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Symmetry Analysis of the 2a Phase of C$_{60}$

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Abstract

A symmetry analysis of the 2*a* phase recently observed in some samples of C_{60} is presented. This phase is described by a unit cell with eight molecules in inequivalent orientations. We first show that if this structure is assumed to be exactly cubic, there are only three allowed space groups, none of which corresponds to the $Pa\bar{3}$ arrangement of threefold axes previously established for C_{60} by several groups. Our calculated powder diffraction spectra for these space groups are not consistent with existing experimental data. Second, if the symmetry of the $Pa\bar{3}$ structure is lowered by a doubling of the unit cell, we show that the resulting structure is trigonal, space group $R\bar{3}$. We calculate powder diffraction spectra for this scenario and thereby place upper limits on both the angular distortion and the trigonal lattice distortion. Third, since the microscopic origin of this distortion probably involves defects of some presently unknown type, we consider a phenomenological scenario for the origin of this trigonal distortion. Within this scenario, we study the symmetry of the interactions needed to explain this structure. We start by giving an analysis of the structural distortion within harmonic lattice dynamics. However, to obtain the correct $(R\bar{3})$ symmetry structure we were forced to study the cubic coupling between zone-corner librons and macroscopic strains. In this way we relate the development of $R\bar{3}$ symmetry from the $Pa\bar{3}$ structure in terms of a phenomenological model of lattice dynamics. Fourth, we extend the above arguments to construct a Landau theory for the hypothesized $Pa\bar{3} \rightarrow R\bar{3}$ phase transition, which occurs as a function of the concentration of the presumed defects. The resulting free energy has no cubic terms (so the transition can be continuous) but has five fourth-order invariants.

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Symmetry analysis of the $2a$ phase of C_{60}

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A symmetry analysis of the $2a$ phase recently observed in some samples of C_{60} is presented. This phase is described by a unit cell with eight molecules in inequivalent orientations. We first show that if this structure is assumed to be exactly cubic, there are only three allowed space groups, none of which corresponds to the $Pa\bar{3}$ arrangement of threefold axes previously established for C_{60} by several groups. Our calculated powder diffraction spectra for these space groups are not consistent with existing experimental data. Second, if the symmetry of the $Pa\bar{3}$ structure is lowered by a doubling of the unit cell, we show that the resulting structure is trigonal, space group $R\bar{3}$. We calculate powder diffraction spectra for this scenario and thereby place upper limits on both the angular distortion and the trigonal lattice distortion. Third, since the microscopic origin of this distortion probably involves defects of some presently unknown type, we consider a phenomenological scenario for the origin of this trigonal distortion. Within this scenario, we study the symmetry of the interactions needed to explain this structure. We start by giving an analysis of the structural distortion within harmonic lattice dynamics. However, to obtain the correct ($R\bar{3}$) symmetry structure we were forced to study the cubic coupling between zone-corner librons and macroscopic strains. In this way we relate the development of $R\bar{3}$ symmetry from the $Pa\bar{3}$ structure in terms of a phenomenological model of lattice dynamics. Fourth, we extend the above arguments to construct a Landau theory for the hypothesized $Pa\bar{3} \to R\bar{3}$ phase transition, which occurs as a function of the concentration of the presumed defects. The resulting free energy has no cubic terms (so the transition can be continuous) but has five fourth-order invariants.

I. INTRODUCTION

Until recently it was established that crystalline C_{60} (which is fcc) underwent an orientational ordering transition[1] at about 250 K from a high-temperature orientational disordered phase[2] into an orientationally ordered structure which was determined to be that of space group $Pa\bar{3}$ (Refs. 3–6) in which the unit cell contains four orientationally inequivalent molecules. In both phases, the centers of mass of the molecules are on a fcc lattice. At much lower temperature ($\sim$ 90 K) there seems to be another transition,[7–9] possibly into a glassy phase, but this transition is of no concern to us here. On the other hand, recently Tendeloo et al.[10] have reported electron diffraction data indicating a doubling of the size of the unit cell relative to the previously established $Pa\bar{3}$ structure. However, it was immediately realized[11] that structures other than the previously established $Pa\bar{3}$ structure could only be consistent with existing experimental powder diffraction data if they were obtained by a small perturbation from the previous $Pa\bar{3}$ structure. Here we will show quite conclusively that the observed powder diffraction spectra are incompatible with the various suggested $2a$ structures. In spite of the disagreement[11] with diffraction experiments, several studies supporting the proposed $2a$ structures have recently appeared.[12–14] However, the conclusions of one of the above-mentioned papers was later withdrawn by the authors.[15] More recently, using differential scanning calorimetry to characterize various samples, Fischer et al.[16] demonstrated that this doubling

of the unit cell is *not* to be associated with perfect single crystals of C_{60}. In fact, Fischer et al. identify a number of higher-order superlattice reflections (indicating unit cells even larger than $2a$) in samples they believe to be imperfect. So although we believe that the $2a$ structure is not an intrinsic property of solid C_{60}, it is unclear how such superlattice reflections are to be understood on a microscopic basis. If they are a result of chemical impurities, one would have to explain why such impurities lead to a doubling of the unit cell. Chemical impurities can lead to a structural phase transition if they relieve local frustration, as was the case for argon doped molecular CO monolayers.[17,18] However, since the C_{60} molecule is so nearly spherical, such a possibility seems unlikely here. Another possibility would be that because of chemical impurities the molecules are not exactly icosahedral, in which case one could imagine an enlargement of the unit cell due to steric packing effects. However, for our purposes we will assume that the solid consists of icosahedral molecules on fcc lattice sites and that the defects, whatever they may be, can be treated as perturbations on the ideal solid C_{60}, which we assume to have the previously proposed $Pa\bar{3}$ structure.

