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Local intermolecular correlations in C_{60}

Ruizhong Hu and T. Egami
Department of Materials Science and Engineering, Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania 19104-6272

Fang Li and J. S. Lannin
Department of Physics, Penn State University, University Park, Pennsylvania 16802

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A neutron-powder-diffraction real-space structural refinement method is applied to study the local intermolecular correlations in bulk C_{60} solid at 10 K. We found that the orientation of the C_{60} molecules often deviates locally from the long-range average structure, and a significant number (30–40%) of molecules have the sixfold face oriented toward adjacent molecules.

The discovery of the fullerene, C_{60}, and its superconducting derivatives, M_3C_{60} (M=K, Rb), has raised hopes that this new form of carbon may produce solids with unusual properties which may be useful in various applications.[1] At room-temperature C_{60} molecules are known to arrange themselves in the face-centered-cubic structure, while they themselves are freely rotating. Below about 250 K, intermolecular orientational correlations set in, and the structure changes to the $Pa\bar{3}$ symmetry.[2–5] In this structure each molecule is rotated from the reference orientation by the same angle, but around four different $\langle 111 \rangle$ axes. At the same time, however, significant structural disorder was found to exist even after annealing.[4] The presence of disorder is obvious in the diffraction pattern because of the strong diffuse scattering intensity (as high as 30% in terms of the total integrated intensities). The disorder can be qualitatively described by the disordering of intermolecular correlation, but its nature has not been well characterized.

In this paper we describe the results of the pulsed neutron atomic pair distribution function (PDF) analysis in determining the nature of the local structural disorder in C_{60} at low temperatures. The analysis of the room-temperature PDF was published in Ref. 6. The PDF describes the distribution of interatomic distances, and can be obtained by Fourier-transforming the normalized scattering intensity. Since the PDF is determined from both the Bragg and diffuse scattering intensities, it can describe the interatomic correlations accurately even in the presence of disorder, while in the conventional crystallographic structural analysis disorder can be handled only approximately. For this reason the PDF analysis has traditionally been applied exclusively to liquids and glasses,[7,8] but recently it has been applied to disordered crystalline solids such as superconducting oxides and yielded important information that is practically unattainable by other techniques.[9,10]

A 580-mg powder samples was prepared by the standard chromatographic separation procedure.[11] Fourier-transform infrared analysis confirmed the high purity of the C_{60} phase, while NMR and neutron absorption prompt γ analysis indicated about 1 at.% of hydrogen. Neutron powder diffraction measurements were performed on the special environment powder diffractometer (SEPD) instrument of the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. The low-temperature measurements were carried out at 10 K with the sample sealed in a vanadium container and cooled by a displex closed-cycle refrigerator.

The powder-diffraction pattern can be indexed using a simple cubic lattice (space group $Pa\bar{3}$) with a lattice parameter equal to 14.05 Å in agreement with other studies.[2–5] The structural coherence length is about 100 Å measured by the width of the Bragg peaks. In spite of the relatively short coherence length compared to other reports, the long-range order of the structure is very similar to what has been observed by other researchers. A careful comparison of the experimental powder-diffraction intensity with a calculated intensity for a structural model with $Pa\bar{3}$ symmetry shows that the rotation angle of each C_{60} molecule around the designated threefold axis is about 25° in agreement with previous studies.[3–5] Two strong diffuse scattering peaks are observed at around $Q=3.4$ and 5.5 Å^{-1} in the diffraction spectrum, where Q is the scattering vector ($=4\pi\sin\theta/\lambda$, where θ is the diffraction angle and λ is the wavelength of incident neutrons), and more are seen in a higher Q range.

