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Orientational ordering of icosahedra in solid C_{60}

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We determine the allowed structures for orientationally ordered icosahedral molecules on a fcc lattice such that there are four molecules per simple-cubic unit cell. The allowed space groups are $Pm3$, $Pn3$, and $Pa3$. In the latter two, an angle of rotation assumes a value not fixed by symmetry. The locations of all 240 atoms in the unit cell as deduced from the powder x-ray data of Heiney *et al.* are tabulated. We discuss a number of minima in the free energy which correspond to the observed $Pa3$ structure of solid C_{60}. We introduce orientational order parameters which lead to a Landau free energy, from which we predict that the orientational transition is discontinuous.

I. INTRODUCTION

The C_{60} fullerene molecule[1] has an interesting structure, whose symmetry is well described by a truncated icosahedron.[2] An icosahedron[2] is a regular solid with 12 vertices, 20 equilateral-triangular faces, and 30 edges of equal length which has twofold, threefold, and fivefold axes of symmetry. A convenient representation of an icosahedron inscribed in a cube is shown in Fig. 1, in which 3 sets of parallel edges are indicated. A truncated icosahedron is derived from the icosahedron when each triangular face is reduced to form a central regular-hexagonal face and five of these new edges from neighboring triangles are then joined to form regular-pentagonal faces, as shown in Fig. 2. The ideal truncated icosahedron has 60 vertices and 32 faces (of which 12 are regular pentagons and 20 are regular hexagons). In C_{60}, the hexagons are distorted,[3,4] bonds belonging to pentagons being the longer single bonds and those between adjoining hexagons being the shorter double bonds. Recently an interesting paper by Heiney *et al.*[5] describes a study of the x-ray powder diffraction pattern from solid C_{60} Fullerite in which an orientational transition is observed at a temperature T_c of about 249 K. For temperature T greater than T_c, they find a phase in which the C_{60} molecules are orientationally disordered[6] and their centers of mass form a fcc lattice.[7] For $T < T_c$ an orientationally ordered phase appears in which, within the resolution of the x-ray data,[5] the orientations of the molecules order without any shift of the centers of mass away from the fcc lattice positions. Accordingly, it is appropriate to attempt to fit the lowest temperature data at $T=11$ K to a model in which the molecules are completely orientationally ordered. Since the powder diffraction peaks could be indexed according to a simple-cubic unit cell containing four molecules, we are interested in understanding the possible orderings for icosahedral molecules on a fcc lattice for which the diffraction peaks retain the selection rules for cubic symmetry. That is, the momentum transfer in the powder diffraction peak associated with indices h, k, and l should be independent of the signs of the indices and independent of different orderings of the indices. The intensities of the various diffraction peaks contain information about the nature of the orientational ordering, and as we shall see, are not invariant under interchange of h and k, for instance. A recent reanalysis[8] is accepted[9] to show that the orientationally ordered phase of solid C_{60} is that of space group $P2_1/a\bar{3}$. In the course of that work several amusing structural questions arose which we will address in the present paper. In addition, due to the brief nature of Ref. 8 (and 9), sufficient details were not actually given to specify completely the structural parameters of the orientationally ordered phase. We give these structural parameters in Table V.

The first, and most obvious, question is what orientationally ordered structures are consistent with the cubic symmetry implied by the fact that the diffraction peaks can be indexed according to a simple-cubic unit cell? As mentioned above we will assume that the centers of mass of the C_{60} molecules form an fcc lattice. To see that the

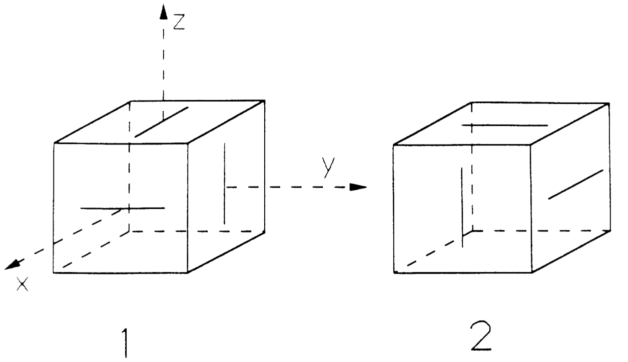

FIG. 1 Schematic representations of an (inscribed) icosahedron. Here we show the icosahedron when it has mirror planes perpendicular to the three ⟨100⟩ directions. In this orientation, six of its edges lie in planes parallel to the mirror planes, so that when the icosahedron is circumscribed by a minimal cube, these edges lie in the cube faces, as shown. A fivefold axis passes through each vertex. Each ⟨1,1,1⟩ direction is a threefold axis. We will refer to these two settings as setting 1 (on the left) and setting 2 (on the right).

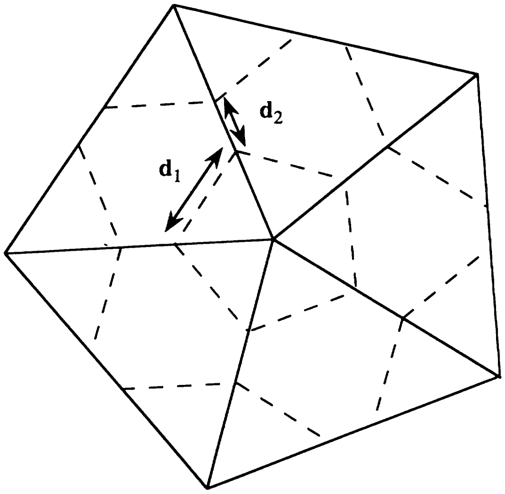

FIG. 2. Construction of a truncated icosahedron from an icosahedron. Here we look along the fivefold axis of the icosahedron with its equilateral-triangular faces whose edges are indicated by solid lines. To construct the truncated icosahedron, each triangle is partitioned into four sectors: one hexagon (that has sides which alternately are of length d_1 and d_2) and three equilateral triangles of side d_1. Each set of five touching triangles of side d_1 is then formed into a single pentagonal face.

above question is not a completely trivial one, we may note that certain orientational arrangements are not in fact possible. For instance, suppose one aligns the fivefold axes of the molecules along the four different ⟨111⟩ directions. Then one may choose, for each molecule, an orientation of the projection of a threefold axis in a plane perpendicular to the ⟨111⟩ direction associated with the molecule in question. It can be seen (see Appendix A) that it is not possible to preserve the equivalence of the three ⟨100⟩ directions and the equivalence of the four ⟨111⟩ directions with such a structure. If such a structure did occur for solid C_{60}, one would observe splittings in the powder diffraction peaks relative to simple-cubic indexing. Of course, if these splittings were small enough, the resolution of an actual experiment might not be good enough to detect them. For the purposes of this paper, we will not consider this possibility: we will assume that the experiments have infinitely good resolution, i.e., that the diffraction peaks indexed assuming a simple-cubic unit cell show no splittings. We are thus left with the purely mathematical question as to what orientational orderings of icosahedra on a fcc lattice are consistent with cubic symmetry and are thus described by one of the cubic space groups.[10]

The second question we address is how many different structures are there which are equivalent, i.e., which cannot be distinguished by any conceivable macroscopic experiment? Perhaps a more precise formulation of this question is as follows. Suppose the orientational structure is defined by orientational order parameters, which we identify below. The orientational free energy is thus considered as a functional of these position-dependent order parameters. As the temperature is lowered towards the orientational ordering temperature, fluctuations will occur in which ordered structures appear over some intervals of time and space (which presumably become larger as the ordering transition is approached, but need not diverge unless the transition is a continuous one). In the case of an Ising ferromagnet or antiferromagnet, there will be two minima of the free energy in phase space where fluctuations will locally be maximal. For a q-state Potts-model ferromagnet there will be q local minima. A slightly less trivial example of counting such minima occurs for the herringbone ordering of molecular dimers (N_2) on a triangular substrate such as Grafoil.[11,12] Here there are three equivalent directions in the herringbone, but in addition, there are two choices of phase, and so there are six equivalent minima in the free energy. Since this model is similar[12] to a Heisenberg model with ⟨100⟩ easy axes, this degeneracy is understandable. Furthermore, if the triple-**q** state of the herringbone (known as the "pinwheel" state) is favored, then there are eight minima, corresponding to the various choices of phase in combining the three **q** vectors which span the triple-**q** state. Since in this case, the model is equivalent to a Heisenberg model with ⟨111⟩ easy axes, we again understand the degeneracy. A final example of this counting occurs for solid H_2 which has a structure[13–15] which we have identified with that of solid C_{60} fullerene.[8,9] For solid H_2 the molecules, whose centers form a fcc lattice, are oriented along different ⟨111⟩ lines which are the local threefold axes of symmetry. In that case there are four ways to identify the molecule at a given site with one particular ⟨111⟩ line. Then there remain two choices for one of the other ⟨111⟩ lines along which to align a neighboring molecule. Having done this, all other orientations are fixed. So for the solid H_2 structure there are eight equivalent local minima in the free energy.[16,17] The question is, how many such minima are there in the orientational free energy for solid C_{60}?

Beyond these structural questions, we consider how the orientational transition can be described within a Landau theory. For that purpose we introduce order parameters and indicate the symmetry of the Landau expansion. We find[18] that the free energy is isomorphic to that which describes orientational ordering in solid orthohydrogen.[16] Since this free energy has a cubic term, Landau theory predicts that the transition is a discontinuous one. Since the observed discontinuity at the transition is small,[5,19] the size of the cubic term cannot be very large. To discuss the size of the cubic term, it is necessary to analyze the fourth-order terms, which depend[12] on the details of the orientational potential. This problem will be discussed elsewhere.[20]

Briefly, this paper is organized as follows. In Sec. II we address the question of possible cubic structures for ordered icosahedra. We show that there are just three possible space-group types for such a structure, one of which is the observed $Pa3$ structure. In Sec. III we discuss the parametrization of this structure and consider some of the symmetry relations in this parameter space. Here, in Table V, we give the structural parameters needed to locate all the atoms in the observed unit cell. In

Sec. IV we discuss the number of equivalent ground states, or phases, which are realized for this structure. In retrospect, it is no surprise that the number of states is the same as for the $Pa3$ structure of solid hydrogen. In Sec. V we discuss the order parameter of the ordered phase and the symmetry of the Landau free energy which describes the orientational ordering. Our conclusions are summarized briefly in Sec. VI.