The data for samples which have been interpreted to have a $2a$ structure are not yet comprehensive enough to be definitive. For instance, the structure of these samples has not been monitored over a sufficient range of temperature. Thus, whether this phase develops directly from the disordered phase or occurs as a result of a thermal instability of the $Pa\bar{3}$ phase is not known with certainty. Here we assume the latter scenario. There are

now two possible interpretations. In the first of these, which we favor, the $2a$ structure forms when the concentration of defects (whatever they may be) is sufficiently large. Therefore, in our interpretation a structural phase transition occurs when the defect concentration passes through a critical value. In the second interpretation, given by Refs. 10 and 14, the instability can be reached starting from the $Pa\bar{3}$ phase of pure C_{60} by reducing the temperature through a critical value, which must be above 113 K (and thus not connected with the transition near 90 K, mentioned above) at which temperature some of the observations of van Tendeloo et al.[10] took place. In either case, it is appropriate to describe this structural phase transition in terms of a Landau expansion. The purpose of this paper is to make a symmetry analysis of this hypothesized structural phase transition. By so doing, we will describe the perturbations that give rise to the $2a$ structure in terms of order parameters. In this way, we will show how the various distortions must be coupled in accordance with their symmetry.

In a Landau expansion the expansion coefficients are usually not actually calculated from a microscopic model. A more quantitative model of this structural phase transition may be obtained by using mean field theory. However, so far, the materials parameters that control the structural phase transition and/or the occurrence of the so-called $2a$ structure have yet to be precisely identified. In these circumstances, no microscopic potential is likely to appear soon to explain this $2a$ phase. In particular, recently proposed potentials[19,20] do not predict such a distortion for pure C_{60}. (This can be seen by the fact that the libron spectrum shows no hint of "softness" or instability anywhere throughout the Brillouin zone,[21,22] nor do explicit calculations of the lattice energies based on the above potential show the possible stability of a $2a$ phase.[23,24]) Accordingly, in this paper we study the existence and evolution (from $Pa\bar{3}$) of this phase on the basis of symmetry considerations that do not invoke specific microscopic models.

The first problem we address is the enumeration of all possible cubic space groups for this $2a$ phase, assuming the C_{60} molecules to be in fixed orientations and to be centered on a fcc lattice. We find three such space groups, none of which are closely related to the $Pa\bar{3}$ structure. We calculate the diffraction spectra for these structures, and show that they violently disagree with the previous experimental data of several groups. These structures could only be possible if the newer samples are very different from those used in the diffraction studies. We discuss the fact that simply doubling the unit cell of the $Pa\bar{3}$ structure in the way proposed in Ref. 10 does not actually lead to another cubic structure, but results in retaining only one of the (1,1,1) directions as a threefold axis. This structure must therefore have an accompanying trigonal lattice distortion. Furthermore, the original proposal[10] that the unit cell is doubled by a microscopic twinning leads to a powder diffraction spectrum[11] that is incompatible with previous experimental work. So microscopic twinning is only tenable if the newer samples are very different from those used in the diffraction studies.

To avoid having to abandon the previous diffraction data we suppose that the $2a$ structure is a small perturbation from $Pa\bar{3}$. In other words, we assume that some as yet unidentified mechanism causes the condensation of a zone corner [wave vector $= \pi(1,1,1)/a$, where a is the simple cubic lattice constant] libron[21] with small amplitude $\Delta\phi$. As a result, half the molecules in the larger unit cell are rotated about their local threefold axis in one sense and half in the other sense, both through an angle $\Delta\phi$. As usual in a situation where symmetry is broken, the intensity of the resulting $2a$ superlattice diffraction peaks will be of order $(\Delta\phi)^2$. If $\Delta\phi$ is small, the results of this model will obviously be close to those for undistorted $Pa\bar{3}$ and thus are guaranteed to be compatible with the large amount of previous diffraction data. Furthermore, the trigonal distortion, mentioned above may not be large enough to have been observed yet. Since the present potentials do not lead to a trigonal distortion, we proceed phenomenologically. That is, we calculate the response of the lattice to a generalized force conjugate to the distortion. Of course, if calculated with the potentials of Ref. 19 or 20 this response would be completely stable. However, we are interested in the symmetry of the response to this generalized force. Accordingly, we study the symmetry of the distorted phase if the force constant associated with the distortion is imagined to vanish. In this way we can make some rather general observations about the way the distorted structure differs from its undistorted parent structure, $Pa\bar{3}$.

In particular, we determine the nature of the orientational and translational phonons that condense when this generalized force is applied. We find, not surprisingly, that there are several equivalent ways in which the distortion can occur. We identify a rather interesting type of distortion: the zone-corner libron that condenses is responsible for the doubling of the unit cell. This libron, when it condenses, induces tipping of the molecular axes so that only one of the (1,1,1) directions remains a threefold axis. This fact, in itself, identifies the distorted structure as trigonal. There is no linear coupling between this libron and any translational phonons.[21] So the doubling of the unit cell takes place only in the orientational degrees of freedom. (Analogously, when an antiferromagnet orders magnetically, the doubling of the unit cell is not accompanied by the condensation of a zone-boundary phonon.) One can go on to consider the coupling (allowed by conservation of wave vector) between two such librons and a zone-center optical phonon. This coupling vanishes because the librons are even parity (under inversion) modes whereas optical phonons are odd parity modes. At this level there is thus no relaxation of the molecular centers within the unit cell due to the angular distortion. As we shall see, the allowed coupling between two zone-corner librons and one zone-center libron does not produce any dramatic effects. Finally, we consider the coupling between two zone-corner librons and macroscopic strains. We show that this coupling is allowed by symmetry and gives rise to shear strains of order $(\Delta\phi)^2$. Thus we conclude that both the splitting of the diffraction peaks due to the trigonal strain and the intensity of the $2a$ superlattice peaks are of order $(\Delta\phi)^2$.