The powder-diffraction spectrum has been corrected for absorption, multiple-scattering, the scattering intensities from background, the vanadium sample container, and the Plazcek shift[12] to obtain the total diffraction intensity. The powder structure factor is defined as

$$S(Q)=I_t/b^2 , \qquad (1)$$

where I_t is the total coherent scattering intensity per atom and b is the neutron scattering length of a C atom. The pair density, or distribution, function (PDF) can be obtained by

$$\rho(r)=\rho_0+\frac{1}{2\pi^2 r}\int Q[S(Q)-1]\sin(Qr)dr , \qquad (2)$$

where ρ_0 is the average density. This function describes the distributions of the atomic distances. In order to include all the available structural information, and at the same time to reduce the termination error which is introduced by the finite range of integration in Eq. (2), the Fourier transformation has been carried out up to 30

Å^{-1}. The details of the method and its error analysis have been described in Ref. 13. The PDF of C_{60} ($G(r)=4\pi r[\rho(r)-\rho_0]$) at 10 K is shown in Fig. 1. A PDF generated from a structural model of a $Pa\bar{3}$ symmetry and with a rotation angle of 25° around the threefold axes has shown a reasonably good agreement with the experimental PDF. However, at distances larger than the size of the fullerene molecule, the experimental PDF oscillates less strongly about the average density, indicating structural disorder. This is in agreement with the strong diffuse scattering in the diffraction pattern.

In the conventional crystallographic methods of structural determination the comparison of the data and model calculation is done in reciprocal space. In such an approach the diffraction intensity is calculated as a function of Q based upon a structural model, and is compared with the measured diffraction intensity. The refinements are made by varying parameters in the model and seeking an optimum agreement between the calculated and measured intensities, often characterized by the R factor or χ^2 factor.[5] On the other hand, our approach is to make the comparison in real space. A PDF is calculated from a structure model and then broadened by a Gaussian function which describes thermal vibration of the atom. The width of the Gaussian function is determined so that it has the best agreement with the experimental PDF, provided that the value is consistent with the Debye frequency of the solid. For different models the width of the Gaussian function usually is taken as a refinable parameter. The model PDF is then compared with the experimental PDF. The agreement factor A to be minimized in the refinement procedure is defined as

$$A^2=\frac{\int_{r_a}^{r_b}[\rho_{\mathrm{obs}}(r)-\rho_m(r)]^2dr}{\int_{r_a}^{r_b}\rho_0^2\,dr}\,, \tag{3}$$

where $\rho_{\mathrm{obs}}(r)$ and $\rho_m(r)$ represent the observed and model PDF, respectively, and the range of integration, from r_a to r_b, is chosen to be consistent with the purpose of analysis as discussed below. The estimated error in the A factor due to statistical fluctuations in the data can be assessed by the procedure of propagating errors.[14]

In order to decouple some of the structure parameters, the general strategy of this study is to use different parts of the PDF to obtain different parameters of the structure. Based upon knowledge of the size of the C_{60} molecule and the lattice parameter, we can divide the PDF into three parts. Each part of the PDF gives information on the atomic pair correlation in different distance ranges. The first part is the PDF up to 3 Å which only includes intramolecular atom-atom correlations. The second part, which is from 3 to 7 Å, includes both intramolecular and first-nearest intermolecular atom-atom correlations. The third part, which is beyond 7 Å, gives general information on the intermolecular atom-atom correlation for the first-nearest neighbors and beyond.

The two bond lengths of the C_{60} molecule are obtained from the first part of PDF. The symmetry of each C_{60} molecule has been kept so that only two bond lengths, which are the edges of the pentagons and the common edges of two hexagons, can be changed in the refinement process. The two parameters, the radius of icosahedra and the ratio of the two bond lengths, plus the width of Gaussian broadening has been refined in the range of 1.0–3.0 Å. The refinement process yielded the bond lengths of 1.40 ± 0.01 Å for the C=C double bond and 1.45 ± 0.01 Å for the C—C single bond, which are consistent with an earlier report,[6] and in good agreement with other studies.[5,15]

The angle of rotation for each C_{60} molecule around the threefold axis was then refined using the data in the 3.0–7.0 Å range which is most sensitive to this parameter. Figure 2 shows the plot of the A factor against the angle of rotation. As we can see, the A factor is a minimum at 25°–29° and at 95°. The first range of angles is consistent with the results of other crystallographic analyses,[3–5] but the second one is not. The value of the A factor in this range is virtually the same at these two rotation angles, and the statistical error in the A factor itself is 0.004. Thus the possibility that some molecules are rotated by about 95° has to be taken seriously. However, the diffraction pattern calculated for a single phase with rotation by 95° shows significant disagreement with the experimental result, indicating that such a rotation angle can

