Comment on "Microscopic Theory of Orientational Disorder and the Orientational Phase Transition in Solid C_{60}"

In a recent paper, Michel, Copley, and Neumann [1] have studied the orientational order-disorder transition of face-centered-cubic fullerite at 250 K, expressing the intermolecular interactions in terms of symmetry-adapted rotator functions; they arrive at the conclusion that the phase transition is driven by a mode of T_{2g} symmetry belonging to the $l = 10$ manifold. This conclusion is arrived at by considering an interaction potential of the Lennard-Jones (L-J) form centered at the atomic sites.

In Ref. [1] the intermolecular potential is expanded in terms of rotator functions. The relative weight of each term in this multipolar expansion [Eq. (6) of Ref. [1]] is given essentially by two factors: the interaction matrix elements, which are averaged over all orientations [Eq. (7), Ref. [1]] and measure the overall strength of the interaction, and the form factors, which depend directly on the location of the interaction sites. The argument of Michel, Copley, and Neumann for choosing $l = l' = 10$ as the leading term is that although the matrix elements for $l = l' = 6$ are about 4 times larger, the form factors are about 8 times smaller, leaving a factor of about 16 in favor of the $l = l' = 10$ terms in the final balance.

It has been shown that the carbon nuclei L-J potential is not a good representation of intermolecular interactions at the distances found in the crystal [2, 3]. At 11 K the ordered structure [4] is obtained by rotating the molecules about the [1,1,1] C_3 crystallographic axis by 98°, starting from the "standard orientation." This potential has its principal minimum at about 40°, and a secondary much shallower minimum at the observed angle [2, 3].

In Fig. 1 we show the molecular-symmetry-adapted functions $S^1_{l(I)}$ (rather than the form factors) for $l = 6$ and 10, for interaction sites located on a molecular symmetry plane. It is clearly seen that the absolute value of $S^1_{6(I)}$ is much smaller than that of $S^1_{10(I)}$ only in the region near the carbon nuclei sites. Therefore the preeminence of the $l = l' = 10$ term is a peculiarity of this particular choice of interaction sites.

Other representations of the intermolecular potential which yield good results for the phase transition and structural properties have been proposed. A twelve pentagon center site L-J potential, which also shows inverted minima, accounts for the order-disorder transition [5], giving a correct transition temperature when a monopolar L-J interaction is added [3]. More complicated potentials correct the problem of the minimum energy structure: Sprik, Cheng, and Klein [6] consider L-J plus electrostatic interactions both at the carbon nuclei and at the double-bond centers, and Lu, Li, and Martin [7] consider L-J interactions of the nuclei plus electrostatic interactions between charges at the centers of the double and
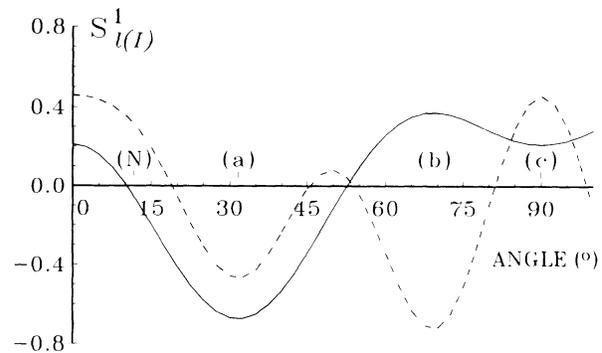

FIG. 1. Molecular-symmetry-adapted functions $S^1_{l(I)}$ for $l = 6$ (full lines) and $l = 10$ (broken lines). High-symmetry sites: (a) center of pentagons (C_{5v}); (b) center of hexagons (C_{3v}); (c) center of double bonds (C_{2v}). (N) indicates the position of the nuclei in the regular configuration.

the simple bonds. Furthermore, for electrostatic interactions it has been found that higher-order multipolar terms ($l = 12$ and $l = 16$) are relevant in determining the intermolecular energy [8]. In general, inclusion with appreciable weight of interaction sites different from the carbon nuclei are indispensable for good agreement with experimental results.

In conclusion, although the theoretical framework of Ref. [1] is not only elegant but also extremely useful, both in reducing the huge number of interaction terms and in acquiring an adequate insight into the nature of the transition, specific conclusions regarding this problem must probably await a more precise knowledge of the interaction potential, since the location of the interaction sites affects much more than the calculated value of the transition temperature.

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