With the above results in hand, it is easy to proceed

more generally to construct a Landau expansion to describe the putative structural phase transition between $Pa\bar{3}$ and the trigonal phase, which we identify as that of space group $R\bar{3}$. We find that the quadratic terms in this expansion are described by a four-component order parameter—one component for each of the orientational sublattices in the parent $Pa\bar{3}$ phase. By wave vector conservation there can be no cubic terms in the Landau expansion. We construct the allowed fourth-order invariants and show that this expansion gives rise to an unusual anisotropy in order parameter space. Normally, the fourth-order terms fix some high-symmetry direction in order-parameter space, to be the equilibrium direction of ordering.[25] Here, the fourth-order terms give the equilibrium direction of ordering (in order-parameter space) to be $(1, \alpha, \alpha, \alpha)$, where α is not fixed by symmetry. This direction in order-parameter space does correspond, not surprisingly, to trigonal (i.e., $R\bar{3}$) symmetry. So we conclude that the Landau expansion allows a continuous structural phase transition between the $Pa\bar{3}$ and the $R\bar{3}$ phases. (If the sign of the fourth-order contribution to the free energy is negative, the transition would be discontinuous, but that cannot be determined on the basis of symmetry.)

Briefly, this paper is organized as follows. In Sec. II we identify the allowed cubic symmetry space groups that have eight molecules per unit cell on a fcc lattice. In Sec. III we present calculations of powder diffraction spectra for these various cubic symmetry space groups and show that only the $Pa\bar{3}$ structure gives agreement with existing experimental data. We also give calculations of the powder diffraction spectrum which show the effects of (a) an angular distortion leading to a doubling of the size of the unit cell and (b) the resulting trigonal lattice distortion. Comparison with experiment enables us to place upper bounds on the magnitude of these distortions. In Sec. IV we summarize the main features and results obtained from the phenomenological model of lattice dynamics, the details of which are presented in Appendix B. In this theory the order parameter is the amplitude of the zone-boundary libron whose condensation causes the doubling of the unit cell. We discuss how the various distortions in the $2a$ phase (relative to the $Pa\bar{3}$ phase) are related to this order parameter. In Sec. V the phenomenological lattice dynamical model is generalized to construct the Landau expansion for the structural phase from $Pa\bar{3}$ to the trigonally distorted $R\bar{3}$ phase. Finally, in Sec. VI the broader implications of our work are discussed and our conclusion are summarized. Several results of this work were reported previously.[11]

II. ALLOWED CUBIC SPACE GROUPS

A. Preliminaries

After some preliminary remarks, we consider in Secs. II B–II D which space groups are allowed for a $2a$ structure and in Sec. II E we discuss some space groups that are not allowed. In Sec. II F we discuss why the $2a$ version of the $Pa\bar{3}$ structure is not cubic.

In this section we discuss what space groups are allowed under the constraints that (a) the centers of the molecules are on a fcc lattice (with nearest neighbor separation $a/\sqrt{2}$), (b) each molecule assumes a fixed definite orientation, and (c) there are eight molecules per unit cell with an associated fcc Bravais lattice (with nearest neighbor separation $a\sqrt{2}$). To compare with the International Tables for Crystallography (ITC),[26] it is convenient to fix the edge of the cubic unit cell to have unit length, or equivalently to set $a = \frac{1}{2}$. In this notation there are molecules at the positions

$$R(l, m, n; j) = \frac{1}{2}[l\hat{i} + m\hat{j} + n\hat{k}] + \tau_j , \qquad (1)$$

where $l + m + n$ must be even, j labels the sublattice, and

$$
\begin{aligned}
\tau_1 &= (0,0,0) ; & \tau_2 &= (0, \tfrac{1}{4}, \tfrac{1}{4}) ; \\
\tau_3 &= (\tfrac{1}{4}, 0, \tfrac{1}{4}) ; & \tau_4 &= (\tfrac{1}{4}, \tfrac{1}{4}, 0) ; \\
\tau_5 &= (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) ; & \tau_6 &= (\tfrac{1}{2}, \tfrac{3}{4}, \tfrac{3}{4}) ; \\
\tau_7 &= (\tfrac{3}{4}, \tfrac{1}{2}, \tfrac{3}{4}) ; & \tau_8 &= (\tfrac{3}{4}, \tfrac{3}{4}, \tfrac{1}{2}) .
\end{aligned}
\qquad (2)
$$

All molecules in the same sublattice have the same orientation.

First we note that τ and $-\tau$ are in the same sublattice. Consequently, the center of each molecule is a center of inversion symmetry. Thus, the possible cubic structures that we are trying to identify are described by a fcc space group with inversion. These groups are (the numbers in parentheses are those used by ITC)

$$Fm\bar{3} \ (202), \ Fd\bar{3} \ (203), \ Fm\bar{3}m \ (225), \ Fm\bar{3}c \ (226),$$

$$Fd\bar{3}m \ (227), \ Fd\bar{3}c \ (228) . \quad (3)$$

Now we discuss where we are allowed to put the eight molecules in the unit cell. (We find it convenient to talk in terms of a unit cell containing eight molecules. In ITC the site multiplicities are calculated on the basis of the conventional unit cell, i.e., a cube with unit length edges. Our discussion will be phrased in terms of multiplicities which are a factor 4 smaller than those in ITC.)