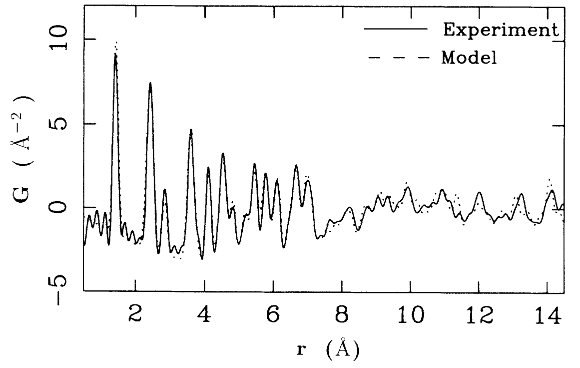

FIG. 1. Comparison of the PDF of C_{60} generated from the structural model with the experimental PDF at 10 K. The structural model has 60% C_{60} molecules with 25° rotation angle and 40% molecules with 85° rotation angle.

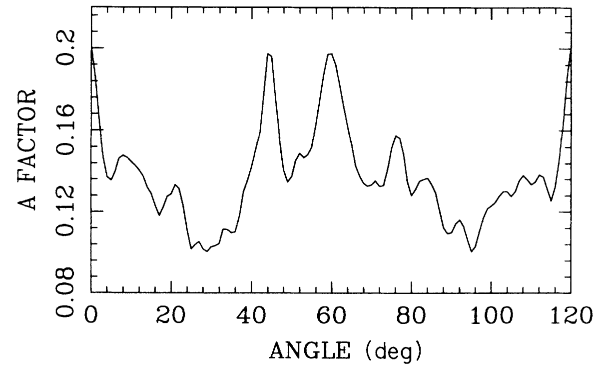

FIG. 2. Variation of the A factor vs the angle of rotation around ⟨111⟩ directions. In each structural model only one rotation angle was used. The agreement factor was calculated over the range of 3–7 Å.

exist only locally.

In order to understand the form of disorder, we constructed a large model including 500 C_{60} molecules. In this structural model a fraction of the molecules (concentration c_α) were rotated by the angle α with the remainder of the molecules having 25° rotation. The value of α was refined using the PDF in the range of 3–14.5 Å. The rotation axis for each molecule was chosen to be the same as the one in the $Pa\bar{3}$ symmetry. The A factor for $c_\alpha = 0.4$ is plotted against α in Fig. 3, showing a minimum at $\alpha = 85°$. Since the statistical error for this A factor is only 0.002 due to a larger range of r values considered, other local minima are outside this error range. However, we cannot rule out the possibility that other angles which show local minima in Fig. 3, such as 39°, 63°, and 108°, are found locally in small amounts. The variation in the A factor when α is fixed at 85° and c_{85} is changed is shown in Fig. 4. The A factor shows a pronounced minimum around 0.3–0.4, indicating that the mixture of these two angles with the compositional ratio of about 2:1 results in much better agreement with the experimental PDF than with any single angle of rotation. The PDF calculated for the model with $\alpha = 85°$ and $c_{85} = 0.4$ is shown in Fig. 1 by a dashed curve.[16] It is of interest to note that the atomic arrangement is not totally dissimilar among these angles of rotation, in the area where two C_{60} molecules face each other at the nearest-neighbor molecular distance as noticed in Ref. 16. A rotation angle of 25° results in an atomic configuration in which a double bond on one C_{60} molecule faces a pentagonal face on the other C_{60} molecule. On the other hand, two molecules rotated by 85° have a double bond facing against a hexagonal face. If a molecule with 25° rotation meets another with 85° rotation, the contact is made between a double bond of one against a hexagonal or a pentagonal face of the other. We also constructed a model suggested by Heiney *et al.*[2] and Copley *et al.*[4] in which about 30% of the molecules are randomly oriented. This model showed slightly better agreement with the experiment than the 25° single angle model, but much less satisfactory agreement than our best model.