II. THE C_{60} SPACE-GROUP PROBLEM

As mentioned above, we assume solid C_{60} to be a cubic structure, so the first question can be phrased as follows: which of the cubic space groups can describe a fcc lattice of statically ordered icosahedra, such that there are four molecules per simple cubic unit cell? (We only consider periodic structures: quenched random orientational disorder is not allowed. Also we assume that the icosahedra are perfectly rigid. In practice, the C_{60} molecules will suffer a distortion consistent with local site symmetry, which is lower than icosahedral. However, this distortion is probably small enough to neglect.) Since the question we address is essentially one of symmetry, we will consider the ordering of icosahedra rather than of truncated icosahedra. In what follows we will frequently refer to space groups by their identifying numbers, as listed in *International Tables for Crystallography.*[10] The fact that there is a finite number (36) of cubic space groups means that our task of enumerating all possible space groups which satisfy our criteria is a finite one. Our procedure will be as follows. We imagine placing infinitesimal icosahedral molecules, each consisting of 12 vertices on a fcc lattice. Note that the question we are addressing is one of symmetry. Thus, the possible space groups for statically ordered actual-sized truncated-icosahedral C_{60} molecules on a fcc lattice are identical to the allowed space groups for statically ordered infinitesimal icosahedra on a fcc lattice. For simplicity we consider the latter problem.

In identifying the fcc lattice with points in the unit cell of some space group, we must not, of course, assume that the four fcc lattice points in the simple-cubic unit cell are at points among which are (0,0,0). Rather, we must allow for use of the points (x,y,z), $(x+\frac{1}{2}a,y+\frac{1}{2}a,z)$, $(x+\frac{1}{2}a,y,z+\frac{1}{2}a)$, and $(x,y+\frac{1}{2}a,z+\frac{1}{2}a)$, where x, y, and z are arbitrary and a is the lattice constant of the sc unit cell. Before starting the discussion we should review briefly the symmetry of a single icosahedron. For the settings shown in Fig. 1, the icosahedron has three mutually perpendicular mirror planes which are perpendicular to the three $\langle 100 \rangle$ directions. Also the icosahedron has threefold axes along each of the $\langle 111 \rangle$ directions.

The fact that the unit cell is sc and *not* fcc or bcc allows us to rule out several space groups. The fifteen remaining eligible candidates are space groups No. 195 $(P23,T^1)$, No. 198 $(P2_13,T^4)$, No. 200 $(Pm\bar{3},T_h^1)$, No. 201 $(Pn\bar{3},T_h^2)$, No. 205 $(Pa\bar{3},T_h^6)$, No. 207 $(P432,O^1)$, No. 208 $(P4_232,O^2)$, No. 212 $(P4_332,O^6)$, No. 213 $(P4_132,O^7)$, No. 215 $(P\bar{4}3m,T_d^1)$, No. 218 $(P\bar{4}3n,T_d^4)$, No. 221 $(Pm\bar{3}m,O_h^1)$, No. 222 $(Pn\bar{3}n,O_h^2)$, No. 223 $(Pm\bar{3}n,O_h^3)$, and No. 224 $(Pn\bar{3}m,O_h^4)$.

Now we start to rule out most of these space groups. First of all, note that an icosahedron is invariant under inversion $(\mathbf{r}\rightarrow-\mathbf{r})$ about its center of mass. This indicates that the fcc crystal has inversion symmetry about each of its sites. So we exclude space groups which lack inversion symmetry. We are then left with only the candidates Nos. 200, 201, 205, 221, 222, 223, and 224. We first deal with space groups Nos. 222 and 223. Consider the locations of the centers of mass of the four icosahedra. These must form a fcc lattice. In space group No. 223, for instance, the centers of the icosahedra cannot occupy b,c,d, . . . etc. sites, because such sites have too high a multiplicity. The a sites form a bcc lattice. So space group No. 223 is ruled out. By similar reasoning group No. 222 is also excluded. Thus space groups No. 200, 201, 205, 221, and 224 are the only space-group types which can describe ordering of inversion symmetric molecules on a fcc lattice with four molecules in a sc unit cell. We now consider the special case when the molecules have icosahedral symmetry.

Consider group No. 224 (with the second choice of origin in Ref. 6). We see that the centers of mass of the icosahedra can occupy either the four b sites or the four c sites. We consider the first case. (The second case is similar.) Consider an icosahedron centered about the origin. The space group symmetry of this crystal structure includes mirror planes perpendicular to $[1\bar{1}0]$, to $[01\bar{1}]$, and to $[10\bar{1}]$. The angle between these vectors is 60°. The icosahedron does not have mirror planes whose normals subtend an angle of 60°. So space group No. 224 is excluded.

Next consider space group No. 221. We place the centers of mass of the icosahedra on one a site and three c sites (or equivalently on one b site and three d sites). Consider the atoms in the icosahedron at the a site at (0,0,0). These 12 atoms cannot come from the eight g sites: there would be four left over which could not be placed on available sites. The only vague possibility is to use the 12 i sites. But these sites have a fourfold axis of local symmetry which the icosahedron does not possess. Thus space group No. 221 is excluded.

Now we consider space group No. 200, which is $P2/m\bar{3}$ (or $Pm3$, for short). Here we put the centers of the icosahedra on the one a site and the three c sites (or equivalently on the one b site and the three d sites). The local site symmetry of these sites is significant. At the a site one has three mirror planes, each perpendicular to a respective $\langle 100 \rangle$ direction. Also there are four threefold axes, one each along a respective $\langle 111 \rangle$ direction. To be consistent with this symmetry, the icosahedron at the origin must be in one of the settings shown in Fig. 1. The symmetry of the c sites is lower, but they have mirror planes perpendicular to each of the $\langle 100 \rangle$ directions. So the icosahedron at $(a/2,a/2,0)$ can be put in one of the settings shown in Fig. 1. But then, the settings of the icosahedra on the two other c sites are completely determined by the fact that a threefold axis passes through the origin. (Notice that we had to use the fact that the molecule being oriented has high enough symmetry so that rotation through 120° about any of the four threefold axes yields the *same* result.) So we can arbitrarily assign ei-

TABLE I. Positions of atoms in oriented icosahedra (not truncated icosahedra) on a fcc lattice for space group $P2_1/a\bar{3}$. This is structure *A*. The positions of atoms in column *I* are for atoms in icosahedron *I*. To make up the complete structure of 48 atoms (for four truncated icosahedra in the unit cell) take two sets of points as listed below, one set of 24 points for the structural parameters *x*, *y*, and *z*, and another set of 24 points for the structural parameters x', y', and z' given in Eqs. (3.1) or (3.2). The actual structural parameters for solid C_{60} are given in Table V. Here $\hat{\mathbf{n}}_I$ is the positive direction of the local threefold axis for icosahedron *I* and *a* is the simple-cubic lattice constant.

$I=1$	$I=2$	$I=3$	$I=4$
x,y,z	$(\frac{1}{2}a+\bar{x},\bar{y},\frac{1}{2}a+z)$	$(\bar{x},\frac{1}{2}a+y,\frac{1}{2}a+\bar{z})$	$(\frac{1}{2}a+x,\frac{1}{2}a+\bar{y},\bar{z})$
z,x,y	$(\frac{1}{2}a+\bar{z},\bar{x},\frac{1}{2}a+y)$	$(\bar{z},\frac{1}{2}a+x,\frac{1}{2}a+\bar{y})$	$(\frac{1}{2}a+z,\frac{1}{2}a+\bar{x},\bar{y})$
y,z,x	$(\frac{1}{2}a+\bar{y},\bar{z},\frac{1}{2}a+x)$	$(\bar{y},\frac{1}{2}a+z,\frac{1}{2}a+\bar{x})$	$(\frac{1}{2}a+y,\frac{1}{2}a+\bar{z},\bar{x})$
$\bar{x},\bar{y},\bar{z}$	$(\frac{1}{2}a+x,y,\frac{1}{2}a+\bar{z})$	$(x,\frac{1}{2}a+\bar{y},\frac{1}{2}a+z)$	$(\frac{1}{2}a+\bar{x},\frac{1}{2}a+y,z)$
$\bar{z},\bar{x},\bar{y}$	$(\frac{1}{2}a+z,x,\frac{1}{2}a+\bar{y})$	$(z,\frac{1}{2}a+\bar{x},\frac{1}{2}a+y)$	$(\frac{1}{2}a+\bar{z},\frac{1}{2}a+x,y)$
$\bar{y},\bar{z},\bar{x}$	$(\frac{1}{2}a+y,z,\frac{1}{2}a+\bar{x})$	$(y,\frac{1}{2}a+\bar{z},\frac{1}{2}a+x)$	$(\frac{1}{2}a+\bar{y},\frac{1}{2}a+z,x)$
$\hat{\mathbf{n}}_1$	$\hat{\mathbf{n}}_2$	$\hat{\mathbf{n}}_3$	$\hat{\mathbf{n}}_4$
$[111]$	$[\bar{1}\bar{1}1]$	$[\bar{1}1\bar{1}]$	$[1\bar{1}\bar{1}]$

ther of the settings of Fig. 1 to the a site and to the c sites. However, if these two settings are the same, then all molecules are equivalent and we have a fcc Bravais lattice with one molecule per unit cell. So the allowed structure for this space group is obtained by arbitrarily choosing one of the settings from Fig. 1 for the icosahedron at the origin and then putting the other three icosahedra on the c sites in the other setting of Fig. 1. In this space group there is no further freedom of rotation of the icosahedra.

