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Short-range antiferromagnetic orientational correlations in Rb_3C_{60}

S. Teslic, T. Egami, and J. E. Fischer
Department of Materials Science and Engineering and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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The neutron pair distribution function (PDF) of Rb_3C_{60} at 10 K reveals local deviations from the Stephens model of merohedral disorder. The experimental PDF in the 3–7 Å range is best represented by a greater fraction of near-neighbor pairs with opposite standard orientations than would be expected from purely random decoration, indicating the presence of *short-range* "antiferromagnetic" orientational correlations.

The average crystal structure of the prototype fullerene superconductor Rb_3C_{60} has been firmly established by Rietveld refinement of powder x-ray diffraction data.[1] The molecules form a face-centered cubic lattice, the tetrahedral and octahedral voids are occupied by Rb ions, and the C_{60}'s are all oriented with twofold axes parallel to cube edges but are randomly distributed over two equally populated "standard orientations" A and B which differ by a $\pi/2$ rotation about any twofold axis. This is referred to as merohedral disorder, space group $Fm\bar{3}m$. The disorder persists at all accessible temperatures[2,3] but may not be the equilibrium ground state.[4–6] Given the sensitivity of the observed superconducting properties[7,8] and the calculated densities of states[9] to differences in orientational correlations, it is important to determine if short-range deviations from the average structure exist.

Here we describe the results of pulsed neutron atomic pair distribution function (PDF) analysis in determining the nature of the local structural disorder in Rb_3C_{60} at 10 K. In this approach [which has been successfully applied to pure C_{60} (Ref. 10)], both the Bragg and diffuse scattered intensities are included without assuming long-range order (and preserving the short-range information), and the comparison between data and structure models is made in real space rather than reciprocal space, with emphasis on differentiating between random and short-range correlated atomic displacements.[11,12] Indeed we find a distinct preference for A-B contact compared to what would obtain with random decoration, but only on the scale of first neighbors. There is no inconsistency with the *globally* equal fractions of A and B, nor is there any evidence for intermediate- or long-range orientational order.[5]

The $\sim$ 1 g sample of nominal Rb_3C_{60} was taken from a larger batch prepared by reacting weighed amounts of Rb and C_{60}. The latter was purchased from TERM USA; purity was checked by HPLC to be better than 99.9%, and the orientational ordering transition was observed at the ideal value 261 K by differential scanning calorimetry. The C_{60} was first ground to a fine powder in an argon-filled glove box. After vacuum sealing in pyrex with the Rb, the solid state reaction was carried out at 433 K for 3 days followed by 4 days at 733 K, then slowly cooled to 300 K over 11 h. High-resolution x-ray diffraction at 300 K revealed no detectable impurity phases at the 2% level. dc magnetization showed a superconducting onset at 28 K with $\sim$100% shielding and $\sim$ 14% Meissner fractions (measured at 10 G). The Hebel-Slichter coherence peak in spin-lattice relaxation rate was observed by μSR, similar to results on a previous sample.[13]

Measurements were carried out at the special environment powder diffractometer at the Argonne Intense Pulsed Neutron Source, using a vanadium container in a closed-cycle refrigerator. Data were collected up to 33 $Å^{-1}$ and analyzed in the usual way[14] to obtain the PDF:

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

where ρ_0 is the average atomic density and $S(Q)$ is the structure function.[14] This is plotted in Fig. 1 as the open symbols. In contrast to x-ray diffraction, the neutron $S(Q)$ is dominated by carbon scattering so $\rho(r)$ is to a good approximation the C-C pair distribution function. Model PDF's were constructed from various real space configurations and convoluted with a normalized Gaussian to describe isotropic harmonic thermal motion.[15] The results of the final refinement (described below) are plotted in Fig. 1 as the solid curve. Refinement of the model PDF with respect to the experimental one is based on varying model parameters to minimize the agreement factor α:

$$\alpha^2 = \int_{r_a}^{r_b} [\rho_{\rm obs}(r) - \rho_m(r)]^2 dr \Big/ \int_{r_a}^{r_b} \rho_0^2 dr \ , \qquad (2)$$

where $\rho_{\rm obs}$(r) and ρ_m(r) are the observed and model PDF's, and the range of integration may be chosen to decouple the various length scales. Intramolecular correlations dominate for r < 3 Å while beyond 7 Å the long-range (crystallographic) information dominates. We focus mainly on the intermediate range 3–7 Å which includes both intramolecular and first-neighbor intermolecular atom-atom correlations. Models consisting of 108 C_{60} molecules were constructed, and the fraction F of nearest neighbors with opposite orientations (i.e., A-B pairs) was chosen as the refinement parameter. While