The first step is simply to list which sites one can possibly occupy with a total of eight entities, without any constraints. This information is catalogued in Table I. Next we select from this list (and show in Table II) only those possibilities where molecules actually form a fcc lattice as specified above, in Eq. (2). The final check we must make is that the site symmetry must be consistent with placing a soccer ball (truncated icosahedron) at the indicated site. In particular, the molecule can be more symmetrical than required by symmetry of the space group. However, the reverse is not allowed: the local site symmetry must not include symmetries not possessed by the icosahedron. Most notable of such unallowed symmetries is a fourfold axis. We now turn to an analysis of each possibility remaining in Table II. In our discussion a crucial point we must consider is how the orientation of one molecule is related by symmetry to another molecule in the unit cell. For this purpose we will often use the relation

TABLE I. Ways to occupy eight sites in the unit cell for possible cubic space groups.

Space group					
$Fm\bar{3}$ (202)	$8f$	$6e + 2c$	$6e + b + a$	$6d + 2c$	$6d + b + a$
$Fd\bar{3}$ (203)	$8e$	$4d + 4c$	$4d + 2b + 2a$	$4c + 2b + 2a$	
$Fm\bar{3}m$(225)	$8f$	$6e + 2c$	$6e + b + a$	$6d + 2c$	$6d + b + a$
$Fm\bar{3}c$(226)	$6d + 2b$	$6d + 2a$	$6c + 2b$	$6c + 2a$	
$Fd\bar{3}m$(227)	$8e$	$4d + 4c$	$4d + 2b + 2a$	$4c + 2b + 2a$	
$Fd\bar{3}c$(228)	$8c$	$8b$			

$$\sigma R_\theta(\mathbf{n})\sigma = R_{-\theta}(\sigma\mathbf{n}) , \qquad (4)$$

where σ represents a reflection through a mirror plane and $R_\theta(\hat{n})$ is a rotation through an angle θ about a rotation axis $\hat{n}$. Alternatively we write this as
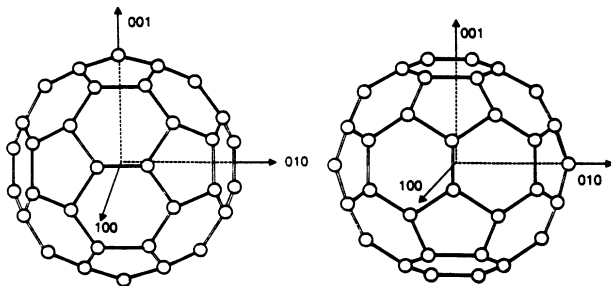
$$\sigma R_\theta(\mathbf{n}) = R_{-\theta}(\sigma\mathbf{n})\sigma . \qquad (5)$$

What this says is that under reflection a rotation becomes a negative rotation about the transformed (reflected) axis. The minus sign in front of the rotation angle occurs because the cross product of two vectors is a pseudovector. Obviously, if we compound two reflections, we have

$$\sigma_1\sigma_2 R_\theta(\mathbf{n}) = R_\theta(\sigma_1\sigma_2\mathbf{n})\sigma_1\sigma_2 . \qquad (6)$$

These relations will tell us how rotating a molecule on one sublattice is related to the consequent rotations of molecules on other sublattices.

At this point we review some basic facts about the molecular geometry of C$_{60}$.[27] The molecule is in the shape of a truncated icosahedron having 60 equivalent sites for carbon atoms. In Fig. 1 we depict two "standard" orientations of the C$_{60}$ molecule such that all three (1,0,0) directions are twofold axis of symmetry. In these orientations there are threefold axes aligned along each of the (1,1,1) directions. Standard orientation B can be obtained from A by either a 90° rotation about a (1,0,0) direction or by a suitable rotation about a (1,1,1) direc-

tion. If $|A\rangle$ ($|B\rangle$) denotes a molecule in standard orientation A (B), then Eq. (5) gives

$$\sigma R_\theta(\mathbf{n})|A\rangle = R_{-\theta}(\sigma\mathbf{n})\sigma|A\rangle . \qquad (7)$$

If the reflection is through a (1,0,0) plane, then $\sigma|A\rangle = |A\rangle$. If the reflection is through a (1,1,0) plane, then $\sigma|A\rangle = |B\rangle$.

B. Occupying eight c sites in space group $Fd\bar{3}c$

We start with space group $Fd\bar{3}c$ (228), assuming molecular centers at the eight c sites, using origin choice 2 in Ref. 26. Since the c site at (0,0,0) has a threefold axis with inversion along (1,1,1) we can place a C$_{60}$ molecule there, rotating it by a setting angle ϕ starting from a standard orientation, say, A,[27] so its orientation is $R_\phi(1,1,1)|A\rangle$. We now wish to deduce the positions of the other seven symmetry-related orientations in the unit cell. For that purpose we first list all the c sites:

$$(0,0,0), \ (\tfrac{1}{4},\tfrac{\bar{1}}{4},\tfrac{1}{2}), \ (\tfrac{\bar{1}}{4},\tfrac{1}{2},\tfrac{1}{4}), \ (\tfrac{1}{2},\tfrac{1}{4},\tfrac{\bar{1}}{4}), \ (\tfrac{\bar{1}}{4},\tfrac{1}{4},0),$$

$$(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}), \ (\tfrac{1}{4},0,\tfrac{\bar{1}}{4}), \ (0,\tfrac{\bar{1}}{4},\tfrac{1}{4}) . \quad (8)$$

