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Structure and phase transition of the 6,5-annulene isomer of $C_{61}H_2$

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We have used differential scanning calorimetry and x-ray diffraction to study the crystalline phases of the 6,5-annulene isomer of $C_{61}H_2$. At 308 K the methylenated fullerenes are orientationally disordered in a face-centered cubic lattice with lattice parameter 14.19 ± 0.02 Å. Below $T_c = 290$ K the symmetry is lowered to $Pa\bar{3}$, a simple cubic structure. At 20 K the lattice parameter is 14.06 ± 0.02 Å, with substantial statistical disorder remaining. The transition temperature in $C_{61}H_2$ is slightly higher than in $C_{60}O$ and higher still than in C_{60}, but the three compounds exhibit orientationally ordering transitions between qualitatively similar phases.

I. INTRODUCTION

C_{60} and its derivatives continue to attract considerable attention, due to both the elegant molecular structures involved and the intriguing structural, dynamic, and electronic properties of the solid phases of fullerenes.[1] Pristine C_{60}, which has the form of a spherical shell, undergoes a transition from a high-temperature orientationally disordered face-centered cubic (fcc) phase (i.e., a plastic crystal) to a low-temperature orientationally ordered simple cubic (sc) phase.[2] This transition, and the structures of the high- and low-temperature phases, have been the objects of numerous experimental[3-5] and theoretical[6] studies.

Due to the nearly spherical shape of the C_{60} molecule, one might expect that the angular component of the intermolecular van der Waals interactions would be relatively small, and that the molecules would be disordered down to quite low temperatures. In fact, Coulomb interactions arising from excess charge in the vicinity of the double bonds also play an important role, both in stabilizing the observed $Pa\bar{3}$ simple cubic structure and in raising the transition temperature.[7-9] Presumably, further deviations from spherical symmetry should increase the transition temperature.

To establish these systematics, it is instructive to consider the thermal behavior of solids composed of molecules that are closely related to, or derived from, C_{60}. Compounds that are derived from C_{60} by adding large side groups[10] are orientationally ordered at room temperature and are quite likely to remain so up to the decomposition temperature of the solid; if the structure is perturbed far from spherical symmetry then rotational motion is no longer possible. By contrast, the addition of a single oxygen atom to form the fullerene epoxide $C_{60}O$ is a relatively small perturbation to the molecular architecture, and as such the solid state structure of $C_{60}O$ may be expected to be quite similar to that of C_{60}, even though the symmetry of the constituent molecules has been drastically reduced. A calorimetry and x-ray powder diffraction (XRPD) study[11] of crystalline $C_{60}O$ confirmed that this is the case. At room temperature, $C_{60}O$ is orientationally disordered with a fcc lattice, $a = 14.185$ Å. However, the entropy is reduced by the requirement that the epoxide moieties point towards octahedral or tetrahedral voids. Upon cooling, an orientational ordering transition at 278 K leads to a low-temperature simple cubic phase. At 19 K, this phase is

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qualitatively similar to the orientationally ordered $Pa\bar{3}$ phase of C_{60}, with $a = 14.062$ Å, but with additional randomness due to a distribution of orientations of the epoxide atoms, which again are found only within the octahedral and tetrahedral voids.

The above observations lead us to observe that the increase in transition temperature from C_{60} to $C_{60}O$ may actually be primarily an entropic, rather than energetic, effect. The orientations of the C_{60} shells are essentially the same in the low-temperature phases of C_{60} and $C_{60}O$. Thus, the ground state structure is primarily determined by the nonspherical component of the C_{60}-C_{60} interactions, but the entropy of the high-temperature phase is reduced by the steric requirement that oxygen atoms be found in voids. This has the net effect of driving up the transition temperature.

