$K_3Na(CrO_4)_2 < K_3Na(SO_4)_2$. This accounts for the trend of decreasing phase-transition temperatures in this sequence [in $K_3Na(SO_4)_2$ this has not been observed above 100 K]. So, we may conclude that the ferroelastic phase transition in this sequence, which is accompanied by the rotation of tetrahedral anions and simultaneous shift of cations, is affected mainly by the bonding of the K(2) cation. On the other hand it is reasonable to expect that the bonding of the K(2) cation is also a function of the size of tetrahedral anion. The larger anion is expected to cause the atom K(2) to be located in a larger cavity, and therefore be more loosely bound. Thus $K_3Na(MoO_4)_2$ and $K_3Na(WO_4)_2$ at room temperature may also be monoclinic and ferroelastic, though the powder data (PDF 28-801 and PDF 28-802, respectively) do not report doubling of the *c* axis.

The growing intensity – when the temperature is lowered – of the reflections which develop below the phase transition at 346 K seems to indicate an increasing structural distortion from the parent phase.

Concluding remarks

A precession photograph of $K_3Na(CrO_4)_2$ has revealed that the *c* axis also doubles its length below the ferroelastic phase-transition point. Thus the low-temperature phases of $K_3Na(SeO_4)_2$ and $K_3Na(CrO_4)_2$ are most probably isostructural. The structure determination of the ferroelastic phase of $K_3Na(CrO_4)_2$ is now being examined.

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Structure of C_{60}: Partial Orientational Order in the Room-Temperature Modification of C_{60}

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Abstract

Using published synchrotron X-ray data, the room-temperature scattering density distribution of pure C_{60} has been parametrized in terms of a combination of eight oriented symmetry-related images of the molecule, and of a freely spinning molecule. Corresponding populations are 61 and 39%. The oriented

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part of the model is obtained, in good approximation, by imposing $m\bar{3}m$ symmetry on the energetically more favourable major orientation in the low-temperature structure of C_{60}. The model was refined using angle restraints to impose the icosahedral molecular symmetry and displacement-factor restraints to restrict thermal movements to rigid-body translations and librations. Translational displacement factors are in the range 0.017–0.023 Å^2. The orientational probability density distribution obtained from the model shows maxima for C_{60} orientations possessing $\bar{3}m$ crystallographic site symmetry. It is also relatively large for the C_{60} orientations with cubic site symmetry $m\bar{3}$. The smallest energy barrier for reorientation between different $\bar{3}m$ orientations *via* an $m\bar{3}$ orientation appears to be less than 2 kJ mol^{-1}. On average, 75% of the intermolecular contacts of the oriented molecules are longer than those observed in the low-temperature structure, the other 25% are less favourable. The second orientation of C_{60} found in the low-temperature structure could not be identified at room temperature.

Introduction

Crystal structures of C_{60} provide a basis for an understanding of the interactions between these highly symmetric molecules and of their motion in the solid state. In pure C_{60}, the molecules exhibit cubic close packing. Occasional stacking faults may produce growth twins across the plane (111) (Chow *et al.*, 1992). Crystals of C_{60} undergo a first-order phase transition at about 250 K (Heiney *et al.*, 1991). Below the transition temperature, the space-group symmetry is $Pa\bar{3}$, $a = 14.067\,(6)$ Å at 200 K; the crystals are merohedrally twinned and the diffraction symmetry is therefore $Fm\bar{3}m$. Neutron powder diffraction (Hu, Egami, Li & Lannin, 1992; David, Ibberson, Dennis, Hare & Prassides, 1992) and X-ray twinned-crystal analyses (Bürgi *et al.*, 1992) have shown that the molecules lock into two alternative, well defined orientations both of which possess the *crystallographic* molecular site symmetry $\bar{3}$. They are therefore defined by one rotation angle about the threefold axis. It is noteworthy that the three *molecular* mirror planes which intersect in the threefold axis are very close to the *crystallographic* planes $(1\bar{1}0)$, $(\bar{1}01)$ and $(01\bar{1})$; these planes are mirror planes in $Fm\bar{3}m$ but not in $Pa\bar{3}$. From the coordinates of Bürgi *et al.* (1992), the angles between molecular and crystallographic planes at 110 K are $\varphi_M = 2.2°$ for the major orientation (population 76%) and $\varphi_m = 64.4°$ for the minor orientation (population 24%). These angles change little with temperature; at 200 K, they are $\varphi_M = 2.5$ and $\varphi_m = 64.8°$. Occupation probabilities between 90 and 250 K appear to be in thermal equilibrium (Bürgi *et al.*, 1992; David *et al.*, 1992).