Now we are left with only space group types 201 ($P2/n\bar{3}$) and 205 ($P2_1/a\bar{3}$) to consider. These are the space groups (in short notation) $Pn3$ and $Pa3$, respectively. The former was used in the initial fit to the structure of solid C_{60} fullerite by Heiney *et al.*[5] and the latter was later[8] shown to be the correct structure. So we now look in detail at these two allowed space groups, $Pn3$ and $Pa3$. For $Pa3$ we have sites at positions given in Tables I and II. There are two distinct realizations of this space group which we label *A* and *B*. As explained in Sec. 8 of Ref. 10, two different structures are attributed to the same *space-group type* if two conditions are fulfilled. The first is that their space groups are isomorphic. In this isomorphism, any element *G* of the first space group and the corresponding element G' of the second space group are related by $G'=P^{-1}GP$, where *P* is an operation which takes one structure into the other. The second condition is that it is possible to choose the operation *P* so that it is a "proper" rotation, i.e., a pure rotation with or without an accompanying translation. (In other words, two groups which differ only in their handedness would not satisfy this condition to belong to the same space-group type. As explained in Ref. 10, such a pair of space groups which differ only in their handedness are enantiomorphic pairs and are considered to be distinct space-group types.) An operation *P* which takes the structure in Table I into that in Table II is a reflection through a $\{1\bar{1}0\}$ plane. However, this transformation is not a proper one. We identify the proper operation *P* to be an inversion followed by a reflection through a $\{1\bar{1}0\}$ plane. This is equivalent to a rotation of 180° about $\langle 1\bar{1}0\rangle$. This transformation takes a point with coordinates (u,v,w) into one with coordinates $(\bar{v},\bar{u},\bar{w})$. Thus the point $\mathbf{r}_1\equiv(\frac{1}{2}a+\bar{x},\bar{y},\frac{1}{2}a+z)$ is transformed into $P\mathbf{r}_1\equiv\mathbf{r}_2=(y,\frac{1}{2}a+x,\frac{1}{2}a+\bar{z})$. Since this operation *P* is *not* one of the symmetry operations of this structure, when it operates on the set of points listed in Table I, it will indeed produce a structure which cannot be realized by the set of points in Table I. To get the points in the form listed in Table II, one should apply *P* to all the points in Table I and then interchange the *parameters* *x* and *y*, so that the point $\mathbf{r}_2$ above becomes $(x,\frac{1}{2}a+y,\frac{1}{2}a+\bar{z})$, which is listed in Table II. For space group $Pn3$ we have sites at the positions given in Table III.

TABLE II. Positions of atoms in oriented icosahedra (not truncated icosahedra) on a fcc lattice for space group $P2_1/a\bar{3}$. This is structure *B*. For notation and explanation, see Table I.

$I=1$	$I=2$	$I=3$	$I=4$
x,y,z	$(\frac{1}{2}a+\bar{x},y,\frac{1}{2}a+z)$	$(x,\frac{1}{2}a+y,\frac{1}{2}a+\bar{z})$	$(\frac{1}{2}a+x,\frac{1}{2}a+\bar{y},z)$
z,x,y	$(\frac{1}{2}a+\bar{z},x,\frac{1}{2}a+y)$	$(z,\frac{1}{2}a+x,\frac{1}{2}a+\bar{y})$	$(\frac{1}{2}a+z,\frac{1}{2}a+\bar{x},y)$
y,z,x	$(\frac{1}{2}a+\bar{y},z,\frac{1}{2}a+x)$	$(y,\frac{1}{2}a+z,\frac{1}{2}a+\bar{x})$	$(\frac{1}{2}a+y,\frac{1}{2}a+\bar{z},x)$
$\bar{x},\bar{y},\bar{z}$	$(\frac{1}{2}a+x,\bar{y},\frac{1}{2}a+\bar{z})$	$(\bar{x},\frac{1}{2}a+\bar{y},\frac{1}{2}a+z)$	$(\frac{1}{2}a+\bar{x},\frac{1}{2}a+y,\bar{z})$
$\bar{z},\bar{x},\bar{y}$	$(\frac{1}{2}a+z,\bar{x},\frac{1}{2}a+\bar{y})$	$(\bar{z},\frac{1}{2}a+\bar{x},\frac{1}{2}a+y)$	$(\frac{1}{2}a+\bar{z},\frac{1}{2}a+x,\bar{y})$
$\bar{y},\bar{z},\bar{x}$	$(\frac{1}{2}a+y,\bar{z},\frac{1}{2}a+\bar{x})$	$(\bar{y},\frac{1}{2}a+\bar{z},\frac{1}{2}a+x)$	$(\frac{1}{2}a+\bar{y},\frac{1}{2}a+z,\bar{x})$
$\hat{\mathbf{n}}_1$	$\hat{\mathbf{n}}_2$	$\hat{\mathbf{n}}_3$	$\hat{\mathbf{n}}_4$
$[111]$	$[1\bar{1}\bar{1}]$	$[\bar{1}\bar{1}1]$	$[\bar{1}11]$

TABLE III. Positions of atoms in oriented icosahedra (not truncated icosahedra) on a fcc lattice for space group $P2/n\bar{3}$. The notation and explanation is the same as in Table I.

$I=1$	$I=2$	$I=3$	$I=4$
x,y,z	$(\frac{1}{2}a+\bar{x},\frac{1}{2}a+\bar{y},z)$	$(\frac{1}{2}a+\bar{x},y,\frac{1}{2}a+\bar{z})$	$(x,\frac{1}{2}a+\bar{y},\frac{1}{2}a+\bar{z})$
z,x,y	$(\frac{1}{2}a+\bar{z},\frac{1}{2}a+\bar{x},y)$	$(\frac{1}{2}a+\bar{z},x,\frac{1}{2}a+\bar{y})$	$(z,\frac{1}{2}a+\bar{x},\frac{1}{2}a+\bar{y})$
y,z,x	$(\frac{1}{2}a+\bar{y},\frac{1}{2}a+\bar{z},x)$	$(\frac{1}{2}a+\bar{y},z,\frac{1}{2}a+\bar{x})$	$(y,\frac{1}{2}a+\bar{z},\frac{1}{2}a+\bar{x})$
$\bar{x},\bar{y},\bar{z}$	$(\frac{1}{2}a+x,\frac{1}{2}a+y,\bar{z})$	$(\frac{1}{2}a+x,\bar{y},\frac{1}{2}a+z)$	$(\bar{x},\frac{1}{2}a+y,\frac{1}{2}a+z)$
$\bar{z},\bar{x},\bar{y}$	$(\frac{1}{2}a+z,\frac{1}{2}a+x,\bar{y})$	$(\frac{1}{2}a+z,x\frac{1}{2}a+y)$	$(\bar{z},\frac{1}{2}a+x,\frac{1}{2}a+y)$
$\bar{y},\bar{z},\bar{x}$	$(\frac{1}{2}a+y,\frac{1}{2}a+z,\bar{x})$	$(\frac{1}{2}a+y,\bar{z},\frac{1}{2}a+x)$	$(\bar{y},\frac{1}{2}a+z,\frac{1}{2}a+x)$
$\hat{\mathbf{n}}_1$	$\hat{\mathbf{n}}_2$	$\hat{\mathbf{n}}_3$	$\hat{\mathbf{n}}_4$
[111]	$[11\bar{1}]$	$[1\bar{1}1]$	[111]

In summary, mathematically, there are only three possible space-group types for orientationally ordered icosahedra centered on fcc lattice points such that the simple-cubic unit cell contains four molecules: $Pm3$, $Pn3$, and $Pa3$. In $Pm3$, the orientation of the molecules is completely determined (apart from a degeneracy with respect to interchange of settings 1 and 2 of Fig. 1). In Fig. 3 we show comparisons between the experimental powder intensity data versus scattering angle and the corresponding theoretical intensities calculated assuming the appropriate atomic form factors for carbon atoms located at their positions in the C_{60} molecule. For the $Pn3$ and $Pa3$ structures the theoretical curves were optimized with respect to the setting angle ϕ, which in both cases was 24.0°. These fits were supplied to us by Dr. D. Cox. Apart from the overall fit, one should notice that there is predicted intensity in a (6,1,0) reflection in the experimental and $Pa3$ theoretical curves which is lacking in the $Pm3$ and $Pn3$ structures. One can see that the fits given by the $Pm3$ and $Pn3$ structures are nowhere near as good as that for the $Pa3$ structure.

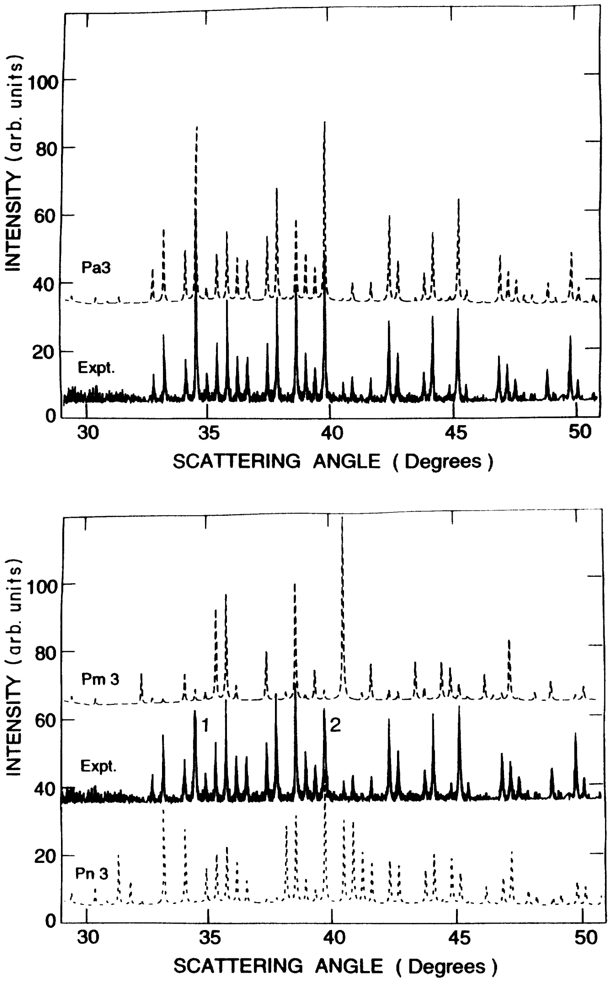

FIG. 3 Comparison of experimental and theoretical powder x-ray diffraction vs scattering angle. Top: comparison with $Pa3$. Bottom: comparison with $Pm3$ and $Pn3$. For clarity the experimental intensity below a baseline of about 6 (arbitrary units vertical scale) is not shown. The (6,1,0) peak in the experimental data is indicated by an arrow. In the comparison with the $Pm3$ and $Pn3$ structures, the experimental peaks labeled 1 and 2 are truncated, but can be seen on the other panel. The setting angle ϕ was optimized for the $Pa3$ structure to be 21.5° and for the $Pn3$ structure to be 21.6°. The calculations were done by D. M. Cox and the data is from P. A. Heiney *et al.* (unpublished).

