.189(9)	C5 7–C5 10 3.459(12)	C2–C1 6 3.502(8)	C2 2–C2 4 3.497(10)
C4 3–C4 9 3.476(9)	C4 5–C5 8 3.401(9)	C4 7–C5 6 3.394(10)	C2–C2 6 3.374(10)	C2 2–C1 4 3.339(9)
C4 3–C5 9 3.483(9)	C4 2–C5 8 3.549(10)	C4 7–C5 10 3.532(10)	C3 3–C1 6 3.381(7)	C1 2–C3 7 3.509(7)

ancy can be explained by the difference in intermolecular contacts in C_{60} and C_{70} . For C_{60} there is only one type of contact which can be described as the inter-pentagon bond of one molecule facing a fivefold ring in the other molecule, the latter which is composed of all single bonds [4]. When the minor orientation of C_{60} is taken into account, a double bond facing a sixfold ring is found [3]. For C_{70} there are five crystallographically independent contacts, all of which are essentially different from the major one in C_{60} : the close packing of the oriented molecules does not allow a fivefold ring to participate in the contact. The three independent contacts within one layer ($z = \frac{1}{4}$) involve atoms in the distorted sixfold rings of the equatorial band of C_{70} (Figs. 2a–2c, Table 3). As determined by symmetry, the C5 atoms of both molecules lie in one plane for all rotations and translations. Common to these contacts is that directly facing atoms in the equatorial plane are avoided. The symmetry forbids the double bond involved (No. 7) to be oriented to face the middle of a hexagon. Two more contacts are found between molecules of neighbouring layers (Figs. 2d and 2e). Now it is found that a double bond (No. 2) is facing a ring, although this necessarily is a sixfold ring, which involves both double (No. 2) and single bonds (No. 1 and No. 3).

4. Conclusions

The low-temperature structure of crystalline C_{70} has been determined to be an ordering of the molecules on an orthorhombic $a \times \sqrt{3}a \times c$ supercell with symmetry Pbnm. The geometry of C_{70} was found to be in accordance with theoretical calculations on the free molecule. The crystal is shown to contain stacking faults connecting regions of identical hexagonal close

packing, but with relative shifts involving a non-crystallographic translation vector. The volume fraction of alternative positions of the hcp regions is independent of the temperature, and in particular is not related to the phase transitions.

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