Above the transition temperature, the diffraction symmetry, and probably also the space-group symmetry are $Fm\bar{3}m$; $a = 14.16\,(1)$ Å at room temperature.

Powder diffraction data have been interpreted assuming freely spinning molecules (Heiney *et al.*, 1991). Chow *et al.* (1992) have recently shown using single-crystal synchrotron X-ray data that this assumption is too simplistic. A good fit of calculated and observed structure amplitudes was obtained with a scattering density parametrized in terms of spherical harmonics up to $l = 18$ and a single isotropic displacement parameter $U_{\text{iso}} = 0.0223\,(3)$ Å^2. The corresponding atomic number density showed regions of density deficiency of 16% centred on the threefold axes ⟨111⟩ and a set of symmetry-equivalent broad peaks of density in excess of 10% centred roughly on ⟨321⟩. This result shows that some orientations of the molecule are more probable than others. Therefore, we felt that it ought to be possible to interpret the same experimental data with a more classical crystallographic model in terms of atomic coordinates, displacement factors and population parameters, which would give more explicit and direct information on preferred molecular orientations, intermolecular interactions and molecular motion.

Structure refinements

Since it is evidently not feasible to refine the parameters of independent atoms in this severely disordered structure, the models used in the present work are built from rigid, strictly icosahedral C_{60} molecules executing rigid-body movements; pentagons are regular and hexagons are semi-regular with alternating long and short bonds enclosing angles of 120°. This geometry can be imposed by fixing the angles between edges and between diagonals of the polygons. We used angle restraints to achieve this goal. The two C—C bond lengths, or alternatively the ratio of the bond lengths and the diameter of the molecule, are then effective adjustable quantities. For site symmetry $\bar{3}$, the molecular orientation is described by one effective parameter, the angle φ between the molecular mirror plane and $(1\bar{1}0)$; for site symmetry $\bar{3}m$, the molecular orientation is fixed, $\varphi = 0$ or 60°. With additional distance restraints, the shape of the molecule may be completely specified and the number of effective parameters is then reduced by two. Rigid-body libration and translation of the molecules (Schomaker & Trueblood, 1968) is ensured with rigid-link restraints which prescribe equal mean-square displacements of two atoms along their interatomic vector (Didisheim & Schwarzenbach, 1987). The displacements of molecules with site symmetry $\bar{3}$ or $\bar{3}m$ are then described by four effective parameters, *i.e.* two librational and two translational terms. The total number of effective parameters per molecule is therefore seven for $\bar{3}$ and six for $\bar{3}m$.

Structure refinements with respect to 320 $|F|^2$ values obtained from Chow *et al.* (1992) were carried out with the programs *LSRES* and *LSLS* (Blanc & Schwarzenbach, 1992). Although the Bragg intensities decrease rapidly with increasing scattering angles, as may be expected for a highly disordered structure, the data collected with synchrotron radiation are of high resolution and contain a large number of $|F|^2 > 3\sigma(|F|^2)$ (Table 1). For a molecule with $\bar{3}$ symmetry, the numbers of refined positional and anisotropic displacement parameters were 30 and 60, respectively; the corresponding numbers of angle and displacement parameter restraints were 58 and 148, respectively. For a molecule with $\bar{3}m$ symmetry, these numbers were 16, 32, 31 and 84, respectively. Angle restraints were given weights of $(0.02^\circ)^{-2}$, the weights of displacement parameter restraints were $(0.0001\ \text{Å}^2)^{-2}$. The weights of the $|F|^2$ values were $\sigma^{-2}(|F|^2)$. Additional refined parameters were a scale factor and a secondary-extinction factor as in Chow *et al.* (1992). Shift-limiting restraints (Flack & Schwarzenbach, 1988) and partial shift factors were used to reach convergence. Refinements were terminated when final shifts were smaller than 0.02 e.s.d.'s. Obviously, the normal equations matrix becomes increasingly ill conditioned with increasing weights of the restraints. The above-mentioned weights resulted in up to 150 correlation coefficents between refined parameters larger than 0.95. Assigning larger weights would result in numerical problems.