III. PARAMETRIZATION OF THE $Pa3$ STRUCTURE

Since it is now accepted[8,9] that the space-group type of solid C_{60} fullerite is $Pa3$, we will confine our attention to this space-group type. First of all, we wish to understand how the points listed in Table I, for instance, represent an icosahedron. For simplicity we will first carry out the discussion as if C_{60} were an icosahedron with 12 vertices. The modification needed to discuss C_{60}, which is a truncated icosahedron with two bond lengths, is given later in this section.

We start by considering an icosahedron in the "standard" orientation, i.e., in an orientation when its three mirror planes are perpendicular to the three $\langle 111 \rangle$ directions. There are two such "standard" orientations, 1 and 2, which are shown in Fig. 1. Orientation 2 can be obtained from orientation 1 by a 90° rotation about a $\langle 100 \rangle$ direction. But more interestingly, orientation 2 can be obtained from orientation 1 by a rotation through an angle—ϕ_0 about the $\langle 111 \rangle$ direction, where[21] $\phi_0=\cos^{-1}(\frac{1}{4})\approx 75.52°$. This rotation is equivalent to one through an angle of $120°—\phi_0$. (The rotation angle ϕ corresponds to a right-handed rotation through an angle ϕ

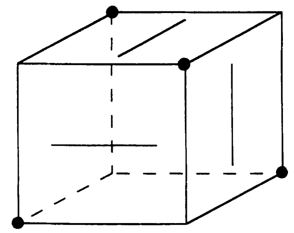

FIG. 4. Definition of the local symmetry axes about which molecules are rotated away from their initial settings as in Fig. 1. A positive rotation angle indicates a right-handed rotation relative to the positive direction. For each $\langle 111 \rangle$ direction, the positive direction is the direction from the center of the cube to the vertex indicated by a dot. When specifying a rotation axis, as in the tables, we always give the positive direction of the axis.

about the positive direction of the local [111] axis as shown in Fig. 4 and as listed in Tables I and II.) For either of these "standard" orientations the $\langle 111 \rangle$ direction is an axis of threefold symmetry. Therefore, for either orientation, the 12 points of the icosahedron can be obtained as two sets of six points, each set being obtained from the basis points (x,y,z), etc. listed in column 1 of Table I. Since two sets of points are needed, the vertices of an icosahedron will be specified by the structural parameters x, y, z, x', y', and z', i.e., by the two seeds $\mathbf{r}=(x,y,z)$ and $\mathbf{r}'=(x',y',z')$. However, it is clear that rotating the icosahedron about [111] merely involves a modified choice of these structural parameters. Of course, as the icosahedron at (0,0,0) is rotated about [111] and these structural parameters are correspondingly modified, the other icosahedra in the unit cell, whose points are given in columns 2, 3, and 4, are rotated about their respective threefold axes. This is equally true for both structures A and B. If we start from standard orientation 1, we can rotate icosahedron 1 about its local threefold axis through an angle ϕ. In this case the structural parameters assume the values

$$x_1=[(1+2\cos\phi)+(1+2\cos\phi_+)\eta]b\ , \tag{3.1a}$$

$$y_1=[(1+2\cos\phi_-)+(1+2\cos\phi)\eta]b\ , \tag{3.1b}$$

$$z_1=[(1+2\cos\phi_+)+(1+2\cos\phi_-)\eta]b\ , \tag{3.1c}$$

$$x_1'=[(1+2\cos\phi)-(1+2\cos\phi_+)\eta]b\ , \tag{3.1d}$$

$$y_1'=[(1+2\cos\phi_-)-(1+2\cos\phi)\eta]b\ , \tag{3.1e}$$

$$z_1'=[(1+2\cos\phi_+)-(1+2\cos\phi_-)\eta]b\ , \tag{3.1f}$$

where $\phi_\pm=\phi\pm120°$, $\eta=(\sqrt{5}-1)/2$, and the subscript 1 indicates that these parameters are based on the initial "standard" orientation 1. Each atom in this icosahedron is at a distance d from the center of the icosahedron with $d^2=9b^2(5-\sqrt{5})/2$. These parameters apply to both structures A and B. If the initial state is the "standard" orientation 2, then we have

$$x_2=[(1+2\cos\phi_+)+(1+2\cos\phi)\eta]b\ , \tag{3.2a}$$

$$y_2=[(1+2\cos\phi)+(1+2\cos\phi_-)\eta]b\ , \tag{3.2b}$$

$$z_2=[(1+2\cos\phi_-)+(1+2\cos\phi_+)\eta]b\ , \tag{3.2c}$$

$$x_2'=[(1+2\cos\phi_+)-(1+2\cos\phi)\eta]b\ , \tag{3.2d}$$

$$y_2'=[(1+2\cos\phi)-(1+2\cos\phi_-)\eta]b\ , \tag{3.2e}$$

$$z_2'=[(1+2\cos\phi_-)-(1+2\cos\phi_+)\eta]b\ . \tag{3.2f}$$

We now parametrize the orientations of actual C_{60} molecules. We need to give ten sets of positions (x_i,y_i,z_i) for $i=1,10$, from which, using Table I (or II), we can generate the positions of all 240 atoms in the unit cell. These ten positions are obtained as follows. We start by specifying three seed vectors:

$$\mathbf{r}_1=\tfrac{1}{2}(d_2,0,\alpha)\ , \tag{3.3a}$$

$$\mathbf{r}_2=\tfrac{1}{2}(\alpha-d_1\eta,d_1+d_2,d_1/\eta)\ , \tag{3.3b}$$

$$\mathbf{r}_3=\tfrac{1}{2}[\alpha-(d_1+d_2)\eta,d_1,(d_1+d_2)/\eta]\ , \tag{3.3c}$$

where $\alpha=(2d_1+d_2)/\eta$ and $\eta=(\sqrt{5}-1)/2$. Here d_1 is the bond length of the side of a pentagonal face, d_2 is the length of an edge between two hexagons, and the distance R from the center of the molecule to any atom is given by $R=\frac{1}{2}[d_2^2+\alpha^2]^{1/2}$. We use values of the bond lengths d_1 and d_2 as determined from NMR:[4] $d_1=1.45$ Å and $d_2=1.40$ Å. To obtain the positions of the atoms in the unit cell from the three seed vectors of Eq. (3.3) we proceed as follows. Using the operations which take (x,y,z) into (x,y,z), $(-x,y,z)$, $(x,-y,z)$, and $(-x,-y,z)$, the three seeds of Eq. (3.3) generate distinct points $\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{10}$. When acted on by the 24 elements of the $Pa3$ space group, as indicated in Tables I and II, it is easy to see that these ten points generate four identically oriented molecules, the jth column in Tables I and II giving the six image points in the molecule j associated with each one of the ten $\mathbf{r}_i$'s.

The above prescription gives the coordinates of all the atoms in the unit cell when each molecule has mirror planes perpendicular to the $\langle 100 \rangle$ directions in orientation 1 of Fig. 1. Accordingly, to obtain the actual structure of C_{60}, we need to rotate the molecules through an angle ϕ about their local threefold axis. This we do by setting

$$\begin{bmatrix} x_i' \\ y_i' \\ z_i' \end{bmatrix} = \frac{1}{3}\begin{bmatrix} 1+2\cos\phi & 1+2\cos\phi_+ & 1+2\cos\phi_- \\ 1+2\cos\phi_- & 1+2\cos\phi & 1+2\cos\phi_+ \\ 1+2\cos\phi_+ & 1+2\cos\phi_- & 1+2\cos\phi \end{bmatrix}\begin{bmatrix} x_i \\ y_i \\ z_i \end{bmatrix}\ . \tag{3.4}$$

Now the ten vectors $\mathbf{r}_i'=(x_i',y_i,z_i')$ are the structural parameters which, when input into Table I, give the correct structure. The best fit to the x-ray diffraction data gives[8] $\phi=26°$, and the vectors $\mathbf{r}_i$ for this case are given in Table V. In the next section we will discuss how other symmetry related structures (which thus must have the same free energy) can be constructed.

Now we make some comments on the structure factor for the $Pa3$ crystal. If we denote the structure factor for a single sc unit cell by $F(\mathbf{k})$, then, if $\mathbf{k}$ is a sc reciprocal lattice vector, we have for structure A

$$F_A(\mathbf{k})=f_1(\mathbf{k})+\sigma_1\sigma_3 f_2(\mathbf{k})+\sigma_2\sigma_3 f_3(\mathbf{k})+\sigma_1\sigma_2 f_4(\mathbf{k}) , \tag{3.5}$$

where $f_I(\mathbf{k})$ is the structure factor of molecule I (for structure A) calculated taking the origin at the center of mass of molecule I, and $\sigma_i=\cos(\frac{1}{2}ak_i)$, where k_μ is the μth Cartesian component of $\mathbf{k}$. Note that σ_i is real ($\sigma_i=\pm 1$), since $\mathbf{k}$ is a sc reciprocal lattice vector. From Table I, we see that for a structure of type A we have the relations

$$f_2(k_x,k_y,k_z)=f_1(k_x,k_y,-k_z) , \tag{3.6a}$$

$$f_3(k_x,k_y,k_z)=f_1(k_x,-k_y,k_z) , \tag{3.6b}$$

$$f_4(k_x,k_y,k_z)=f_1(-k_x,k_y,k_z) . \tag{3.6c}$$

Thus for structure A

$$F_A(\mathbf{k})=f_A(k_x,k_y,k_z)+\sigma_1\sigma_3 f_A(k_x,k_y,-k_z) +\sigma_2\sigma_3 f_A(k_x,-k_y,k_z)+\sigma_1\sigma_2 f_A(-k_x,k_y,k_z) , \tag{3.7}$$

where the subscript A emphasizes that f is the structure factor of the molecule at the origin in the A structure. Because the [111] direction is a threefold axis, it satisfies

$$f_A(k_x,k_y,k_z)=f_A(k_y,k_z,k_x)=f_A(k_z,k_x,k_y) . \tag{3.8}$$

It is clear that if we displace the crystal so that the molecule previously at the origin now occupies another site in the unit cell, the structure factor suffers only a phase change, involving a product of σ's, which will not affect the observable quantity $|F_A(\mathbf{k})|^2$.