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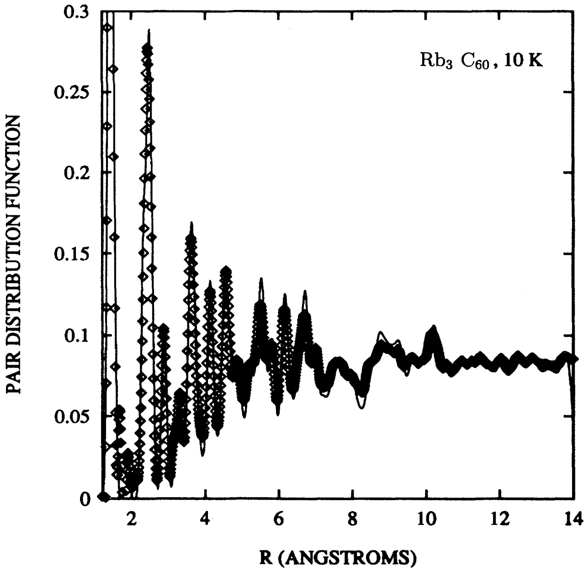

FIG. 1. Open symbols: pair distribution function of Rb_3C_{60} at 10 K derived from neutron scattering data up to $Q = 33$ Å^{-1}. Solid curve: final refined model PDF in which the fraction of A-B near-neighbor pairs is 0.6451; the limits for no correlations and maximum antiferromagnetic correlations are 0.5 and 0.67, respectively. Also, all molecules are rotated by 2° about randomly chosen ⟨100⟩ axes from the A and B standard orientations (see text).

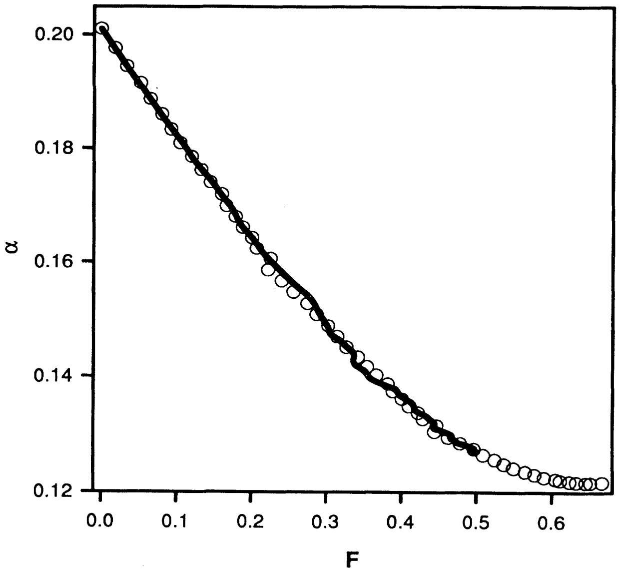

FIG. 2. Variation of the agreement factor α with the fraction of nearest neighbors having opposite orientations. The solid curve is for a model in which the molecules are oriented randomly in one of the two standard orientations A and B, or "spin" states. The open circles describe results of a model in which a degree of short-range order is introduced by controlled decoration of the four sc sublattices of the fcc structure. In both cases α is based on the PDF in the 3–7 Å range to emphasize near-neighbor correlations. The statistical error on A in this range is ± 0.002.

this is not unique (i.e., many structures with the same F may be constructed), it was found that α in the 3–7 Å range depended only on F and was not sensitive to other features of a particular decoration scheme. Note also that, whereas the fractions of A and B in our 108-molecule system will not be equal for arbitrary F, the real material can be envisaged as many such systems in half of which the roles of A and B are reversed, thus maintaining the *globally* equal population of the Stephens model.