One can see (from the list of coordinates in ITC) that the environs of each of these sites are obtained from those of the first site at (0,0,0) by the operations

$$[E], \ [\sigma_x\sigma_y], \ [\sigma_x\sigma_z], \ [\sigma_y\sigma_z], \ [\sigma_{yz}\sigma_x\sigma_z], \ [\sigma_{xz}],$$

$$[\sigma_{xz}\sigma_x\sigma_z], \ [\sigma_{yz}\sigma_y\sigma_z] , \quad (9)$$

where E is the identity operation, σ_α is a reflection through a plane perpendicular to the α axis. [Similarly, σ_{xy} denotes a reflection through a plane perpendicular to the (1,1,0) direction.] Note that the first four sub-

Standard Orientation A   Standard Orientation B

FIG. 1. Two "standard" orientations for the C$_{60}$ molecule. In these orientations the molecule has twofold axes of symmetry along all the (1,0,0) directions. There are threefold axes along all the (1,1,1) directions. Orientations B can be obtained from A by either a rotation of 90° about a (1,0,0) direction or by a suitable rotation about a (1,1,1) direction.

TABLE II. Possible ways to occupy eight sites in the unit cell of the relevant space groups so as to realize a fcc lattice.

Space group		
$Fm\bar{3}$ (202)	$6e + 2c$	$6d + 1b + 1a$
$Fd\bar{3}$ (203)[a]	$8e$ ($x = \tfrac{1}{4}$)	$4d + 4c$
$Fm\bar{3}m$ (225)	$6e + 2c$	$6d + 1b + 1a$
$Fm\bar{3}c$ (226)	$6d + 2b$	$6c + 2a$
$Fd\bar{3}m$ (227)[a]	$8e$ ($x = \tfrac{1}{4}$)	$4d + 4c$
$Fd\bar{3}c$ (228)	$8c$	$8b$

[a]x refers to the second setting.

lattices are obtained via an even number of reflections, whereas the last four sublattices involve an odd number of reflections. Hence a rotation through an angle ϕ in the first sublattice induces a rotation through $+\phi$ about the transformed axes of sublattices 2–4, and a rotation through $-\phi$ about the transformed axes of sublattices 5–8. In the cases of sublattices 5–8 the reflection about a $(1,1,0)$ plane converts the initial standard orientation A into B. The transformed $(1,1,1)$ axes are

$$(1,1,1),\ (\bar{1},\bar{1},1),\ (\bar{1},1,\bar{1}),\ (1,\bar{1},\bar{1}),\ (\bar{1},\bar{1},1),\ (1,1,1),$$

$$(\bar{1},1,\bar{1}),\ (1,\bar{1},\bar{1})\ . \quad (10)$$

So the molecules in sublattices 1–4 are rotated through an angle ϕ *starting from setting* A and molecules in sublattices 5–8 are rotated through an angle $-\phi$, *starting from setting* B. Comparing the orientations of the local threefold axes with the associated τ we see that the placement of these axes is characteristic of $Pn\bar{3}$. (In Table III we list the arrangement of threefold axes for space groups $Pa\bar{3}$ and $Pn\bar{3}$.)

We should also remark that $Fd\bar{3}c$ with setting angle ϕ gives a different powder diffraction spectrum than the same structure with setting angle $-\phi$. One might not expect this to be the case, since these operations seem to be related by a reflection through a plane perpendicular to $[1,\bar{1},0]$. (This operation interchanges x and y.) However, the actual effect of such a reflection is to take a rotation through an angle ϕ starting from initial standard orientation A into a rotation through an angle $-\phi$ starting from initial orientation B. So there is no relation whose only effect is to change the sign of ϕ. Similarly, the "special" value $\phi = 0$ does not introduce additional symmetry operations. Therefore this special value of ϕ is still within space group $Fd\bar{3}c$.

C. Occupying four c and four d sites for space group $Fd\bar{3}$

We now consider space group $Fd\bar{3}$ (203), assuming molecular centers at the four c and four d sites. Consider the four c sites that (using origin choice 2 in ITC) are at

$$(0,0,0),\ (\tfrac{1}{4},\tfrac{1}{4},0),\ (\tfrac{1}{4},0,\tfrac{1}{4}),\ (0,\tfrac{1}{4},\tfrac{1}{4})\ . \quad (11)$$

These sites have a threefold symmetry axis with inversion. The c sites are obtained from that at $(0,0,0)$ by the operations

$$[E],\ [\sigma_x\sigma_y],\ [\sigma_x\sigma_z],\ [\sigma_y\sigma_z]\ . \quad (12)$$

Note that these all involve an even number of reflections, and hence a rotation through an angle ϕ in sublattice one induces a rotation through $+\phi$ about the transformed axes of sublattices 2–4. The transformed $(1,1,1)$ axes are

$$(1,1,1),(\bar{1},\bar{1},1),(\bar{1},1,\bar{1}),(1,\bar{1},\bar{1}). \quad (13)$$

Again we have the arrangement of threefold axes as in $Pn\bar{3}$. So, we may orient the first four sublattices like $Pn\bar{3}$ with an angle ϕ. We can do the same construction for sublattices 5–8 on the four d sites, with an angle ψ not related to ϕ. So this structure may be called two sublattice $Pn\bar{3}$. If $\phi = \psi$, this reduces to space group $Pn\bar{3}$, with four molecules per unit cell. Also, if $\psi = \phi_0 - \phi$, where $\cos(120° - \phi_0) = \tfrac{1}{4}$, then this structure becomes $Fd\bar{3}c$.