Similarly for structure B, we have the structure factor

$$F_B(\mathbf{k})=f_B(k_x,k_y,k_z)+\sigma_1\sigma_3 f_B(-k_x,k_y,k_z) +\sigma_2\sigma_3 f_B(k_x,k_y,-k_z)+\sigma_1\sigma_2 f_B(k_x,-k_y,k_z) . \tag{3.9}$$

It should be obvious that if structure A is realized in one experiment, then structure B will be realized in some other experiment. The relation between these structures implies that

$$f_B(k_x,k_y,k_z)=f_A(k_y,k_x,k_z) . \tag{3.10}$$

Substituting this into Eq. (3.9) we see that

$$F_B(k_x,k_y,k_z)=F_A(k_y,k_x,k_z) . \tag{3.11}$$

If a monodomain sample is obtained, a diffraction experiment will determine whether the sample in question happens to be structure A or structure B. The Bragg peaks will come at the same locations, of course, but their intensities will differ for the two structures. That is, if the reflections are indexed by h, k, and l as usual for a simple-cubic Bravais lattice, then the intensities associated with these indices obey $I(h,k,l)=I(k,l,h)=I(l,h,k)$, but in general $I(h,k,l)\neq I(k,h,l)$. Thus although this system is cubic, it may be surprising, but it is true that for a monodomain sample $I(3,2,1)\neq I(2,3,1)$. [The intensities from one structure or domain can be obtained from those of the other one by reflection, as in Eq. (3.11).] However, if the sample is a powder, then the angular deflection depends only on $h^2+k^2+l^2$. From Eq. (3.11) it is then clear that the two structures will have the same powder pattern of diffraction intensities.

Finally we mention briefly several very recent experimental results. Copley *et al.*[22] have used neutron diffraction at $T=14$ K to study the orientationally ordered phase in a sample which has[9] fewer stacking faults than that used in the original work.[5] Their data is well fitted by a model in which the ordered phase has $Pa3$ structure, but also allows for the presence of a non-negligible amount of disorder (as did previous fits[5,8]). From these measurements they deduce the value $\phi=24°$. We did not redo our calculations with this value of ϕ, since our qualitative results depend on the symmetry of the $Pa3$ structure. We should also point out that further confirmation of the $Pa3$ structure comes from a pulsed neutron study of the pair-correlation function.[23] This data is best modeled by the $Pa3$ structure taking $\phi=26°$. So experimental evidence seems to be clearly in favor of the $Pa3$ structure, although some details concerning disorder remain to be resolved.

We also note an experiment on a single crystal sample,[24] where a result consistent with the simultaneous existence of domains of both structures was observed. Since the orientational ordering transition is expected to be a first-order one,[18] it may be difficult to prevent nucleation of the ordered phase at different locations with the concomitant creation of a multidomain sample. Perhaps an inhomogeneous cooling process could be used to create a monodomain from a single "seed" location whose temperature is colder than that of the crystal as a whole.

IV. NUMBER OF EQUIVALENT STATES

In this section we count the number of symmetry-related minima in the free energy for the $Pa3$ structure. First of all, as in solid H_2, there are eight ways to assign the local $\langle 111\rangle$ directions to the four sites in the unit cell.[16,17] To see this, note that there are four ways to assign a given molecule to the origin with a threefold axis along $\langle 111\rangle$. The additional factor of 2 in the degeneracy comes from the fact that there are two independent ways one can choose the threefold axis for one of the other sites in the unit cell. This choice corresponds to choosing either the structure of Table I or the structure of Table II. After this choice the orientations of the threefold axes for the other molecules in the unit cell are fixed by the threefold axis of symmetry which passes through the origin. Here we have to see whether or not the fact that there are two "standard" initial configurations of the icosahedra and the possibility of rotating either through an angle ϕ or $-\phi$ leads to further degeneracy.

We now discuss the symmetry operations in terms of these structural parameters. Let $|\phi,X,n\rangle$ denote the crystal one obtains when one starts with the icosahedron at the origin in "standard" orientation n ($n=1$ or 2) and rotates through an angle ϕ about the local axes positioned as in structure X, where X is either A or B as in Tables I and II.

First consider the effect of a rotation about the threefold axis through the angle $\phi_0=\cos^{-1}(\frac{1}{4})\approx 75.52°$, mentioned above, which takes orientation 2 of Fig. 1 into orientation 1, or equivalently rotation through an angle $120° - \phi_0 \approx 44.5°$ which takes setting 1 into setting 2. Thus

$$|\phi, A, 1\rangle = |\phi+\phi_0, A, 2\rangle \ , \tag{4.1a}$$

$$|\phi, B, 1\rangle = |\phi+\phi_0, B, 2\rangle \ , \tag{4.1b}$$

as can be verified by checking that $x_1(\phi)=x_2(\phi+\phi_0)$, etc. Thus any structure obtained from one "standard" orientation can equally well be obtained from the other one.

We see that Eq. (4.1) relates standard orientations 1 and 2. We can also get a relation between structures A and B by considering the effect of σ_{xz}, a reflection through the plane $x=y$. Accordingly, we now identify $\sigma_{xz}|\phi, A, 1\rangle$. The atomic positions in the structure $|\phi, A, 1\rangle$ are given by the entries in Table I with x_1, y_1, z_1, etc. given as in Eq. (3.1). Applying the operation σ_{xz} interchanges the first and third components of the position vectors. Thus this operation takes the list of points in Table I into that of Table II providing one interchanges the parameters x_i and z_i. Thus $\sigma_{xz}|\phi, A, 1\rangle$ is a structure of type B with structural parameters $\hat{x}_1=z_1(\phi)$, $\hat{y}_1=y_1(\phi)$, $\hat{z}_1=x_1(\phi)$, etc. But

$$x_1(\phi)=z_2(-\phi) \ , \tag{4.2a}$$

$$y_1(\phi)=y_2(-\phi) \ , \tag{4.2b}$$

$$z_1(\phi)=x_2(-\phi) \ . \tag{4.2c}$$

So $\sigma_{xz}|\phi, A, 1\rangle$ is a structure of type B with structural parameters $\hat{x}_1=x_2(-\phi)$, $\hat{y}_1=y_2(-\phi)$ $\hat{z}_1=z_2(-\phi)$. This means that

$$\sigma_{x,z}|\phi, A, 1\rangle = |-\phi, B, 2\rangle \tag{4.3a}$$

or

$$\sigma_{x,z}|\phi, A, 1\rangle = |-\phi, B, 2\rangle = |-\phi-\phi_0, B, 1\rangle \ . \tag{4.3b}$$

Now we address the question of how two structures with opposite signs of ϕ differ, it at all. Intuitively, it might seem that changing the sign of ϕ leads to an equivalent structure. This is not so. The simplest proof of this is as follows. First consider the rotation of a single icosahedron starting from setting 1 of Fig. 1. A rotation through the angle $-\phi_0$ about the positive sense of the local body diagonal, as indicated in Fig. 2, takes standard orientation 1 into standard orientation 2 in which the mirror planes are again perpendicular to the (1,0,0) directions. Rotation through ϕ_0 leads to an orientation in which the mirror planes are not perpendicular to the (1,0,0) directions. (If this were not so, then rotation through $2\phi_0$ would be a symmetry operation of the icosahedron, which it is not.) Now consider the relation between structure (a) in which all molecules in the unit cell are rotated through an angle ϕ, and structure (b) in which they are all rotated through an angle $-\phi$. Arguing as before, we see that these two structures cannot in general be equivalent because they are not equivalent when $\phi=\phi_0$.

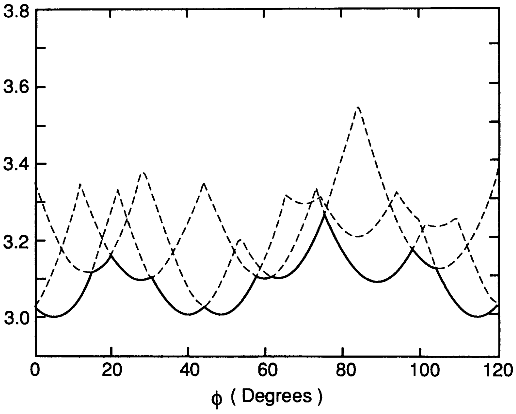

FIG. 5. The three smallest separations r_1, r_2, and r_3 between an atom on one molecule and an atom on a nearest-neighboring molecule vs the structural parameter ϕ. The angle ϕ is that for structure A when measured relative to orientation 1 of Fig. 1. Orientation 2 of Fig. 1 corresponds to $\phi=120°-\phi_0\approx 44.5°$ and has the same set of r_i's as orientation 1 ($\phi=0°$). Note that there is no symmetry about $\phi=0°$ or about $\phi=\phi^*\equiv\frac{1}{2}(120°-\phi_0)\approx 22°$.

We know from Eq. (4.1a) that $|120°-\phi_0, A, 1\rangle = |0, A, 2\rangle$. Since the free energies of $|0, A, 2\rangle$ and $|0, A, 1\rangle$ must be the same, we can say that the free energies of the structures $|0, A, 1\rangle$ and $|120°-\phi_0, A, 2\rangle$ are the same. This relation suggests that possibly there is symmetry about the value $\phi^*\equiv 60°-\frac{1}{2}\phi_0\approx 23°$. (This value is rather close to that, 26°, determined[8] for solid C_{60}.) Accordingly, one might ask whether or not $|\phi^*+\delta, A, 1\rangle$ and $|\phi^*-\delta, A, 1\rangle$ are symmetry-related structures. But in general, this is not true. To see this note that $|\phi^*-\delta, A, 1\rangle = |\phi^*+\delta, B, 2\rangle$. But since $|\phi^*+\delta, A, 1\rangle$ is not in general equivalent to $|\phi^*+\delta, B, 2\rangle$ for an arbitrary value of δ, there is no such symmetry about ϕ^*.