In view of the small deviations from an isotropic density distribution (Chow *et al.*, 1992), one may think that any model based on specific disordered molecular orientations would have to be ambiguous at best. The results of our analysis do not rule out alternative interpretations of the diffraction data. They do show, however, that certain models are incompatible with the diffaction data and that others are physically untenable. These are given below in summary form together with a more detailed discussion of the model which we consider to be superior from a chemical, physical and crystallographic point of view.

The search for trial models was guided by the observation that the maxima of excess density found by Chow *et al.* (1992) form hexagons around $\langle 111 \rangle$ with an edge length of 1.4–1.5 Å. This might indicate that some of the six-membered rings of the C_{60} molecules are oriented perpendicular to a threefold axis as in the low-temperature structure (LTS). Therefore, the most obvious recipe for devising a trial model of the room-temperature structure (RTS) of C_{60} consists of imposing the symmetry $Fm\bar{3}m$ on the coordinates of the LTS. Since the site symmetries of the molecular centres in the RTS and LTS are $m\bar{3}m$ and $\bar{3}$ with multiplicities of 48 and 6, respectively, this procedure generates in the RTS eight superimposed molecules for each of the two molecular orientations in the LTS. Two of these images, *i.e.* those related by the diagonal mirror planes $(1\bar{1}0)$, nearly coincide since a molecular mirror plane is close to $(1\bar{1}0)$ as described above. Therefore, a simpler RTS can be imagined by assuming the molecular mirror planes to coincide exactly with the crystallographic $(1\bar{1}0)$ mirror planes. The molecular site symmetry is then $\bar{3}m$; four orientations in the RTS with their threefold axes aligned along the four $\langle 111 \rangle$ directions now correspond to one molecular orientation in the LTS.

Initial refinements were carried out including both a major and a minor orientation as in the LTS, and assuming all combinations of $\bar{3}$ and $\bar{3}m$ site symmetries. These converged to R values somewhat larger than those of Chow *et al.* (1992), $wR(|F|^2) \simeq 0.07$ for $\bar{3}$ and $\simeq 0.08$ for $\bar{3}m$. However, the mean-square rigid-body translation for the minor orientation perpendicular to the threefold axis $T_{m,\text{perp}}$ was consistently negative. In addition, the resulting C—C bond lengths were far from the expected values, the 6,6 bond being much too short and the 5,6 bond too long: respective values were in the range 1.26–1.29 and 1.45–1.48 Å for the major orientation. Values for the minor orientation were even further off. The average value of the diameter of the molecular spheres, however, was near 6.95 Å in all cases. The librational displacement factors of the major orientation refined to about 100 deg^2. The librational correction of the diameter is therefore roughly 0.1 Å and the diameter obtained in the refinements is thus in reasonable agreement with the expected value of 7.07 Å (Bürgi *et al.*, 1992). The population factors of the two orientations could not be refined together with all the other parameters. Assuming total populations for major/minor of 0.50/0.50, 0.60/0.40 and 0.67/0.33 resulted in slight, but model-dependent variations of the R values.

Next, the bond lengths were fixed to $d_{5,6} = 1.425$ and $d_{6,6} = 1.364$ Å, calculated from the expected bond-length ratio of 1.045 and the sphere diameter of 6.95 Å. These refinements with symmetries $\bar{3}$ $[wR(|F|^2) \simeq 0.11]$ did not change appreciably the parameters of the major orientation. The molecule of minor orientation, however, turned to a position near $\varphi \simeq 24^\circ$ intermediate between the major and minor orientations observed at low temperature. $T_{m,\text{perp}}$ remained negative. Fixing the minor orientation at $\varphi \simeq 60^\circ$ (symmetry $\bar{3}m$) increased the R value substantially. Additional models were tested comprising three and even four molecular orientations with site symmetry $\bar{3}$ and fixed bond lengths. These refinements were stable; the lowest $wR(|F|^2) \simeq 0.066$ was obtained for $\varphi = 0$, 32.6, 37.8 and 67.4°, but one rigid-body translation, $T_{m,\mathrm{perp}}$ or $T_{m,\mathrm{paral}}$, of two of the minor orientations remained negative. Corresponding librational displacements of these orientations, $L_{m,\mathrm{paral}}$ or $L_{m,\mathrm{perp}}$, were $\simeq$ 120 deg^2. Constraining the displacement parameters of the minor orientations equal to those of the major orientation increased $wR(|F|^2)$ to 0.09.