D. Occupying one a, one b, and six d sites for space group $Fm\bar{3}$

Next we consider space group $Fm\bar{3}$ (202) assuming molecular centers on the six d sites, the a site, and the b site. The site symmetry of all these sites is such that their icosahedra must be in standard orientations, not necessarily the same for a, b, and/or d sites. To go from one d site to another one, we either invoke a threefold rotation about $(1,1,1)$ or a reflection through a $(1,0,0)$ plane. In either case, we do not change the standard orientation. So all molecules on the d sites are in the same standard orientation. Let us say they are in orientation A. If the a and b sites are both in orientation A, all molecules are equivalent and the unit cell contains only one molecule. So this possibility is rejected. If the a and b sites are both in orientation B, the structure can be described as having four molecules per unit cell and it reduces to[27] $Pm\bar{3}$. This possibility is therefore also rejected. The only allowed possibility is that in which sublattices a and b are in different standard orientations. This structure is therefore a sort of antiferromagnetic $Pm\bar{3}$.

E. Unallowed structures of Table II

Here we consider the other possibilities listed in Table II and show that they are not allowed under our conditions. We first consider space group $Fd\bar{3}c$ (228) when the centers of the molecules are on the eight b sites. These sites have a threefold axis along $(1,1,1)$ and a twofold axis along $(1,1,0)$. But this is *not* consistent with an icosahedron. It would require a mirror plane along $x = y$. So this possibility must be excluded.

Next, consider space group $Fd\bar{3}m$ (227), assuming

TABLE III. Arrangement of threefold axes for $Pa\bar{3}$ and $Pn\bar{3}$ space groups.

Sublattice	Position[a]	$Pa\bar{3}$[b]	$Pa\bar{3}$[c]	$Pn\bar{3}$
1	(0,0,0)	$(1,1,1)$	$(1,1,1)$	$(1,1,1)$
2	(1/2,0,1/2)	$(\bar{1},\bar{1},1)$	$(1,\bar{1},\bar{1})$	$(\bar{1},1,\bar{1})$
3	(0,1/2,1/2)	$(\bar{1},1\bar{1})$	$(\bar{1},\bar{1},1)$	$(1,\bar{1},\bar{1})$
4	(1/2,1/2,0)	$(1,\bar{1},\bar{1})$	$(\bar{1},1,\bar{1})$	$(\bar{1},\bar{1},1)$

[a]Positions are for a simple cubic unit cell whose edges are of unit length.
[b]This choice of the two settings for $Pa\bar{3}$ is the one used for explicit calculations in this paper.
[c]This second, but equivalent, setting is not used for calculations in this paper.

molecular centers at the eight e sites. Here, using origin choice 2 of ITC we must set $x = \frac{1}{4}$ in order to put the molecular centers on a fcc lattice. These sites have a threefold axis along $(1,1,1)$ and a $(1,1,0)$ mirror plane. This indicates a mirror plane containing the threefold axis. This is *not* consistent with an icosahedron. So this case is excluded. Consider this same space group, assuming molecular centers at the four c and four d sites. Again these sites have a mirror plane containing a threefold axis. Since this is not consistent with an icosahedron, this possibility is ruled out.

Next we consider space group $Fm\bar{3}c$ (226) when six molecules are on d sites and two are on b sites. This possibility is immediately ruled out because in this space group the d sites have a fourfold axis, which is inconsistent with an icosahedron. The same reasoning leads to rejection of the possible occupation, in this space group, of six c sites and two a sites. Likewise the presence of a fourfold axis rules out the possibility of occupying six e sites and two c sites in space group $Fm\bar{3}m$ (225).

Space group $Fm\bar{3}m$ using six d, one b, and one a sites is excluded because the a site has a threefold axis in a mirror plane, which is inconsistent with an icosahedron.

Next consider space group $Fd\bar{3}$ (203), assuming molecular centers at the eight e sites. Using origin choice 2 of ITC, we must set $x = \frac{1}{4}$ to put the molecular centers on a fcc lattice. The positions of the e sites are

$$(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4}),\ (0,0,\tfrac{1}{4}),\ (0,\tfrac{1}{4},0),\ (\tfrac{1}{4},0,0),\ (\tfrac{\bar{1}}{4},\tfrac{\bar{1}}{4},\tfrac{\bar{1}}{4}),\ (0,0,\tfrac{\bar{1}}{4}),$$

$$(0,\tfrac{\bar{1}}{4},0),\ (\tfrac{\bar{1}}{4},0,0)\ . \quad (14)$$

One can see (from the list of coordinates in ITC) that the environs of each of these sites are obtained respectively from the first site at $(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4})$ by the operations

$$[E],\ [\sigma_x\sigma_y],\ [\sigma_x\sigma_z],\ [\sigma_y\sigma_z],\ [\sigma_y\sigma_x\sigma_z],\ [\sigma_z],\ [\sigma_y],\ [\sigma_x]\ . \quad (15)$$

Note that the first four sublattices involve an even number of reflections, and hence a rotation through an angle ϕ in sublattice one induces a rotation through $+\phi$ about the transformed axes of sublattices 2–4, and a rotation through $-\phi$ about the transformed axes of sublattices 5–8. The transformed $(1,1,1)$ axes are

$$(1,1,1),\ (\bar{1},\bar{1},1),\ (\bar{1},1,\bar{1}),\ (1,\bar{1},\bar{1}),\ (\bar{1},\bar{1},\bar{1}),$$

$$(1,1,\bar{1})\ (1,\bar{1},1),\ (\bar{1},1,1)\ . \quad (16)$$

Note that rotating through ϕ about $[1,1,1]$ is identical to rotating through $-\phi$ about $[\bar{1},\bar{1},\bar{1}]$. Thus sublattices 5–8 are identical to sublattices 1–4 and we have a unit cell containing four molecules, which is actually $Pn\bar{3}$. Since this structure does not have eight molecules per unit cell, we discard it.