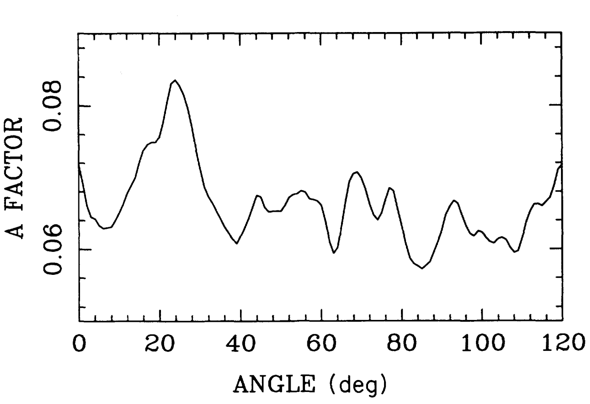

FIG. 3. Variation of the A factor vs angle of rotation for the case of a mixture of two rotation angles. In each model, 60% of C_{60} molecules are rotated through 25° and 40% take the rotation angle shown. The agreement factor was calculated over the range of 3–14.5 Å.

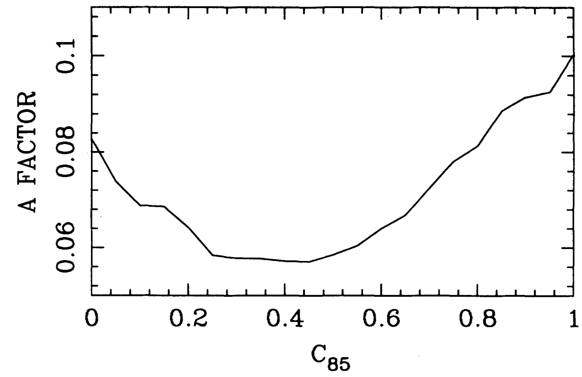

FIG. 4. Variation of the A factor vs concentration of C_{60} molecules with the rotation angle of 85°. In each model, the remaining molecules are rotated by 25°.

The present result suggests that while the long-range order of C_{60} at low temperatures can be described well with a crystallographic structure with the symmetry of $Pa\bar{3}$ and a rotation angle of 25°, locally there are numerous deviations from the long-range structure. While the long-range structure has a pentagonal face of each molecule facing a double bond on an adjacent molecule, locally the molecule can also have a hexagonal face opposite a double bond. In both atomic configurations, the part of molecule with a high electron density faces the part with a low electron density. While a pentagon has five single bonds and a hexagon has three double and three single bonds, a hexagon is larger in area than a pentagon. As these two might be equally preferred from the local electron density point of view alone, it is not unreasonable that both are found in the C_{60} solid at low temperatures. The fact that the long-range order is formed with a pentagonal face close to another molecule may imply that the configuration with the pentagonal face is slightly preferred. When the long-range order sets in at 249 K, locally the molecules can take other angles due to the entropical reason, in particular if other angles, such as $\alpha = 85°$, are easily reachable energetically. Such orientational disorder can be locally frozen in during the cooling for kinetic reasons. The kinetic barrier for rotation is estimated to be about 250 meV below the structural transition temperature.[17] Thus it is most likely that the energy difference between two configurations, with $\alpha = 25°$ and 85°, is significantly smaller than the barrier for rotation, resulting in the freeze-in of disorder at low temperatures.

Orientational disorder is known to exist in the superconducting phase, K_3C_{60}, in which the C_{60} molecules randomly choose between two local orientations.[18] Both in pure C_{60} and in K_3C_{60} the orientational disorder most likely would have significant effects on the electronic structure, as suggested by a recent calculation.[19] In addition accurate characterization of the orientational disorder will be important in understanding the nature of the intermolecular interactions.[20] This rather surprisingly high degree of orientational disorder indicated by the present result suggests that disorder is an inherent nature of the low-temperature phase of C_{60}, and any theory must take this fully into account.

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