In this paper we report a combined XRPD and calorimetry study of the 6,5-annulene isomer of $C_{61}H_2$ (Fig. 1). The methylene group is larger than the epoxide moiety in $C_{60}O$ and projects farther from the surface. Thus, there are two natural possibilities for the structure: essentially the same sequence from orientationally disordered to sc may be followed, but with a higher transition temperature, or the symmetry at all temperatures may be lowered by orientational ordering of the methylene groups. (For example, if the methylene groups acquired "ferromagnetic" order so that they all pointed in the same direction, the lattice symmetry would necessarily be lower than cubic.) In fact, we observe that the 6,5-annulene isomer of $C_{61}H_2$ is very similar in its behavior to C_{60} and $C_{60}O$.

There are two known isomers of $C_{61}H_2$: the 6,5-annulene and the cyclopropane. The 6,5-annulene isomer[12] [Fig. 1(a)] has a nine-membered ring which derives from a hexagon and a pentagon, with a methylene unit bridging what used to be a shared bond between the two rings. The cyclopropane or 6:6 isomer[13] of $C_{61}H_2$ is composed of a three-membered ring possessing a methylene unit that bridges two hexagons [Fig. 1(b)]. It is
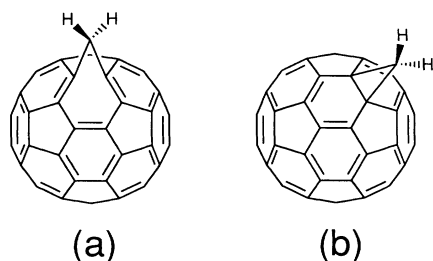

(a)   (b)

FIG. 1. The two known isomers of $C_{61}H_2$. (a) shows the 6,5-annulene isomer in which a nine-membered ring is formed from a hexagon and a pentagon, and the carbon in the methylene group does not form a ring with the two carbon atoms to which it bonds, but instead leaves an "open" structure. This is the isomer discussed in this paper. (b) shows the cyclopropane isomer recently synthesized by Smith et al. (Ref. 13), in which the methylene group bridges two hexagons of the C_{60} cage. Notice that the methylene group in this case is part of a three-membered ring. This is the methylene analog of $C_{60}O$.

an isostere of $C_{60}O$, wherein an oxygen atom bridges a 6,6-ring fusion. Future work will address the solid state structure of the cyclopropane isomer.

The remainder of this paper is organized as follows. In Sec. II we discuss sample preparation and characterization. In Sec. III we describe the acquisition and analysis of XRPD data. Section IV describes the results of XRPD measurements at 308 K and Sec. V describes the calorimetric evidence for a phase transition and the results of XRPD measurements at 20 K. We conclude with a brief discussion of our results in Sec. VI.

II. SAMPLE PREPARATION AND CHARACTERIZATION

Our synthesis of the annulene isomer of $C_{61}H_2$ follows the procedure outlined by Suzuki et al.;[12] here we report more extensive details. Chromotographically pure C_{60} was prepared as previously described[14] with an additional purification via flash column chromatography on Norit A and Silica (2:1 wt:wt mixture[15]). A solution of C_{60} (100 mg, 0.14 mmol) in toluene (200 ml) was then treated with ethereal diazomethane (0.31M, 0.45 ml) at 0 °C. The resultant pyrazoline was isolated in solution via column chromatography on SiO_2; following elution of unreacted C_{60} with 10:1 hexane/toluene, the solvent polarity was gradually increased to 10:1 toluene/hexane, affording a brown solution of the pyrazolines. The pyrazoline solution (ca. 0.25mM) was then immediately heated to reflux until the color of the solution turned to purple. Concentration of the solution (in vacuo) afforded pure $C_{61}H_2$ (30 mg, 30% yield) as a black solid. The sample was further dried at 10^{-7} Torr at 25 °C for 24 h, and then sealed in a capillary under primary vacuum.