Next consider space group $Fm\bar{3}$ (202), assuming molecular centers at the two c and six e sites, with $x = \frac{1}{4}$ so that the molecules are centered on a fcc lattice. The site symmetries are such that all molecules must be in

TABLE IV. Allowed cubic structures.

Space group	Angles	Initial orientation	Site[a]	Site symmetry
$Fm\bar{3}$ (202)	0	A	24d	2/m
T_h^3	0	A	4a	$m\bar{3}$
	0	B	4b	$m\bar{3}$
$Fd\bar{3}$ (203)[b,c]	ϕ	A	16d	$\bar{3}$
T_h^4	ψ	A	16c	$\bar{3}$
$Fd\bar{3}c$ (228)[b,d]	ϕ	A	16c	$\bar{3}$
O_h^8	$-\phi$	B	16c	$\bar{3}$

[a]Here we use the convention in ITC based on a sc conventional unit cell.

[b]In these space groups the arrangement of the local threefold axes along the various $(1,1,1)$ directions is similar to that in space group $Pn\bar{3}$, as explained in the text.

[c]When $\psi = \phi$ this structure belongs to space group $Pn\bar{3}$. This structure belongs to space group $Fd\bar{3}c$ for $\psi = \phi_0 - \phi$, where ϕ_0 is the angle required to rotate from setting B to setting A: $\cos(120° - \phi_0) = \frac{1}{4}$, so that $\phi_0 \approx 44.48°$.

[d]This structure is defined more completely in the text. It could also be described as having angles ϕ and $\phi_0 - \phi$, both referred to initial setting A. For $\phi = \phi_0/2$ this structure is actually $Pn\bar{3}$.

one of the two standard orientations. We go from one e site to another via a threefold rotation about $(1,1,1)$ either with or without inversion. However, such a rotation and inversion both take a standard orientation into itself. So all e sites are in one standard orientation and the c sites are in the other standard orientation. (If they were both in the same standard orientation we would have a unit cell with only one molecule in it.) This structure is simply $Pm\bar{3}$ and is simple cubic[27] and we do not consider it further.

The allowed structures are summarized in Table IV.

F. Why is the 2a version of the $Pa\bar{3}$ structure noncubic?

Finally, consider the structure in which we have molecules:

$$(0,0,0)\quad [1,1,1]_{\phi_1}, \quad (17)$$

$$(\tfrac{1}{4},\tfrac{1}{4},0)\quad [1,\bar{1},\bar{1}]_{\phi_1}, \quad (18)$$

$$(\tfrac{1}{4},0,\tfrac{1}{4})\quad [\bar{1},\bar{1},1]_{\phi_1}, \quad (19)$$

$$(0,\tfrac{1}{4},\tfrac{1}{4})\quad [\bar{1},1,\bar{1}]_{\phi_1}, \quad (20)$$

$$(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})\quad [1,1,1]_{\phi_2}, \quad (21)$$

$$(\tfrac{3}{4},\tfrac{3}{4},\tfrac{1}{2})\quad [1,\bar{1},\bar{1}]_{\phi_2}, \quad (22)$$

$$\left(\tfrac{3}{4}, \tfrac{1}{2}, \tfrac{3}{4}\right) \quad [\bar{1}, \bar{1}, 1]_{\phi_2}, \tag{23}$$

$$\left(\tfrac{1}{2}, \tfrac{3}{4}, \tfrac{3}{4}\right) \quad [\bar{1}, 1, \bar{1}]_{\phi_2}. \tag{24}$$

Here the first triad of components gives the location in the unit cell, and the second triad the axis around which rotations are taken. The subscript ϕ_k indicates the angle of rotation. Note that this is a $Pa3$-like structure with a doubled unit cell, as considered in Ref. 10. Since this doubling does preserve the threefold axis at the origin, it might still seem to be cubic. We now show that (in agreement with the previous results of this section, as summarized in Table IV) this is *not* the case.

To show this, look at the environs of $\left(\tfrac{1}{4}, \tfrac{1}{4}, 0\right)$ to see if this site still has threefold symmetry about $(1, \bar{1}, \bar{1})$. Its neighbors are

$$(0,0,0) \text{ and } \left(\tfrac{1}{2}, \tfrac{1}{2}, 0\right) \quad [1, 1, 1]_{\phi_1}, \tag{25}$$

$$\left(\tfrac{1}{2}, \tfrac{1}{4}, -\tfrac{1}{4}\right) \text{ and } \left(0, \tfrac{1}{4}, \tfrac{1}{4}\right) \quad [\bar{1}, 1, \bar{1}]_{\phi_1}, \tag{26}$$

$$\left(\tfrac{1}{4}, \tfrac{1}{2}, -\tfrac{1}{4}\right) \text{ and } \left(\tfrac{1}{4}, 0, \tfrac{1}{4}\right) \quad [\bar{1}, \bar{1}, 1]_{\phi_1}, \tag{27}$$

$$\left(0, \tfrac{1}{2}, 0\right) \text{ and } \left(\tfrac{1}{2}, 0, 0\right) \quad [1, 1, 1]_{\phi_2}, \tag{28}$$

$$\left(0, \tfrac{1}{4}, -\tfrac{1}{4}\right) \text{ and } \left(\tfrac{1}{2}, \tfrac{1}{4}, \tfrac{1}{4}\right) \quad [\bar{1}, 1, \bar{1}]_{\phi_2}, \tag{29}$$

$$\left(\tfrac{1}{4}, 0, -\tfrac{1}{4}\right) \text{ and } \left(\tfrac{1}{4}, \tfrac{1}{2}, \tfrac{1}{4}\right) \quad [\bar{1}, \bar{1}, 1]_{\phi_2}. \tag{30}$$