The calculations described so far all indicate the presence of the major orientation, but they do not produce meaningful results for other orientations of C_{60}. Fig. 1 shows that the atomic number density found by Chow *et al.* (1992) is indeed qualitatively explained by a superposition of the eight molecules of the major orientation with symmetry $\bar{3}$. For some atoms, the large positive displacements arising from $L_{m,\mathrm{paral}}$ and $L_{m,\mathrm{perp}}$ of the putative minor orientations can be shown to be compensated for by corresponding negative terms $T_{m,\mathrm{perp}}$ and $T_{m,\mathrm{paral}}$ to maintain non-vanishing electron densities at the corresponding sites. This suggests a new and much simpler model consisting of a set of molecules in major orientation ($\varphi_0 \simeq 0°$) superimposed on a spherical electron-density distribution representing freely spinning C_{60} molecules. The total electron density is then

$$\rho_{\mathrm{total}} = p\rho_{\mathrm{major}} + (1-p)\rho_{\mathrm{spin}},$$

where p is a population parameter. The Fourier transform of ρ_{spin} is

$$f_{\mathrm{spin}} = 60 f_C \exp(-k^2 U_{\mathrm{spin}}/2)(\sin kR/kR), \qquad (1)$$
$$k = 4\pi \sin\theta/\lambda.$$

$R = 3.53$ Å is the libration-corrected radius of the C_{60} sphere obtained for the major orientation, U_{spin} is an isotropic displacement parameter, and f_C is the form factor of a C atom. This model was refined using only angle and rigid-link restraints and assuming site symmetry $\bar{3}$. The effective number of parameters is 11, *i.e.* population factor p, orientation angle φ_0, bond lengths, rigid-body translations and librations, U_{spin}, scale factor and extinction factor (Becker & Coppens, 1974). Convergence was easily reached at $wR(|F|^2) = 0.067$. All parameters assume reasonable values (Tables 1, 2).* Secondary-extinction corrections were large only for the two strongest reflections 111 and 220. The model used by Chow *et al.* (1992) uses 16 variable parameters and converged at a similar agreement factor of $wR(|F|^2) = 0.064$.

In order to confirm the absence of another preferred orientation at a different φ angle, a molecule in the minor orientation near $\varphi = 60°$ was added to the set of major orientations and the freely spinning C_{60} molecule. Refinement with fixed bond lengths again rotated the minor molecule to $\varphi \simeq 21°$ and resulted in negative rigid-body translations and very large librations.

Discussion

In the room-temperature structure, 61.1 (8) % of the molecules have one of their threefold axes aligned with a crystallographic threefold axis. Their orientation angle φ_0 is 7.1 (1)°. Population and orientation are comparable to the corresponding quantities of the major orientation at low temperaure (LT). The minor orientation at LT is replaced by freely spinning molecules at room temperature (RT). However, disorder increases in going from LT to RT even for the oriented part of the stucture. At LT, a molecule is orientated on only one threefold axis and with one rotation angle $\varphi_M \simeq +2°$, whereas at RT each molecule may be aligned along any of the four directions [111], [$\bar{1}$11], [1$\bar{1}$1] and [11$\bar{1}$], and may assume two rotation angles $\varphi_0 = \pm 7.1°$. Thus, the oriented part

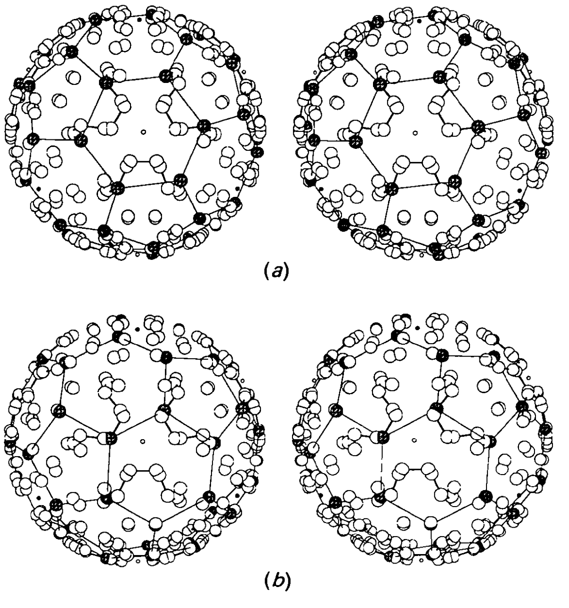

Fig. 1. Distribution of the atoms of eight superimposed molecules. The stereoviews are down the crystallographic threefold axis. Only the upper part of the sphere is drawn. Thick lines show distances shorter than 0.6 Å, thin bonds identify one of the C_{60} molecules, aligned on [111, $+\varphi_0$] in (*a*) and on [$\bar{1}$11, $-\varphi_0$] in (*b*). Dots and small circles identify the ⟨100⟩ and ⟨111⟩ directions, respectively. The distribution of atoms in this figure is to be compared with the continuous atomic number density distribution in Fig. 1 of Chow *et al.* (1992). The plots have been prepared with *ATOMS* (Dowty, 1991).