It is well known that residual solvent can dramatically affect the crystal structures and transitions of fullerenes.[3,15,16] Most of the probes which have been used to detect traces of solvent in C_{60} and C_{70}, such as nuclear magnetic resonance, infrared absorption, or prompt γ activation analysis, are sensitive to the presence of hydrogen atoms or C-H stretches. Such tests are clearly more difficult to apply to a hydrogen-containing compound such as $C_{61}H_2$, wherein the mere observation of C-H stretch modes is not enough to indicate the presence of solvent. We have nevertheless attempted to characterize our samples using Fourier transform infrared reflectance (FTIR). While some infrared band structure was observed in the C-H stretch region of the spectrum, we observed none of the absorption peaks characteristic of intercalated toluene, as seen previously, for example, in C_{70}.[16] We conclude, therefore, that our sample did not contain substantial amounts of toluene.

The sample was additionally characterized via differential scanning calorimetry measurements using a TA Instruments 2100 thermal analyzer. An 8 mg sample was heated in an aluminum crimped pan and cooled using liquid nitrogen. The results from these measurements will be presented in Sec. V.

III. X-RAY DATA ACQUISITION AND METHOD OF ANALYSIS

The XRPD data were collected on Beamline X3B1 at the National Synchrotron Light Source, Brookhaven National Laboratory. An incident beam of wavelength 1.150 75 Å was selected by a Si(111) monochromator and monitored by an ion chamber. The diffracted beam was detected using a Ge(111) analyzer crystal and a NaI scintillation counter. Complete diffraction profiles were collected between 5° and 43° at 20 K, 268 K, and 308 K, counting for an average of 4 sec at intervals of 0.005°. Data were normalized to counts per second at a synchrotron ring current of 100 mA. The actual ring current varied between 90 and 250 mA. The sample was cooled in an APD Cryogenics model DE201A closed-cycle cryostat, in a He atmosphere contained in a Be can at the sample temperature. In the low-temperature data sets, the sample temperature fluctuated from 15 to 30 K. Close to the phase transition, the stability was on the order of 0.3 K, with an absolute calibration accuracy of 1 K.

An individual background scattering profile was estimated for each temperature profile by linear interpolation between data points far from diffraction peaks. Initial Rietveld refinements of the data were complicated by stacking faults, which resulted in small symmetry-dependent shifts in Bragg peak position and line shape. Accordingly, the final analysis was accomplished using least-squares fits to previously fitted peak integrated intensities. To model the individual peak shapes, which were in many cases somewhat asymmetric, we used a function consisting of a Gaussian plus an asymmetric Lorentzian:

$$I(q) = I_p \left\{ \frac{f}{\delta} \sqrt{\frac{4\ln 2}{\pi}} \exp\left[-4\ln 2 \left(\frac{q-q_0}{\delta}\right)^2\right] + \frac{(1-f)}{\pi(\kappa_1 + \kappa_2)} \frac{1}{\frac{1}{4} + \left(\frac{q-q_0}{\Gamma(q)}\right)^2} \right\},$$

$$\Gamma(q) \equiv \begin{cases} \kappa_1, & q < q_0, \\ \kappa_2, & q \geq q_0, \end{cases} \tag{1}$$

where f is the fraction of Gaussian component, q_0 is the peak position, and κ_1, κ_2, and δ are adjustable half-widths. The Gaussian and Lorentzian components are normalized such that the area under each is unity. The half-widths (half widths at half maximum) had values between 5×10^{-3} Å^{-1} and 1×10^{-1} Å^{-1}, with κ_1 and κ_2 differing by up to 20% in a given peak. f was always in the range 0.0 to 0.2, indicating that the peaks were primarily Lorentzian in nature.