This last point leads to a very important observation. The value of ϕ can not be constrained by symmetry (unless ϕ is zero or its equivalent). Thus, in the observed structure ϕ must be a function of temperature which depends in detail on the orientational interaction potential. To further emphasize this point, and also to elucidate the way two neighboring C_{60} molecules arrange themselves, we show in Fig. 5 the three smallest distances between atoms on nearest-neighboring molecules as a function of the structural parameter ϕ for the $|\phi, A, 1\rangle$ structure.[25] In particular, note that there is no symmetry about either $\phi=0°$ or about $\phi=\phi^*$.

V. LANDAU THEORY

Now we make some observations about the form of Landau theory to describe the orientational ordering into the $Pa3$ structure. Basically, the discussion[17] is an extension of that given by Cullen *et al.*[16] for the orientational ordering in solid hydrogen. First we have to decide how to describe the ordering of a rigid body. This can be done using Euler angles, but that is clearly not convenient. Rather we introduce the order parameter $\sigma^{(m)}(I)$ for molecule I via

$$\sigma^{(m)}(I) \propto \langle \sum_{i \in I} r_i^6 Y_6^m(\theta_i,\phi_i) \rangle_T \tag{5.1a}$$

$$= C_0 \langle \sum_{i \in I} Y_6^m(\theta_i,\phi_i) \rangle_T \ , \tag{5.1b}$$

where C_0 is a normalization constant, the sum is over all atoms i in molecule I, r_i is the displacement of atom i relative to the center of gravity of the molecule, θ_i and ϕ_i are the polar and azimuthal angles of the ith atom, and $\langle \ \rangle_T$ indicates a thermal average at temperature T. Since r_i is the same for all atoms in the molecule, we incorporate a factor r_i^6 into the constant C_0, whose value will be fixed later. Observe that

$$[\sigma^{(m)}(I)]^* = (-1)^m \sigma^{(-m)}(I) \ . \tag{5.2}$$

This tensor order parameter is a logical one, because multipoles of nonzero order lower than 6 vanish independent of the orientation of the molecule.

We now construct a density matrix ρ which gives the probability distribution P for the Euler angles α_I, β_I, and γ_I of the Ith molecule [with $P=\rho/(8\pi^2)$]. Within mean-field theory ρ is taken to be a product of single-molecule density matrices:

$$\rho(\{\alpha,\beta,\gamma\}) = \prod_I \rho_I(\alpha_I,\beta_I,\gamma_I) \ . \tag{5.3a}$$

Here

$$\rho_I(\alpha,\beta,\gamma) = 1 + C_1 \sum_{m=-6}^{6} \sigma^{(m)} \sum_{i \in I} [Y_6^m(\theta_i,\phi_i)]^* \ , \tag{5.3b}$$

where C_1 is a constant fixed by requiring that Eq. (5.3) reproduce Eq. (5.1b). The right-hand side of Eq. (5.3) is indeed a function of the Euler angles since the spherical angles θ_i and ϕ_i implicitly depend on the Euler angles. We determine C_1. Equation (5.1b) is

$$\sigma^{(m)}(I) = C_0 \frac{1}{8\pi^2} \int d\alpha_I \sin\beta_I d\beta_I d\gamma_I \sum_{i \in I} Y_6^m(\hat{\omega}_i) \left[1 + C_1 \sum_n \sigma^{(n)} \sum_{j \in I} [Y_6^n(\hat{\omega}_j)]^* \right] , \tag{5.4}$$

where $\hat{\omega}_i \equiv (\theta_i,\phi_i)$. Now for notational convenience we write symbolically

$$\mathrm{Tr} \equiv \prod_I \left[\frac{1}{8\pi^2} \int d\alpha_I \sin\beta_I d\beta_I d\gamma_I \right] . \tag{5.5}$$

The virtue of introducing a normalized trace (e.g., $\mathrm{Tr}1=1$) is that one usually does not have to specify the molecules over which the average is taken. To evaluate the integral in Eq. (5.4) we note that the only rotational invariant to survive the average over Euler angles gives

$$\sigma^{(m)}(I) = C_0 C_1 \sigma^{(m)}(I) \mathrm{Tr} \sum_{i,j \in I} Y_6^m(\hat{\omega}_i) [Y_6^m(\hat{\omega}_j)]^* \tag{5.6a}$$

$$= C_0 C_1 \sigma^{(m)}(I) \tfrac{1}{13} \sum_\nu \sum_{i,j \in I} Y_6^\nu(\hat{\omega}_i) [Y_6^\nu(\hat{\omega}_j)]^* \ . \tag{5.6b}$$

So

$$C_1^{-1} = \frac{C_0}{4\pi} \sum_{i,j \in I} P_6(\cos\theta_{ij})$$

$$= \frac{15}{\pi} C_0 \sum_{i \in I} P_6(\cos\theta_{ij}) \tag{5.7a}$$

$$\equiv \frac{15}{\pi} C_0 Z \ , \tag{5.7b}$$

where $\cos\theta_{ij} = \mathbf{r}_i \cdot \mathbf{r}_j / (r_i r_j)$. Using the structural parameters given in Table V, we evaluated the constant $Z = 0.105\,67$.

Now we develop mean-field theory as a functional of the order parameters by writing

$$F(\{\sigma\}) = \sum_I \mathrm{Tr} V_I \rho_I + \sum_{I<J} \mathrm{Tr} V_{IJ} \rho_I \rho_J + kT \sum_I \mathrm{Tr} \rho_I \ln\rho_I \ , \tag{5.8}$$

where V_I, the crystal field, is the orientational potential of molecule I when its neighbors are disordered and V_{IJ} is the orientational potential energy of interaction between molecules I and J. Up to quadratic order the free energy is of the form

$$F = F_0 + \tfrac{1}{2} \sum_{m,m'} \sum_{I,I'} [\sigma^{(m')}(I')]^* \sigma^{(m)}(I) \chi^{-1}(m',I';m,I) \ , \tag{5.9}$$

where χ^{-1} is the inverse susceptibility, which we regard as a matrix in the scripts m and I. In Eq. (5.9) the term F_0 includes "noncritical" contributions, including the non-symmetry-breaking crystal-field term similar to that found in the orientational ordering of monolayers.[12]

By expanding Eq. (5.8) up to order σ^2, one can show that Eq. (5.9) is of the form

$$\chi^{-1}(m',I';m,I) = s_0 kT \delta_{m,m'} \delta_{I,I'} + V(m',I';m,I) \ , \tag{5.10}$$

where V is essentially the orientational potential between molecules, the form of which, unfortunately, is not well known; we used Eq. (5.7) to determine s_0 as

$$s_0 = C_1^2 \mathrm{Tr} \sum_{i,j} Y_6^m(\hat{\omega}_i) [Y_6^m(\hat{\omega}_j)]^* = C_1 / C_0 \ . \tag{5.11}$$

TABLE IV. Order parameters $C_0^{-1}\sigma^{(m)}(I)$ for the molecules in the unit cell for structure A, calculated from the structural parameters given in Table V. These structural parameters are based on the NMR work (Ref. 4) for bond lengths, and the x-ray diffraction work (Ref. 8) for the angle ϕ specifying the orientation of the molecules in the unit cell.

m	$\mathbf{r}_I=(0,0,0)$	$\mathbf{r}_I=(a/2,a/2,0)$	$\mathbf{r}_I=(a/2,0,a/2)$	$\mathbf{r}_I=(0,a/2,a/2)$
-6	(0.135, 0.766)	(0.135, −0.766)	(0.135, 0.766)	(0.135, −0.766)
-5	(0.330, −0.405)	(−0.330, −0.405)	(−0.330, 0.405)	(0.330, 0.405)
-4	(0.666, 0.064)	(0.666, −0.064)	(0.666, 0.064)	(0.666, −0.064)
-3	(0.714, 0.626)	(−0.714, 0.626)	(−0.714, −0.626)	(0.714, −0.626)
-2	(−0.200, −0.561)	(−0.200, 0.561)	(−0.200, −0.561)	(−0.200, 0.561)
-1	(−0.535, 0.590)	(0.535, 0.590)	(0.535, −0.590)	(− 0.535, −0.590)
0	(−0.356, 0.000)	(−0.356, 0.000)	(−0.356, 0.000)	(−0.356, 0.000)
1	(0.535, 0.590)	(−0.535, 0.590)	(−0.535, −0.590)	(0.535, −0.590)
2	(−0.200, 0.561)	(−0.200, −0.561)	(−0.200, 0.561)	(−0.200, −0.561)
3	(−0.714, 0.626)	(0.714, 0.626)	(0.714, −0.626)	(−0.714, −0.626)
4	(0.666 −0.064)	(0.666, 0.064)	(0.666, −0.064)	(0.666, 0.064)
5	(−0.330, −0.405)	(0.330, −0.405)	(0.330, 0.405)	(−0.330, 0.405)
6	(0.135, −0.766)	(0.135, 0.766)	(0.135, −0.766)	(0.135, 0.766)

After Eq. (5.14) below we fix the value of C_0: $C_0=0.743$, so that by Eq. (5.7b), $C_1=2.666$, from which we get $s_0=3.586$. Although the orientational potential is not well known, we can nevertheless construct the order parameter tensor from the known[8] orientation of the molecules. This information is given in Table IV. In fact, one can see that this four-sublattice structure involves spatial Fourier components at wave vectors

$$Q_x=2(\pi/a)\hat{i}\ ,\quad Q_y=2(\pi/a)\hat{j}\ ,$$

$$Q_z=2(\pi/a)\hat{k}\ ,\quad Q_0=0\ . \tag{5.12}$$

We are mainly interested in the amplitudes at the nonzero wave vectors: they are the quasicritical ones. (We do not have true criticality because in fact the orientational transition will be seen to be discontinuous.) Then one has

$$\sigma_A(Q_x)=C_0(0,0.330,0,0.714,0,-0.535,0,0.535,0,-0.714,0,-0.330,0)\ , \tag{5.13}$$

where we define the wave-vector-dependent order parameter as

$$\sigma(\mathbf{q})^{(m)}=N^{-1}\sum_I \sigma^{(m)}(I)e^{i\mathbf{q}\cdot\mathbf{r}_I}\ , \tag{5.14}$$

where N is the total number of C_{60} molecules in the system. We fix $C_0=0.743$ by requiring the order-parameter vector in Eq. (5.13) (which is essentially its value at zero temperature) to have unit norm, in which case

$$\sigma_A(Q_x)=(0,0.245,0,0.531,0,-0.398,0,0.398,0,-0.531,0,-0.245,0)\ . \tag{5.15a}$$