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* Lists of anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71107 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Results of the least-squares refinement*

p is the total population of the eight superimposed oriented molecules, the population of the homogeneous sphere is $1 - p$. D is the diameter of the molecule, the second number for the distances is the libration-corrected value. L and T are the librational and translational displacement factors of the oriented molecule parallel and perpendicular to the threefold axis. $y_{\min}$ is the smallest extinction factor. S is the goodness of fit including diffraction data and restraints. $R(|F|)$ includes reflections with $|F|^2 > 3\sigma(|F|^2)$, $wR(|F|^2)$ and S include all reflections. The weighted R value for $|F|^2$ is $wR(|F|^2) \simeq 2wR(|F|)$. All other symbols are explained in the text. E.s.d.'s are given in parentheses.

p	0.611 (8)
φ_0 (°)	7.1 (1)
$d_{6,6}$ (Å)	1.440 (6), 1.453 (6)
$d_{5,6}$ (Å)	1.359 (6), 1.372 (6)
D (Å)	6.992 (4), 7.057 (4)
L_{paral} (deg^2)	60 (1)
L_{perp} (deg^2)	61 (1)
T_{paral} (Å^2)	0.019 (2)
T_{perp} (Å^2)	0.022 (2)
U_{spin} (Å^2)	0.017 (3)
$y_{\min}(|F|^2)$	0.69
$(\sin\theta/\lambda)_{\max}$ (Å^{-1})	0.767
No. of observations	320
No. of $|F|^2 > 3\sigma(|F|^2)$	189
No. of restraints	206
No. of variables	94
S	1.24
$R(|F|)$	0.0358
$wR(|F|^2)$	0.0670

Table 2. *Positional, displacement and site occupation parameters of* C_{60} *at room temperature*

Sph is the sphere with constant electron density, p is the population factor. Eight molecular orientations are obtained with the following symmetry operations:
$[111, +\varphi_0]$: $\pm(x, y, z; z, x, y; y, z, x)$; $[111, -\varphi_0]$: $\pm(y, x, z; z, y, x; x, z, y)$;
$[1\bar{1}\bar{1}, +\varphi_0]$: $\pm(\bar{x}, y, z; \bar{z}, x, y; \bar{y}, z, x)$; $[1\bar{1}\bar{1}, -\varphi_0]$: $\pm(\bar{y}, x, z; \bar{z}, y, x; \bar{x}, z, y)$;
$[\bar{1}1\bar{1}, +\varphi_0]$: $\pm(x, \bar{y}, z; z, \bar{x}, y; y, \bar{z}, x)$; $[\bar{1}1\bar{1}, -\varphi_0]$: $\pm(y, \bar{x}, z; z, \bar{y}, x; x, \bar{z}, y)$;
$[\bar{1}\bar{1}1, +\varphi_0]$: $\pm(x, y, \bar{z}; z, x, \bar{y}; y, z, \bar{x})$; $[\bar{1}\bar{1}1, -\varphi_0]$: $\pm(y, x, \bar{z}; z, y, \bar{x}; x, z, \bar{y})$.
$p(\text{Sph}) = 0.3888\ (78)$; $p(\text{C1 to C10}) = [1.0 - p(\text{Sph})]/8 = 0.0764$; $U_{\text{eq}}(\text{C1 to C10}) = 2U_{\text{libration}}/3 + U_{\text{translation}} = 0.1730\ (35)$ Å^2; $U(\text{Sph}) = 0.0169\ (33)$ Å^2; $T_{\text{eq}} = \exp[-8\pi^2 U_{\text{eq}}(\sin\theta/\lambda)^2]$.

	x	y	z
C1	0.21002 (30)	0.12271 (51)	−0.04251 (13)
C2	0.19585 (18)	0.13925 (33)	0.05683 (22)
C3	0.11937 (23)	0.20551 (14)	0.06706 (20)
C4	0.08629 (38)	0.22991 (20)	−0.02596 (23)
C5	0.14231 (40)	0.17874 (40)	−0.09368 (24)
C6	0.10142 (53)	0.14382 (39)	−0.17321 (22)
C7	−0.05079 (56)	0.20626 (22)	−0.12582 (48)
C8	−0.00749 (56)	0.24329 (15)	−0.04158 (36)
C9	−0.07374 (33)	0.23305 (20)	0.03490 (44)
C10	−0.15798 (28)	0.18972 (26)	−0.00209 (49)
Sph	0.0	0.0	0.0

is disorded over eight symmetry-equivalent positions. Fig. 1 shows the distribution of the atoms resulting from these eight superimposed molecules.