The results of the above fits were then used in two ways. The peak positions q_0 were used to determine the cubic lattice parameter, while the integrated peak intensities I_p were used as input to refinements of various postulated structures. The significance of new parameters introduced into the model structures was assessed using Hamilton's significance tests.[17] Parameters which failed to decrease the weighted R factor at the 5% confidence level were rejected.
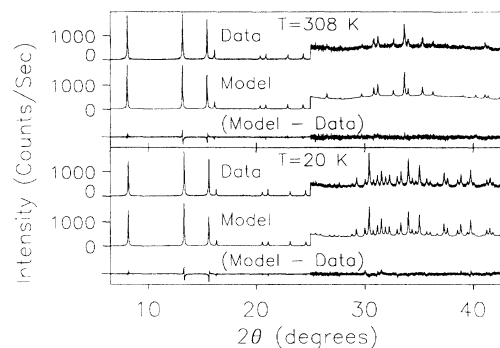

FIG. 2. X-ray powder diffraction profiles, model profiles, and (model−data) for the 6,5-annulene isomer of $C_{61}H_2$ at 308 K and 20 K. Intensity is shown in counts per second normalized to a synchrotron ring current of 100 mA. The typical counting time was 4 sec. At 308 K the molecules are orientationally disordered in a face-centered cubic lattice, with the methylene groups preferentially pointing toward octahedral voids. At 20 K the structure is simple cubic, space group $Pa\bar{3}$, with the methylene group again occupying octahedral voids.

The total uncertainty in the integrated peak intensities $\sigma(I)$ was given by the sum in quadrature of the variance from counting statistics, σ_c^2, and a typical 3% replication uncertainty:[11] $\sigma^2(I) = \sigma_c^2 + (0.03I)^2$. To illustrate the quality of our model fits, in Fig. 2 we plot calculated diffraction patterns using Lorentzian line shapes with integrated intensities generated by our model calculations.

IV. ANALYSIS OF 308 K PROFILE

The room-temperature lattice was determined to be fcc with a cubic lattice parameter of 14.19 ± 0.02 Å. Unlike the case of C_{60}, for which the symmetry of the molecules permits in principle an orientationally ordered structure with space group $Fm\bar{3}$, the low symmetry of the $C_{61}H_2$ molecule implies that the fcc lattice must incorporate molecular orientational disorder. For a detailed structural model, we are guided by previous experience with $C_{60}O$.[11] In both $C_{60}O$ and the 6,5 isomer of $C_{61}H_2$, the epoxide or methylene groups are too large for the molecule to have completely random orientations given the observed lattice parameters, and the orientational disorder is constrained by the requirement that the additional group point toward a void. X-ray diffraction measures the time average of Fourier transforms of "snapshots" of the structure. Thus, the quantity of interest is the average molecular structure. An XRPD measurement does not in general distinguish between static and dynamic disorder. In the high-temperature phase of $C_{60}O$, it was found that on average approximately $\frac{2}{3}$ of the oxygen atoms pointed randomly along the $\langle 100 \rangle$ axes and $\frac{1}{3}$ along the $\langle 111 \rangle$ axes, and that each molecule was cylindrically disordered about the axis of its oxygen atom, with additional librational motion which smeared the average charge density into an almost smooth sphere.

For our analysis, we assumed as above that the methy-

lene groups occupied either octahedral voids (along $\langle 100 \rangle$ directions) or tetrahedral voids (along $\langle 111 \rangle$ directions) with adjustable probabilities α and $1 - \alpha$. Clearly, from the symmetry of the system, the methylene group must have an equal probability $\frac{\alpha}{6}$ of occupying each octahedral site and an equal probability $\frac{1-\alpha}{8}$ of occupying each tetrahedral site. Thus, the average molecule used in the XRPD analysis had up to 14 fractional methylene groups. In practice, we found that the occupation of the tetrahedral voids refined to zero, so that $\alpha = 1.0 \pm 0.1$. Our constraint on the methylene group position does not completely determine the orientation of the cage, but only constrains it to rotate along one of three octahedral axes. Thus each molecule must exhibit cylindrically symmetric statistical disorder along a randomly chosen [100] direction to preserve the cubic symmetry. Since we expected that, as in the case of $C_{60}O$, librational modes would tend to further average the orientational disorder, the carbon shell was modeled by a smooth sphere of charge.