In addition to random decoration, we considered two possibilities for near-neighbor orientational correlations, hereafter referred to as ferromagnetic and antiferromagnetic by analogy to magnetic systems with A and B playing the roles of spin up and spin down. Neither of these can exist at long range in Rb_3C_{60}; ferromagnetic ordering would violate the observed cubic symmetry by singling out a unique [100] direction, and antiferromagnetic ordering is frustrated on the fcc lattice.[16] Our initial attempt consisted of randomly distributing variable fractions of the A and B orientations. The results are shown as the solid curve in Fig. 2. When $F = 0$ we have all A or all B and ferromagnetic order is imposed on the length scale of our system size; this gives the worst agreement. The degree of ferromagnetic order is decreased as F increases; α decreases monotonically with increasing F, reaching a minimum $\alpha_{\min} = 0.1266$ at $F = 0.5$. This corresponds to the Stephens merohedrally disordered structure on our scale of 108 molecules; the best fit for random decoration naturally corresponds to equal populations. Note also that the largest physically meaningful value of F for random decoration is 0.5.

Next we allowed a preference for opposite near-neighbor orientations by decorating the four simple cubic sublattices in a controlled manner capable of creating varying sizes and shapes of ferromagnetic and antiferromagnetic clusters, the former dominating for $F < 0.5$, the latter for $F > 0.5$. The results are plotted in Fig. 2 as the open circles. Ferromagnetic order ($F = 0$) again gives the worst agreement. In this model, as F increases from 0 to 0.5 the ferromagnetic clusters get smaller and/or less numerous, and the agreement gets better in a manner very similar to what was found with random decoration. But now the physical limit on F is 2/3 (corresponding to the maximum antiferromagnetic correlation), and as F increases beyond 0.5 we find a broad minimum in α near $F = 0.6$ and a lower minimum, $\alpha_{\min} = 0.1216$, than was obtained with random decoration. The improvement, while small, is statistically significant and indicates a preference for antiferromagnetic short-range order.

We simulated the effect of fluctuations in cluster size by convoluting α with a binomial distribution; the effect was insignificant. In order to determine the range of the antiferromagnetic correlations (i.e., the size of the clusters), we extended the comparison of the above two models to the interval 7–14 Å in $\rho(r)$ in which second-neighbor intermolecular correlations dominate. In contrast to the above analysis which emphasized the near-neighbor scale, we now found a distinct preference for random decoration over antiferromagnetic order, the respective $\alpha_{\min}$'s in this range being 0.0800 and 0.0878 (the *absolute* improvement

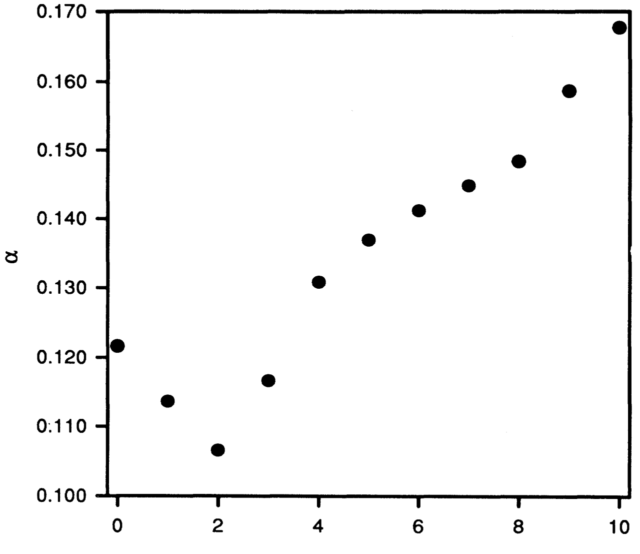

FIG. 3. Variation of α with angle of rotation about random (100) axes; other features of the model are the same as the open circles in Fig. 2.

compared to the above discussion is most likely due to the larger range of r). Thus the preference for A-B contact is restricted to near neighbors only.

At this point in the refinement strategy, the agreement with experiment is quite good but the model PDF oscillates more strongly about ρ_0 than the measured one, indicating additional randomness in the real structure. We thus added to the antiferromagnetic cluster model a small deviation away from the A and B standard orientations by an angle $\pm\sigma$ about randomly chosen $\langle 100\rangle$ axes. The result of refining σ is shown in Fig. 3, yielding a pronounced minimum at 2°. This gave a statistically significant further reduction in $\alpha_{\min}$ in the 3–7 Å range to 0.1065. This small disorder in orientations could be static or dynamic; in the latter case, σ simulates a librational Debye-Waller factor, while the Gaussian broadening described earlier represents thermal motion of the centers of mass. X-ray profile refinements are similarly improved by explicitly accounting for orientational disorder associated with librations.[2,3] The optimized value of σ is about twice the directly measured librational amplitude at this temperature.[17] The final PDF with $F = 0.6451$ and $\sigma = 2°$ is plotted as the solid curve in Fig. 1.