The molecular thermal displacements are not far from isotropic. The translational displacements are somewhat larger than U_{spin} and compare reasonably well with the value of 0.0223 (3) Å^2 obtained by Chow *et al.* (1992). The r.m.s. librational displacements are 7.8 (1)°. This value gives a rough indication of a vibrational amplitude, but should not be taken at face value. Rather, it ought to be considered together with the orientation angle φ_0 as a parametrization of a strongly anharmonic libration as may be shown from the following considerations.

First we note that the C_{60} molecules of the oriented part can assume 480 distinct but symmetry-equivalent preferred orientations O_n $(1 \leq n \leq 480)$: each of the 20 hexagons may be placed perpendicular to each of the four crystallographic threefold axes and rotated about any of these axes to the six equivalent positions at $\pm\varphi_0$, $120 \pm \varphi_0$, $240 \pm \varphi_0$ $(20 \times 4 \times 6 = 480)$. Alternatively, one may say that a molecule with icosahedral symmetry is invariant with respect to 60 rotations and that the crystallographic symmetry $m\bar{3}m$ creates eight distinguishable, but equivalent orientations of C_{60}. Next, we define a reference orientation O_0 of C_{60} with crystallographic symmetry $\bar{3}m$; the $\bar{3}$ axis is along [111] and one of the mirror planes of C_{60} coincides with $(\bar{1}10)$. Any other orientation of C_{60} may be described with three angular coordinates (Θ, Φ, φ) where Θ and Φ define the direction of a rotation axis $\mathbf{r}$, Θ being the angle between $\mathbf{r}$ and [111]; starting from O_0, the orientation (Θ, Φ, φ) is realized by a rotation through the angle φ about $\mathbf{r}$. These angles span the configuration space for molecular reorientation. Thus, a rotation about [111] is specified by $(0, 0, \varphi)°$ and the two preferred orientations nearest to O_0 have coordinates $(0, 0, \pm\varphi_0)°$. At $(0, 0, \pm 22.24)°$, the crystallographic site symmetry of a C_{60} molecule is $m\bar{3}$. Finally, we consider an instantaneous orientation O_{inst} a molecule may assume in the course of its thermal displacements; O_{inst} is defined by $(\Theta_{\text{inst}}, \Phi_{\text{inst}}, \varphi_{\text{inst}})$. We wish to calculate the probability $P(O_{\text{inst}})$ of observing O_{inst}. This quantity is a function of the libration tensor $\mathbf{L}$ obtained in the structural refinement: $\mathbf{L}$ is the variance–covariance tensor of a Gaussian distribution which permits calculation of the probability that a molecule with orientation O_n librates to O_{inst}. The general problem to be solved is to find the 480 rotation axes and rotation angles $(\mathbf{r}_{n,\text{inst}}, \varphi_{n,\text{inst}})$ transforming each of the 480 O_n's into the same O_{inst}. These quantities are readily obtained from the corresponding orthogonal transformation matrices. The variance $L_{n,\text{inst}}$ for the rotation axis $\mathbf{r}_{n,\text{inst}}$ is easily computed from $\mathbf{L}$. Thus, $P(O_{\text{inst}})$ is the sum of 480 Gaussian distributions and of a constant term which takes into account the freely spinning molecules,

$$P(\Theta_{\text{inst}}, \Phi_{\text{inst}}, \varphi_{\text{inst}}) = (p/480) \sum_{n=1}^{480} (2\pi L_{n,\text{inst}})^{-3/2} \times \exp[-\varphi^2_{n,\text{inst}}/2L_{n,\text{inst}}] + 3(1-p)/4\pi^4. \qquad (2)$$

$p = 0.611$ is the population factor of the oriented part of the structure. Not all O_{inst} need be considered, but only an asymmetric region in configuration space.