Also

$$\sigma_A(Q_y)=i(0.568,0,0.048,0,-0.4170,0,0,0.417,0,-0.048,0,-0.569)\ , \tag{5.15b}$$

$$\sigma_A(Q_z)=i(0,-0.301,0,0.466,0,0.438,0,0.438,0,0.466,0,-0.301,0)\ , \tag{5.15c}$$

where the subscript A indicates that it is for structure A. Here we list the components $\sigma_A(Q_\alpha)^{(m)}$ in the order $\sigma^{(-6)},\sigma^{(-5)},\ldots,\sigma^{(6)}$. Since reflection about (1,1,0) takes structure A into structure B, we can write down the analogous order parameters for structure B:

$$\sigma_B(Q_x)=i(0.569,0,-0.048,0,-0.417\ 0,0,0,0.417,0,0.048,0,-0.569)\ , \tag{5.16a}$$

$$\sigma_B(Q_y)=i(0,-0.245,0,0.531,0,0.398,0,0.398,0.0.531,0,-0.245,0)\ , \tag{5.16b}$$

$$\sigma_B(Q_z)=(0,0.301,0,0.466,0,-0.438,0,0.438,0,-0.466,0,-0.301,0)\ . \tag{5.16c}$$

Using rotation matrices we checked that successive rotations through 120° about (1,1,1) takes the 13-component eigenvector $\sigma_A(Q_x)$ into $\sigma_A(Q_y)$ into $\sigma_A(Q_z)$.

Now we truncate the Landau free energy to keep only these quasicritical Fourier components. Furthermore, we will only keep fluctuations associated with the eigenvectors listed in Eqs. (5.15) and (5.16). In other words the density matrix of molecule I is of the form

$$\rho_I = 1 + C_1 \sum_{X=A,B} \sum_{\alpha=x,y,z} \xi_X(Q_\alpha) e^{i\mathbf{Q}_\alpha \cdot \mathbf{r}_I} \sum_m \sigma_X(Q_\alpha)^{(m)} \sum_{i \in I} [Y_6^m(\hat{\omega}_i)]^* , \tag{5.17}$$

where $\sigma_X(Q_\alpha)^{(m)}$ are the coefficients given in Eqs. (5.15) and (5.16) and $\xi_X(Q_\alpha)$ are the amplitudes associated with those "normal modes." Three of these normal modes are associated with structure A and three with structure B. So to quadratic order we have

$$N^{-1}F = \tfrac{1}{2} s_0 k(T - T_0) \sum_{X,\alpha} \xi_X(Q_\alpha)^2 . \tag{5.18}$$

Next we consider the term F_3 in the free energy of order ξ^3. It comes exclusively from expanding the entropy contribution $\mathrm{Tr}\rho \ln\rho$ up to third order in σ. Summing this contribution over all molecules will enforce the condition that the sum of the wave vectors should be a vector of the fcc reciprocal lattice. This can only happen if we combine fluctuations at different wave vectors. Thus

$$N^{-1}F_3 = -\tfrac{1}{6} kTC_1^3 \sum_{X,Y,Z} \xi_X(Q_x)\xi_Y(Q_y)\xi_Z(Q_z) \sum_{l,m,n} \sigma_X(Q_x)^{(l)} \sigma_Y(Q_y)^{(m)} \sigma_Z(Q_z)^{(n)} \times \sum_{i,j,k \in I} \mathrm{Tr}\{[Y_6^l(\hat{\omega}_i)]^* [Y_6^m(\hat{\omega}_j)]^* [Y_6^n(\hat{\omega}_k)]^*\} . \tag{5.19}$$

To simplify this result note that the trace vanishes unless $l+m+n=0$. As a consequence, we only obtain a nonzero contribution if we combine one even-parity (in m) mode with two odd-parity modes. Since only two of the modes in Eqs. (5.15) and (5.16) are even, there are only four possible combinations of the labels X, Y, and Z in Eq. (5.19). Of these combinations, only two can actually satisfy $l+m+n=0$. As a result, we have

$$F = \frac{s_0}{2}(T - T_0) \sum_{X=A,B} \sum_{\alpha=x,y,z} \xi_X(Q_\alpha)^2 - kTw \sum_{X=A,B} \xi_X(Q_x)\xi_X(Q_y)\xi_X(Q_z) + O(\xi^4) . \tag{5.20}$$

The expression and numerical value for w are obtained in Appendix B. The form of Eq. (5.20) is equivalent to that given in Ref. 16 for solid hydrogen.

It is easy to see that this type of Landau free energy does describe the eight realizations of the observed[8,9] $Pa3$ structure. We see that for a given value of the quadratic part of the free energy, we should minimize the term of order ξ^3 to determine the actual phase. To do this we can either have an A phase or a B phase. To see this set

$$x \equiv \xi_A(Q_x)^2 + \xi_A(Q_y)^2 + \xi_A(Q_z)^2 \tag{5.21a}$$

and

$$y \equiv \xi_B(Q_x)^2 + \xi_B(Q_y)^2 + \xi_B(Q_z)^2 . \tag{5.21b}$$

Fixing the value of x^2+y^2 defines a surface on which the quadratic term is fixed. On this surface it is easy to see that the cubic term (when minimized) is proportional to $-|w|(x^3+y^3)$ and is therefore largest in magnitude (i.e., minimal) when $x=0$ or $y=0$. Q.E.D. Now assume we condense into the A structure. Then one sees that a minimum in F occurs when all the ξ_A's are equal in magnitude and their product has the same sign as w, which we find to be positive in Appendix B. If we take all the ξ_A's to be positive, we obtain the structure as listed in Table I. Changing the signs to any two of the ξ_A's leads to an equivalent minimum free energy and amounts to a relabeling of the sublattices. Changing the signs of *all* the ξ_A's is *not* a symmetry operation and leads to a higher free energy. Since the above discussion applies equally to either A or B variables, there are eight minima in the free energy, as expected from structural considerations.

It is clear from the fact that the cubic term is nonzero, that the orientational transition is a first-order one. The data in Ref. 5 suggest a first-order transition with a small jump in the order parameter at the phase transition. Reference 19 suggests that possibly this jump is very small, if not zero. In the above free energy one sees that $w=0$ is a multi critical point where the transition is continuous. However, to reach such a point it would be, in general, necessary to adjust two parameters, not only the temperature, say, but also another variable, perhaps the pressure. Then one would observe a first-order transition whose associated discontinuity would vanish as the pressure was adjusted to its critical value on the $p(T)$ line. It

TABLE V. Values of the structural parameters (in angstroms) for the orientationally ordered phase. We used the x-ray data (Ref. 8) to set ϕ in Eq. (3.4) to be 26° (for setting 1 of structure A) and the NMR data (Ref. 4) to set $d_1 = 1.45$ Å and $d_2 = 1.40$ Å in Eq. (3.3). At low temperature the lattice constant of the sc Bravais lattice is (Ref. 5) 14.04. (This set of structural parameters is not unique. Any vector $\mathbf{r}_i$ can be replaced by $G\mathbf{r}_i$, where G is an element of the space group.)

i	x_i (Å)	y_i (Å)	z_i (Å)
1	1.595	−0.540	3.123
2	0.279	−0.917	3.417
3	2.866	1.910	0.852
4	2.912	0.899	1.819
5	3.463	−0.769	0.084
6	3.215	−0.464	1.428
7	−2.831	0.277	2.121
8	−1.973	−0.510	2.907
9	−2.234	−2.402	1.353
10	−1.669	−1.864	2.516

should also be pointed out, in this connection, that passing to the other sign of w would lead to a different phase altogether. If we were dealing with liquid crystals, characterized by a Y_2^m-type order parameter, then changing the sign of the order parameter would correspond to going from ordinary liquid crystals to discotic liquid crystals. Here, perhaps such a transformation would be to a phase in which the molecules were rotating about a fixed axis, and thus would be partially ordered in a different way than the one envisaged here. It will thus be interesting to see experimentally if w can be tuned. Until a realistic orientational potential is available, it will not be possible to have a theoretical prediction of the magnitude of the discontinuity in the order parameter at the phase transition, because this quantity depends on terms in the Landau expansion up to order ξ^4 and the ξ^4 terms have contributions from the noncritical modes[12] which depend on the details of the orientational potential.

VI. CONCLUSIONS

We may summarize our conclusions as follows.

(i) The only possible cubic space groups which describe orientationally ordered icosahedra on a fcc lattice such that the simple-cubic unit cell contains four molecules are $Pm3$, $Pn3$, and $Pa3$. Of these, the first has the molecular orientations constrained so that each molecule has mirror planes perpendicular to the $\langle 100 \rangle$ directions. For the other space groups, the molecules can be rotated, each about a local symmetry axis, through an angle ϕ whose value must be nonzero but which is otherwise not fixed by symmetry.

(ii) We emphasize the unusual symmetry corresponding to the existence of two distinct space groups associated with the same space-group *type*. This degeneracy manifests itself in the two possible distinct (but, symmetry-related) choices for the local threefold axes. It would be possible to distinguish these two structures by a diffraction experiment if one had a monodomain specimen. (As mentioned, to do this may require inhomogeneous cooling to avoid nucleation of a multidomain sample.)

(iii) A convenient representation of the order parameter of the Ith molecule is through the quantity

$$\sigma^{(m)}(I) = C_0 \langle \sum_{i \in I} Y_6^m(\theta_i, \phi_i) \rangle_T \ , \tag{6.1}$$

where the sum is over atoms i in molecule I. Actual values of this order parameter as obtained from experimentally determined orientations of the molecules are given in Table IV for one of the two choices of the local threefold axes. Values for the other choice can be obtained by a suitable reflection of coordinates.

