Comment on "Orientational Ordering Transition in Solid C_{60}"

In an interesting Letter, Heiney et al. [1] study the x-ray scattering from powdered solid C_{60}. For temperatures above 249 K they find an orientationally disordered phase in which the freely rotating molecules form an fcc lattice. At lower temperatures their data indicate an orientationally ordered structure (OOS), which, within their resolution, occurs without motion of the centers of the molecules away from their fcc positions. All the powder-diffraction peaks could be indexed according to a simple-cubic unit cell containing four C_{60} molecules. However, since their fit to the intensities showed some discrepancies, we considered other structures for oriented icosahedra on an fcc lattice which would be consistent with simple-cubic indexing. We determined that most of the fifteen simple-cubic space groups [2] are excluded. For instance, when the icosahedra are on an fcc lattice their symmetry is higher (containing an inversion element) than permitted for space groups 195 and 198. In fact, there are two main possibilities [3]: the one actually used in Ref. [1], $P2/n\overline{3}$ (or $Pn3$), and that [4] of solid H_2, $P2_1/a\overline{3}$ (or $Pa3$), which Heiney et al. mentioned but did not actually use. These differ only in the way the molecular threefold axes are distributed over various $\langle 111 \rangle$ directions.

The most general OOS for space group $P2_1/a\overline{3}$ is obtained as follows. Start from a fcc crystal in which all molecules have their twofold axes aligned along the three (1,0,0) directions. Then 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 rotated through an angle $\phi \neq 0$ about the $(1,1,1)$, $(1,\overline{1},\overline{1})$, $(\overline{1},\overline{1},1)$, and $(\overline{1},1,\overline{1})$ directions, respectively, so that the 240 atoms in the unit cell occupy ten sets of "d" sites [2]. Even after this rotation, these directions remain threefold axes for each of the four sites in the unit cell.

The calculated powder-diffraction intensity for the $Pa3$ structure was optimized with respect to the angle ϕ and the authors of Ref. [1] have kindly supplied the results shown in Fig. 1, which was obtained, following the procedures of Ref. [1], taking the lattice parameter to be
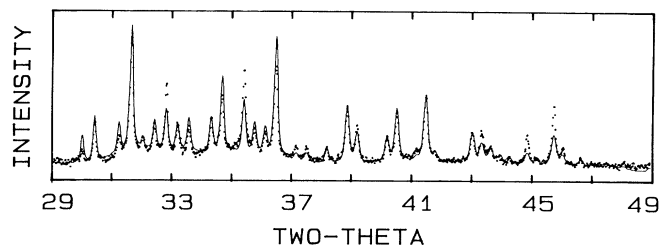

FIG. 1. Dots: A portion of the experimental 11-K x-ray profile from Ref. [1] in which most of the reflections are associated with the OOS. Wavelength 1.1992 Å. Continuous line: Model profile as in Ref. 1 but based on $Pa3$ rather than $Pn3$ space group.

$a = 14.05$ Å and $\phi = 26°$ to best fit the 11-K data. This fit is significantly better than that found in Ref. [1]. We thus conclude that the OOS structure of solid C_{60} is $P2_1/a\overline{3}$. The structural parameters and symmetry will be discussed elsewhere [3].

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[1] P. A Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley, Jr., A. B. Smith, III, and D. E. Cox, Phys. Rev. Lett. **66**, 2911 (1991).

[2] International Tables for Crystallography, edited by Theo Hahn (Reidel, Boston, 1983), Vol. 4.

[3] A. B. Harris and R. Sachidanandam (to be published).

[4] A. B. Harris, S. Washburn, and H. Meyer, J. Low Temp. Phys. **50**, 151 (1983); see Sec. 3.1.