From the 308 K profile in Fig. 2 we extracted 26 intensities, 22 of which were above the baseline uncertainty of approximately 100 counts/sec under the peak. The fitting parameters for the structural model were the radius of the C_{60} shell, the radius of the methylene group (i.e., its distance from the center of the C_{60} shell), and a thermal factor for the entire $C_{61}H_2$ molecule. We rejected the addition of a separate thermal factor for the methylene group because it was not significant at the 5% level.

The probability of the methylene group occupying tetrahedral or octahedral voids was assessed in several ways. We first assumed a variable number of methylene groups per C_{60}. As the number of tetrahedral-site methylene groups per C_{60} was varied from 0 to 1, R_{wi} increased monotonically from 0.13 to 0.16. Conversely, as the number of octahedral-site methylene groups per C_{60} was varied from 0 to 1, R_{wi} decreased from 0.13 to 0.08: a significant decrease at the 0.5% confidence level. When we constrained the number of methylenes per C_{60} to be 1.0 and allowed the parameter α (which as discussed above measures the relative occupancy of octahedral and tetrahedral sites) to vary, we obtained $\alpha = 1.0 \pm 0.1$ indi-

cating a strong preference for octahedral-site occupation and essentially zero tetrahedral-site occupation. In the final refinements, α was fixed at 1.0.

The radius of the carbon shell refined to 3.555 ± 0.007 Å. The thermal factor indicates a 0.12 ± 0.03 Å root-mean-squared (r.m.s.) isotropic displacement of the molecular center of mass. Since the hydrogen atoms make a negligible contribution to the scattered intensity, we disregarded them in our analysis and considered only the methylene carbon atom. The radius of the methylene group in the octahedral void refined to 4.9 ± 0.2 Å. Assuming that the bridging carbons are separated by approximately 1.455 Å as in unmodified C_{60},[18] this yields a methylene group to carbon atom bond length of 1.6 ± 0.2 Å.

The refined values of the parameters are listed in Table I and the profile generated from the results of the refinement is shown in Fig. 2. We obtained $\chi^2 = 1.2$, $R_i = 0.03$, and $R_{wi} = 0.08$. This high level of agreement between model and data indicates that the model captures the essential features of the structure.

V. ANALYSIS OF 20 K PROFILE AND EVIDENCE FOR A PHASE TRANSITION

Differential scanning calorimetry on heating shows a first-order phase transition at 290 ± 5 K with an enthalpy change of 9.0 ± 0.5 $J g^{-1}$ (see Fig. 3). The transition temperature is considerably higher than either the 260 K transition temperature in C_{60} or the 278 K transition temperature in $C_{60}O$. This is consistent with the hypothesis that the epoxide or methylene group has the effect of reducing the entropy of the high-temperature phase, thus driving the transition temperature up. The carbon atom in the methylene group is not at a significantly larger radius than the oxygen atom (4.9 ± 0.2 Å for carbon vs 4.71 ± 0.01 Å for oxygen). However, the two hydrogen atoms which were neglected in structure factor calculations play an important steric role. Our analysis of the high-temperature phase indicates that the probability of finding the methylene group in the tetrahedral sites is

TABLE I. Refined values of parameters for both the 308 K and 20 K profiles. Uncertainties were determined by finding upper and lower values of the parameters which could be rejected at a 10% confidence level using Hamilton's significance tests (Ref. 17).