(iv) A Landau expansion is derived in terms of a simple mean-field density matrix incorporating the order parameters $\sigma^{(m)}(I)$. In this expansion, the most critical fluctuations are described by a six-component theory, which describes two three-state Potts variables. The eight realizations of the orientationally ordered phase are obtained from the minima of this Landau free energy, which is of the same form as that for the orientational ordering of solid orthohydrogen, which forms a very similar $Pa3$ structure.

(v) We call attention to the experimental possibility of adjusting the Landau parameter w which regulates the magnitude of the jump in the order parameter at the transition. If it were possible to change the sign of w, a rather novel type of ordering would result. Also investigation of the multi critical point $w = 0$ would, of course be interesting.

(vi) It is desirable (and we are currently studying this problem) to construct an orientational potential which would explain this observed structure. In the language of the present paper, a correct potential will give a global minimum in the eigenvalues of $\chi^{-1}(\mathbf{q})$ at the wave vectors Q_x, Q_y, and Q_z, and will minimize the energy of the structure for the observed low-temperature value[8] of the rotation angle ϕ.

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APPENDIX A: AN IMPOSSIBLE STRUCTURE

In this appendix we give the argument that one cannot retain cubic symmetry with the icosahedral fivefold axes aligned along the $\langle 111 \rangle$ directions. This conclusion follows, of course, from the arguments of Sec. II. However, these arguments only provide an indirect answer to the question of can the fivefold axes be aligned along $\langle 111 \rangle$ directions? Those arguments certainly do not indicate why this is impossible. Here we provide a more direct answer to that question. Specifically, the question we address is the following. We consider the simple-cubic unit cell to have truncated icosahedra centered at the points $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{2},0,\frac{1}{2})$, and $(0,\frac{1}{2},\frac{1}{2})$ oriented so that each molecule has one of its fivefold axes along a $[111]$ axis. (The fact that the actual C_{60} molecule has different single- and double-bond lengths does not change the argument.) Is it possible to have such a structure but retain indexing of all diffraction peaks relative to a simple-cubic lattice containing the above four molecules? Such indexing implies that all the eight $\langle 111 \rangle$ directions are equivalent and that all the six $\langle 100 \rangle$ directions are equivalent. Two directions are equivalent if there is a symmetry operation of the crystal which takes one into the other.

Clearly, if all four of the $\langle 111 \rangle$ axes are to be equivalent, each of the four molecules in the unit cell will have to have one of its fivefold axes along a different one of the $\langle 111 \rangle$ axes. The particular $[111]$ axis along which

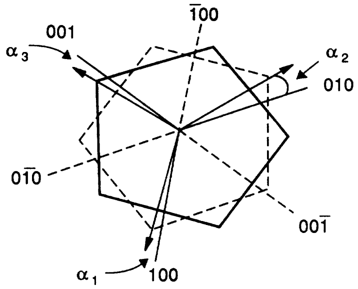

FIG. 6. Projection onto the plane $P_\perp$ of the six $\langle 100\rangle$ directions forming a regular hexagon and of the decagon described in the text. Here the decagon is represented by two pentagons, the one in solid lines nearer the observer, the one in dashed lines further from the observer. We indicate the angle α_n between the nth $\langle 100\rangle$ direction and the closest radial spoke of the decagon.

a given molecule has one of its fivefold axis aligned will be referred to as the local [111] axis. For each molecule, the plane perpendicular to its local [111] axis will be called the plane $P_\perp$.

Now consider one of the molecules in the unit cell. The local [111] axis passing through the center of the molecule passes perpendicularly through the center of two opposite pentagonal faces. When these two pentagonal faces are projected onto the plane $P_\perp$, their vertices define a regular decagon. Similarly, when the six points $\pm(a,0,0)$, $\pm(0,a,0)$, and $\pm(0,0,a)$ are projected onto the plane $P_\perp$, they define a regular hexagon. This situation is shown in Fig. 6. If we make the same construction for the other three molecules in the unit cell, the relative orientations of the hexagon and the decagon must be the same, up to a reflection, if all the $\langle 111\rangle$ axes are to be equivalent.

Now number the radial spokes of the hexagon $1,2,\ldots,6$ in order and let the minimum *magnitude* angle between the nth radial spoke of the hexagon (which represents one of the $\langle 100\rangle$ directions) and a radial spoke of the decagon be α_n. Different molecules have the same set of α_n although their ordering may not be the same for different molecules. By symmetry $\alpha_n=\alpha_{n+3}$ for $n=1$, 2, or 3. It can easily be established that $\alpha_1=\alpha_2=\alpha_3$ is *not* possible. So for each molecule we can uniquely pick out a radial spoke (i.e., a particular [100] direction) by saying it is the one with the minimum value of α, or if this minimum is twofold degenerate (e.g., $\alpha_1=\alpha_2<\alpha_3$) it is the one with the maximum value of α. So we have formulated a rule to uniquely select, for each molecule in the unit cell, an associated $\langle 100\rangle$ axis. In this way we get four choices of $\langle 100\rangle$ axes from the four molecules in the unit cell. These four choices cannot possibly leave the three $\langle 100\rangle$ axes equivalent: each axis cannot be chosen $\frac{4}{3}$ times. So a cubic structure of the type desired with the fivefold axes of the icosahedra oriented along the $\langle 111\rangle$ directions is impossible.

APPENDIX B: MEAN-FIELD EVALUATION OF w

In this appendix we evaluate w. According to Eq. (5.17) we need to evaluate

$$w_{XYZ}\equiv\tfrac{1}{6}C_1^3\sum_{l,m,n}\sigma_X(Q_x)^{(l)}\sigma_Y(Q_y)^{(m)}\sigma_Z(Q_z)^{(n)}T(l,m,n)\ ,\tag{B1}$$

where

$$T(l,m,n)=\sum_{i,j,k\in I}\mathrm{Tr}\{[Y_6^l(\hat\omega_i)]_c^*[Y_6^m(\hat\omega_j)]_c^*[Y_6^n(\hat\omega_k)]_c^*\}\ ,\tag{B2}$$

where the subscript c indicates that the quantization axis is fixed in the crystal. To carry out the trace, as defined in Eq. (5.5), we proceed as follows. We write[26]

$$[Y_6^m(\hat\omega_i)]_c=\sum_\mu[D^6_{m,\mu}(\chi_{c\to\mathrm{mol}})]^*[Y_6^\mu(\hat\omega_i)]_{\mathrm{mol}}\ ,\tag{B3}$$

where the subscript mol means with respect to axes fixed in the molecule and $\chi_{c\to\mathrm{mol}}$ indicates the triad of Euler angles which take the crystal coordinate system into that fixed in the molecule. The trace involves an average over all values of these Euler angles. So

$$\begin{aligned}T(l,m,n)=\frac{1}{8\pi^2}\int d\alpha\,\sin\beta\,d\beta\,d\gamma\\ \times\sum_{\mu,\nu,\rho}[D^6_{l,\mu}(\alpha,\beta,\gamma)]^*[D^6_{m,\nu}(\alpha,\beta,\gamma)]^*\\ \times[D^6_{n,\rho}(\alpha,\beta,\gamma)]^*S_\mu^*S_\nu^*S_\rho^*\ ,\end{aligned}\tag{B4}$$

where the S's are sums over atoms in a single molecule,

$$S_m\equiv\sum_{i\in I}Y_6^m(\hat\omega_i)\ ,\tag{B5}$$

and the D's are rotation matrices.[26] The integration over Euler angles is done using Eqs. (4.22) and (4.62) of Ref. 26:

$$\begin{aligned}T(l,m,n)=\tfrac{1}{13}\delta_{l+m+n,0}\\ \times\sum_{\mu,\nu,\rho}\delta_{\mu+\nu+\rho,0}C(6,6,6;l,m)C(6,6,6;\mu,\nu)\\ \times(-1)^{n+\rho}S_\mu^*S_\nu^*S_\rho^*\ ,\end{aligned}\tag{B6}$$

where the C's are Clebsch-Gordan coefficients. Thus

$$\begin{aligned}w_{XYZ}=\tfrac{1}{78}C_1^3\sum_{l,m}C(6,6,6;l,m)\sigma_X(Q_x)^{(l)}\\ \times\sigma_Y(Q_y)^{(m)}\sigma_Z(Q_z)^{(l+m)*}\\ \times\sum_{\mu,\nu}C(6,6,6;\mu,\nu)S_\mu^*S_\nu^*S_{-\mu-\nu}\end{aligned}\tag{B7a}$$

$$\equiv K_1K_2\ ,\tag{B7b}$$

where K_2 is the last summation over μ and ν and

$$\begin{aligned}K_1=\tfrac{1}{78}C_1^3\sum_{l,m}C(6,6,6;l,m)\sigma_X(Q_x)^{(l)}\\ \times\sigma_Y(Q_y)^{(m)}\sigma_Z(Q_z)^{(l+m)*}\ .\end{aligned}\tag{B7c}$$

We evaluate K_1 using Eqs. (5.14) and (5.15), and setting $C_1=2.666$. Thereby we see that K_1 is only nonzero for $X=Y=Z$ and its value is independent of X:

$K_1=-0.009\,03$. As for K_2 note that it is an invariant: it can be evaluated in any coordinate system. Accordingly we work in a coordinate system in which the quantization axis coincides with a fivefold axis. In that case, S_m vanishes unless m is a multiple of 5, and

$$S_5 e^{-5i\phi}=S_{-5}e^{5i\phi}=\sqrt{\tfrac{7}{11}}S_0 \ , \tag{B8}$$

where ϕ is the angle between the x axis and one of the mirror planes containing the z axis. Thus there is only one independent sum, S_0. For an undistorted truncated icosahedron we find that

$$S_0=2.117\,78 \ . \tag{B9a}$$

For the bond lengths taken from the NMR work[4] ($d_1=1.45$ Å and $d_2=1.40$ Å), we find

$$S_0=1.698\,82 \ . \tag{B9b}$$

To evaluate K_2 we use $C(6,6,6;0,0)=20/\sqrt{(11)(17)(19)}$ and $C(6,6,6;-5,5)=27.5/\sqrt{(11)(17)(19)}$, so that $K_2=-10.2814$. Thus the constant w in Eq. (5.20) is $w=0.928\,54$.

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