We also refined the bond lengths using the PDF from 0 to 3 Å and assuming that the icosahedral symmetry is preserved. This resulted in values of 1.438 ± 0.01 Å for the C=C "double" bond and 1.428 ± 0.01 Å for the C-C "single" bond, i.e., the same within experimental error. This is consistent with results from another compound with three electrons per molecule[18] and with theory.[19]

Alkali metal intercalation introduces new features into the cubic close-packed C_{60} orientational potential.[6] For large tetrahedral ions like Rb, repulsion due to core overlap between alkali ions and carbon atoms is dominant, equally favoring the two standard orientations. This is reflected in the potential as two degenerate minima corresponding to A and B orientations. This interaction alone is therefore insufficient to drive antiferromagnetic correlations since at this stage A and B are equivalent. On the other hand, intermolecular hopping along $\langle 111\rangle$ *via* the tetrahedral ion does show a small preference for A-B over A-A pairs,[4] and the equivalence is broken. However, the competing energies are such that long-range order never develops at any temperature; the barrier for jump rotation from A to B is larger than the energy difference between A-A and A-B pairs, such that the mean field ordering temperature is much less than the temperature at which the rate of thermally activated $A \rightarrow B$ jumps becomes negligible.[6] Thus long-range orientational order in heavy alkali M_3C_{60} compounds is unlikely to be realized on the experimental time scale, and the Stephens model for the average structure reflects quenched disorder. On the other hand, the present work does show the existence of antiferromagnetic correlations on the scale of nearest-neighbors clusters, presumably driven by the small difference between hopping integrals for the two pair configurations as first suggested by Satpathy *et al.*

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[1] P. W. Stephens *et al.*, Nature **351**, 632 (1991); P. W. Stephens *et al*, Phys. Rev. B **45**, 543 (1992).

[2] Q. Zhu, J. E. Fischer, and D. E. Cox, in *Electronic Properties of Fullerenes and Other Novel Materials*, edited by J. Fink, H. Kuzmany, M. Mehring, and S. Roth, Springer Series in Solid State Sciences Vol. 117 (Springer, Berlin, 1994), p. 168.

[3] P. W. Stephens (unpublished).

[4] O. Gunnarsson, S. Satpathy, O. Jepsen, and O. K. Andersen, Phys. Rev. Lett. **67**, 3002 (1991).

[5] I. I. Mazin *et al.*, Phys. Rev. Lett. **70**, 4142 (1993).

[6] T. Yildirim *et al.*, Phys. Rev. B **48**, 12262 (1993).

[7] K. Kniaź *et al.*, Solid State Commun. **88**, 47 (1993).

[8] T. Yildirim *et al.*, Solid State Commun. (to be published).

[9] M. S. Deshpande, S. C. Erwin, S. Hong, and E. J. Mele, Phys. Rev. Lett. **71**, 2619 (1993).

[10] R. Hu, T. Egami, F. Li, and J. S. Lannin, Phys. Rev. B **45**, 9517 (1992).

[11] W. Dmowski *et al.*, Phys. Rev. Lett. **61**, 2608 (1988).

[12] B. H. Toby *et al.*, Phys. Rev. Lett. **64**, 2414 (1990).

[13] R. F. Kiefl *et al.*, Phys. Rev. Lett. **70**, 3987 (1993).

[14] B. H. Toby and T. Egami, Acta Crystallogr. Sect. A **42**, 336 (1992).

[15] The Gaussian width is a parameter which can be deter-

mined by fitting the model to the experimental PDF, provided that the value is consistent with the Debye frequency.

[16] The fcc lattice consists of four interpenetrating simple-cubic (sc) sublattices. If only two orientations are allowed, any two sublattices can take orientation A and the other two orientation B. While 2D antiferromagnetic ordering is possible within a (100) plane, between neighboring planes there are equal numbers of A-A and A-B neighbor pairs. Consequently the coupling between (100) planes is frustrated and *long-range* antiferromagnetic ordering is impossible.

[17] D. Reznik *et al.*, Phys. Rev. B **49**, 1005 (1994).

[18] K. Prassides *et al.*, Science **263**, 950 (1994).

[19] W. Andreoni, J. Phys. Chem. Solids **54**, 1789 (1993).