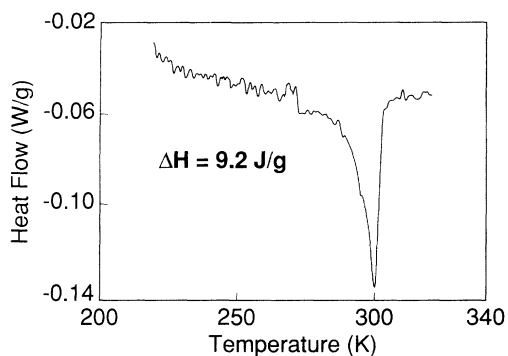| Fitting parameters	308 K	20 K
Lattice parameter	14.19 ± 0.02 Å	14.06 ± 0.02 Å
Methylene radius	4.9 ± 0.2 Å	4.8 ± 0.2 Å
C_{60} shell radius	3.555 ± 0.007 Å	3.555 ± 0.007 Å
Occupancy of octahedral site	1.0 ± 0.1	1.0 ± 0.1
ϕ_1		$24.6° \pm 0.8°$
ϕ_2		$89° \pm 1°$
Occupancy of ϕ_1 orientation		0.66 ± 0.03
$\langle u_s \rangle$ of carbon shell	0.12 ± 0.03 Å	
Goodness of fit		
χ^2	1.2	0.90
R_i	0.03	0.06
R_{wi}	0.08	0.09

FIG. 3. Differential scanning calorimetry scan of $C_{61}H_2$ upon heating showing an enthalpy change of 9.0 ± 0.5 J/g at the transition from simple cubic to face-centered cubic. The onset temperature is 290 ± 5 K. The data were taken on heating at a rate of 5 °C/min.

low. Thus, the high-temperature phase of the 6,5 isomer of $C_{61}H_2$ should have lower entropy than that of $C_{60}O$, and we would expect the transition temperature to be higher.

The existence of a phase transition between 308 K and 268 K is confirmed by XRPD data showing fcc and sc structures, respectively, at those temperatures. Below 290 K the XRPD profile displays peaks with mixed odd and even Bragg indices (see Fig. 2), indicating a simple cubic structure. We extracted 58 intensities, 43 of which were above the baseline uncertainty. On the basis of the systematically absent reflections (i.e., $k = 2n$ for $0kl$), the space group $Pa\bar{3}$ was assigned, like those of orientationally ordered C_{60} and $C_{60}O$. To calculate the molecular structure factor, we used a standard model for the C_{60} carbon cage[19] and appended a methylene group. The methylene group was replaced by a carbon for analysis and centered over the carbon-carbon 6:5 bond at a variable radius from the center of the carbon shell.

$Pa\bar{3}$ symmetry can be achieved by starting with each of the four molecules in the fcc unit cell with its twofold axes along the three $\langle 100 \rangle$ directions. There are two choices for such a "standard orientation;" we use that of Harris and Sachidanandam.[20,21] The molecules centered at $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{2},0,\frac{1}{2})$, and $(0,\frac{1}{2},\frac{1}{2})$ are then rotated through an angle $\phi_1 \neq 0$ about the $(1,1,1)$, $(1,\bar{1},\bar{1})$, $(\bar{1},\bar{1},1)$, and $(\bar{1},1,\bar{1})$ directions, respectively, ϕ_1 being one of the fitting parameters. In C_{60}, it is observed that there is considerable orientational disorder even in the nominally ordered $Pa\bar{3}$ phase. This disorder has been modeled[3,7] as arising from a thermal population of molecules with a second orientation generated by a rotation through ϕ_2. Applying a similar model to $C_{61}H_2$, we find that the fit is improved by incorporation of a second rotation angle. The two angles were found to be $\phi_1 = 24.6° \pm 0.8°$ and $\phi_2 = 89° \pm 1°$. The probability of finding a molecule in the 25° orientation was found to be 0.66 ± 0.03.

The two rotation angles and their respective probabilities were refined without including the contribution to the diffracted intensity from the methylene group. We then used this information to find the bonds on each C_{60} shell which were closest to the octahedral and tetrahedral voids. We next allowed variable occupancies of these selected bonds by methylene units and observed the quality of fit as different bonds were populated.

The symmetry elements of the $Pa\bar{3}$ space group take a general position in the unit cell to 23 other equivalent positions. Thus, if we consider a methylene carbon atom position associated with a 6:5 bond near an octahedral void, there are 24 equivalent positions, all near octahedral voids, corresponding to the six octahedral directions available to each of the four molecules in the unit cell. In order to add a methylene group to a molecule in a manner consistent with $Pa\bar{3}$ symmetry, we therefore added $\frac{1}{6}$ of a methylene group in six different places on the same molecule. Physically, this corresponds to a statistically disordered crystal in which the molecules equally populate six equivalent orientations.