We report here the probability density function $P(0, 0, \varphi_{\text{inst}})$ of molecular libration about the threefold axis [111] (Fig. 2). For all values of φ_{inst}, at most five of the 480 terms have $\varphi_{n,\mathrm{inst}} < 25°$ and contribute significantly. One of them is marked in Fig. 1(*a*), a second in Fig. 1(*b*), and the other three are obtained by rotations of these marked molecules about [111], in Fig. 1(*a*) by $-2\varphi_0$ and in Fig. 1(*b*) by ±120°. At $\varphi_{\mathrm{inst}} = 22.24°$, where the molecule has the cubic site symmetry $m\bar{3}$ and four of the molecular threefold axes coincide with the four crystallographic threefold axes, there are four important contributors with $\varphi_{n,\mathrm{inst}} = 15.1°$.

$P(0, 0, \varphi_{\mathrm{inst}})$ shows two important characteristics: it is monomodal with a single maximum (0.0462) at $\varphi_{\mathrm{inst}} = 0°$, and it has a plateau of constant density ($\simeq 0.0224$) between $\varphi_{\mathrm{inst}} = 21$–$26°$ near the cubic site symmetry at 22.24°. It drops to the constant background value of 0.0030 at $\varphi_{\mathrm{inst}} > 55°$. The minor orientation of the LTS is clearly not a preferred orientation. The shape of the curve shows that the preferred orientation has site symmetry $\bar{3}m$ and that the libration about the $\bar{3}$ axis is highly anharmonic. The plateau indicates that the cubic position is important. Starting from there, a molecule may rotate about any of the crystallographic threefold axes to reach $\bar{3}m$ orientations. The shortest path between two $\bar{3}m$ orientations is a rotation of $\varphi_{\mathrm{inst}} = 36.24°$ about the axis $\Theta_{\mathrm{inst}} = 35.78$, $\Phi_{\mathrm{inst}} = -11.12°$; along this path, P is a superposition of two Gaussians with a minimum exactly midway between the maxima, $P(35.78,\ -11.12,\ 18.12) = 0.0197$. Curves $P(90, \Phi, \varphi_{\mathrm{inst}})$ representing the molecular libration about axes perpendicular to [111] do not show much anharmonicity; peaks of maximum probability at $\varphi_{\mathrm{inst}} = 0$ and $\simeq 68°$ are separated by large regions of minimal probability.

The shape of $P(0, 0, \varphi_{\mathrm{inst}})$ suggests an alternative model where the orientated part is represented by two molecules with different population parameters, one with $\bar{3}m$ and the other one with $m\bar{3}$ site symmetry. This model was indeed successfully refined. It represents an alternative parametrization of the same probability density function, but it uses a larger number of adjustable parameters.

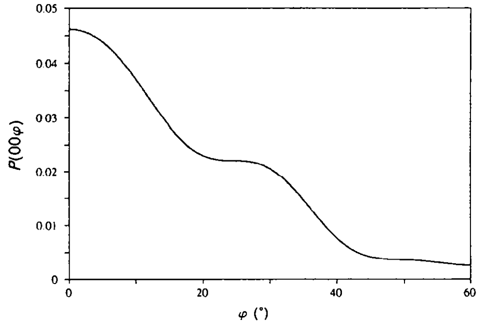

Fig. 2. Probability density function $P(0, 0, \varphi_{\mathrm{inst}})$ for libration of C_{60} about the crystallographic threefold axis [111].

Table 3. *Intermolecular contact distances smaller than 3.5 Å and corrected for librational effects for molecular site symmetry* $\bar{3}m$, $\varphi = 0°$

The symmetry operations listed below and their products with the operations of $\bar{3}m$ generate the atoms next to a molecule centred at 0,0,0: (1) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (2) $\frac{1}{2} - x, \frac{1}{2} - y, z$; (3) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (4) $\frac{1}{2} + x, y, -\frac{1}{2} + z$; (5) $\frac{1}{2} + x, -y, -\frac{1}{2} + z$. Average e.s.d.'s are 0.006 Å. The number of times a distance occurs is shown in square brackets.