For each of the two orientations, 25° and 89°, we used ten inequivalent trial methylene positions, over 6:5 bonds and near lattice voids. Five were near tetrahedral voids, and five were near octahedral voids. For each of these candidate positions, we placed the carbon atom over the center of the 6:5 bond at a variable radius from the carbon shell center. None of the positions near tetrahedral voids improved the fit. For each of the orientations, we found only one position near the octahedral voids which improved the fit at the 5% confidence level; this was the closest bond to the octahedral void. To place limits on the occupancy of the tetrahedral voids, we chose the bond near the tetrahedral void which degraded the fit the least, and varied the relative concentration of the octahedral and tetrahedral voids until R_w increased above the 10% confidence level. We find that there is at most 0.1 of a methylene group near the tetrahedral void. Thus, including the constraint of one methylene unit per C_{60}, we conclude that, as in the high-temperature phase, the octahedral-site occupancy is 1.0 ± 0.1.

In our fits, the radius of the extra carbon refined to 4.8 ± 0.2 Å. Table I shows a list of the refined values of all parameters except the overall amplitude. Neither the addition of a thermal factor for the entire $C_{61}H_2$ molecule nor the addition of a thermal factor for the methylene group alone produced a significant improvement in the fit at the 5% confidence level. The goodness-of-fit parameters $\chi^2 = 0.90$, $R_i = 0.06$, and $R_{wi} = 0.09$ again indicate that our model provides a good description of the data.

VI. DISCUSSION

The 6,5-annulene isomer of $C_{61}H_2$ is similar to $C_{60}O$ in several ways. The high-temperature phase in both compounds consists of orientationally disordered molecules in a fcc lattice. In our model, the CH_2 group or oxygen atom points toward a lattice void while the molecule rotates about the axis passing through the attached group. In both molecules, the octahedral direction was preferred (occupation of octahedral sites were 1.0 ± 0.1 for $C_{61}H_2$, 0.7 ± 0.2 for $C_{60}O$); there appears to be a slightly en-

hanced probability of finding the molecules near octahedral voids in $C_{61}H_2$, consistent with the hypothesis that the transition temperature is driven up by the decrease in entropy of the disordered phase. This hypothesis could in principle be tested by detailed comparison of the transition enthalpies for C_{60}, $C_{60}O$, and $C_{61}H_2$. However, the spread in enthalpies in C_{60} prepared by different methods or different groups is sufficiently large[3,22] that such a comparison is not feasible at this time. Presumably, as larger and larger appendages are added to the C_{60} cage the transition temperature will increase further until one reaches the point where cubic lattices are less thermodynamically stable than lower-symmetry structures.

Riccò et al.,[23] using nuclear magnetic resonance and quasielastic neutron scattering to study mixtures of C_{60} and the 6,5-annulene isomer of $C_{61}H_2$, have observed two relaxation times which are consistent with this model. One corresponds to rotation of the molecule along the axis of the CH_2 group. The second slower mode is interpreted as the axis of rotation jumping from one interstitial (probably octahedral) site to another.

In the low-temperature phase both compounds exhibit $Pa\bar{3}$ symmetry with partial occupation of two angles of rotation near 24° and 89°, and the methylene group or oxygen atom pointing toward an octahedral void. We find a higher degree of orientational disorder, as characterized by the probability of finding the molecule in the 89° orientation: $34\pm3\%$ for the $C_{61}H_2$ as compared to 6% for $C_{60}O$. This may reflect the differing dynamics of the two molecules: if the time scale for reorientation of $C_{61}H_2$ is longer, the orientational disorder will be quenched at a higher temperature, and more disorder should be observed at 20 K.

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