6,6 bond on pentagon	Pentagon on pentagon	6,6 bond on 6,6 bond
(1) 3.253, 3.320, 3.434,	(2) 3.332 [2], 3.435 [2]	(4) 3.090 [2], 3.381 [2]
3.453, 3.482, 3.499	(3) 3.434, 3.435 [3]	(5) 3.183 [2], 3.294 [2]

From the classical Boltzmann distribution

$$P_1/P_2 = \exp[-\Delta E_{1,2}/\mathrm{RT}],$$

energy differences ΔE are 1.7 kJ mol^{-1} between the maximum at $\varphi_{\mathrm{inst}} = 0$ and the plateau at $\varphi_{\mathrm{inst}} = 22°$, and 6.6 kJ mol^{-1} between $\varphi_{\mathrm{inst}} = 0$ and 60°. The latter energy depends, of course, sensitively on the constant background value of P. Our results may be compared with the NMR value of 5.9 (4) kJ mol^{-1} (Johnson, Yannoni, Dorn, Salem & Bethune, 1992), and with the value of 3.4 (1.5) kJ mol^{-1} from coherent quasielastic neutron-scattering measurements (Neumann *et al.*, 1991).

The intermolecular contact distances between oriented molecules are reported in Table 3. They have been calculated for the molecular reference orientation O_0 at the maximum of the monomodal probability density function. The corresponding atomic coordinates were corrected for the effects of librational motion. As in the LTS, each molecule has six neighbours facing a 6,6 bond in the equatorial plane perpendicular to its threefold axis, and six neighbours above and below this plane facing pentagons. Every neighbour may assume four orientations generated by the $m\bar{3}m$ symmetry. This results in three types of contacts: (1) A 6,6 bond is aligned with a pentagon. Contacts in the equatorial plane and out of the equatorial plane are equal. On average, 50% of the contacts are of this type which corresponds to the energetically most favourable arrangement at LT. The shortest distance is 3.25 Å, 0.11 Å longer than at LT where the shortest contact is 3.14 Å. This increase is explained in part by the larger cell constant at RT. (2) A pentagon is aligned with a pentagon. These contacts are realized with 25% probability. They may be somewhat less favourable energetically than (1), but the distances are of comparable lengths, the shortest being 3.33 Å. (3) A 6,6 bond is aligned with a 6,6 bond, with a probability of 25% . The shortest contact in this class, 3.090 Å, is clearly shorter than the contacts at LT. This value should not be taken literally: two molecules in this mutual orientation may well repel each other by about 0.1 Å. This is less than the r.m.s. translational displacement amplitudes of about 0.15 Å. In summary, 75% of the intermolecular contacts are roughly as favourable as those observed at LT. Only one of these 14 favourable contact lengths is considerably shorter than the distance of 3.35 Å between layers in graphite.

Concluding remarks

Although the population factor p of 61.1 (8)% and the most probable orientation angle of C_{60} at RT are comparable to the corresponding quantities at LT, the RTS is probably not simply a somewhat more disordered version of the LTS. At the phase transition which is first order (Heiney *et al.* 1991), the molecular motion is profoundly modified. The molecules seem to move quite freely, but occasionally lock in a position of $\bar{3}m$ symmetry which is energetically favourable and very close to the major orientation of the LTS. A particularly favourable low-energy reorientation pathway which flips a molecule between different $\langle 111 \rangle$ directions passes through an orientation with cubic molecular site symmetry $m\bar{3}$. This transitional position is reached from the most favourable position by a rotation about the threefold axis of only 22°. The average number of favourable intermolecular contacts (75%) is unchanged after the flipping. The minor orientation observed in the LTS is not favoured in the RTS.

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Structure of $K_{1.0}Ti_8O_{16}$ and $K_{0.0}Ti_8O_{16}$

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Abstract

Potassium titanium bronze $K_{1.0}Ti_8O_{16}$ and its chemically oxidized '*exuviae*' oxide $K_{0.0}Ti_8O_{16}$ crystallize in a tetragonal system, $I4/m$, with the hollandite-type one-dimensional tunnel structure. For $K_{1.0}Ti_8O_{16}$, $M_r = 678.13$, $a = 10.1776$ (5), $c = 2.9614$ (2) Å, $V = 306.75$ (3) Å^3, $Z = 1$, $D_x = 3.67$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 5.55$ mm^{-1}, $F(000) = 323$, $T = 298$ K, $R = 0.048$ for 947 unique observations. For $K_{0.0}Ti_8O_{16}$, $M_r = 639.03$, $a = 10.164$ (2), $c = 2.9631$ (7) Å, $V = 306.1$ (1) Å^3, $Z = 1$, $D_x = 3.47$ Mg m^{-3}, $\mu = 5.21$ mm^{-1}, $F(000) = 304$, $R = 0.020$ for 1084 independent reflections. The structural modification caused by K deintercalation *via* oxidation of the host framework is followed using the present data as well as those from two previous studies of the bronze

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