Relative to the site at $\left(\tfrac{1}{4}, \tfrac{1}{4}, 0\right)$ its neighbors which are rotated by ϕ_1 are at

$$\pm\left(\tfrac{1}{4}, \tfrac{1}{4}, 0\right), \quad \pm\left(\tfrac{1}{4}, 0, -\tfrac{1}{4}\right), \quad \pm\left(0, \tfrac{1}{4}, -\tfrac{1}{4}\right). \tag{31}$$

These sites do *not* realize threefold symmetry about $(1, \bar{1}, \bar{1})$. So the only threefold axis is along $(1, 1, 1)$ and this structure is noncubic. We identify the actual space group of this *orientationally* distorted structure to be that of the trigonal space group $R\bar{3}$. (Note that our discussion is valid even if the molecular centers are assumed to remain on fcc lattice sites.) Of special interest is the structure in which the angles ϕ_1 and ϕ_2 assume the values $\phi + \Delta\phi$ and $\phi - \Delta\phi$, respectively, where ϕ is the setting angle determined for the $Pa\bar{3}$ structure and $\Delta\phi$ is small. We will refer to this as the $2a$-$R\bar{3}$ structure. A similar discussion shows that if the threefold axes are arranged as for $Pn\bar{3}$, the structure with a doubled unit cell *is* cubic, in agreement with the results in Table IV.

The above algebraic analysis shows that doubling the $Pa\bar{3}$ unit cell by having two setting angles leaves only one of the $(1,1,1)$ directions a threefold axis. Even so, when one considers a figure of the type given in Refs. 10 and 14 and reproduced (slightly modified) here as Fig. 2, it may still seem paradoxical that this structure is noncubic. From this figure it is hardly apparent which one of the $(1,1,1)$ directions remains an axis of threefold symme-
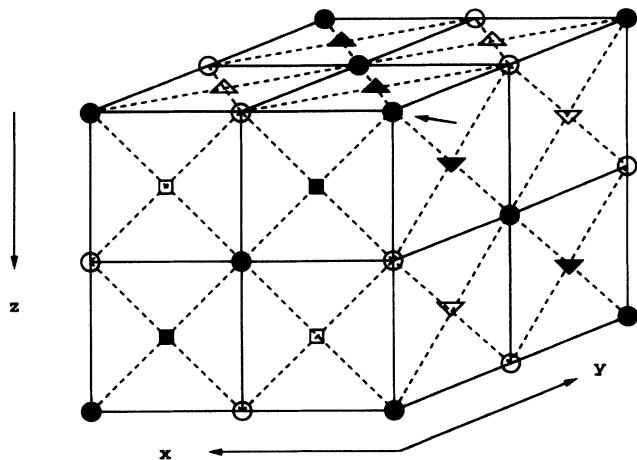

FIG. 2. Doubled unit cell for the $Pa\bar{3}$ structure, after Refs. 10 and 14. The four $Pa\bar{3}$ sublattices (before doubling) are A, B, C, and D, indicated here by circles, inverted triangles, squares, and triangles, respectively. After doubling, the primed and unprimed sublattices have setting angles ϕ_1 and ϕ_2. Here, primed sublattices are indicated by open symbols and unprimed by filled symbols. The arrow points to the origin.

try. To discuss this question, it is convenient to introduce some terminology. We will use the phrase "local rotation axis" to denote the direction of the axis about which each molecule is rotated (starting from one of the standard orientations). Before the unit cell size is doubled, the local rotation axis is the local axis of threefold symmetry. When the unit cell is doubled, as shown in Fig. 2, each site, whether primed (indicated by open symbols) or unprimed (indicated by full symbols), is surrounded by 12 nearest neighboring sites, half of which are primed and half of which are unprimed. Now, for the moment, ignore the fact that all primed (or unprimed) sites are not equivalent. That is, imagine primed sites as being helium atoms and unprimed sites as being argon atoms. In such a structure each site has a local threefold axis. We refer to this axis as the "doubling axis." Looking at Fig. 2, we see that the doubling axis of the sites are along the various $(1,1,1)$ directions. In fact, their arrangement is precisely the same as that of the threefold axes of the $Pn\bar{3}$ structure listed in Table III. Now, for a site in the structure shown in Fig. 2 to really have a threefold axis of symmetry, it is required that its local rotation axis and its doubling axis be collinear.

For which sites in Fig. 2 are these two axes collinear? One cannot say until the local rotation axes are specified. Indeed, in that sense Fig. 2 still has cubic symmetry. In what follows, the reader must keep in mind that the doubling axes are exactly the $Pn\bar{3}$ axes listed in Table III. Now consider possible choices for the arrangement of the local rotation axes. For instance, if the local rotation axes of the A or A' molecules is $(1,1,1)$, then *only* for the A and A' molecules will the local rotation axis and the doubling axis coincide to yield a threefold axis of symmetry. (This can easily be seen from Table III: only for

the site at the origin do the $Pn\bar{3}$ and $Pa\bar{3}$ axes coincide.) In this case, only the $(1,1,1)$ direction remains a three-fold axis. Another possibility is that the local rotation axis of the B and B' sites lies along $(1,-1,-1)$. In that case one can determine that only for B and B' sites do the local rotation axes coincide with the doubling axes and, consequently, in this case only the $(1,-1,-1)$ direction remains an axis of threefold symmetry. In fact, we can choose any one of A, B, C, D to have coincident local rotation and doubling axes. Having made this choice, the other three of A, B, C, D will have local rotation axes which are different from their doubling axes. As a result, only one of the $(1,1,1)$ directions will remain a threefold axis after doubling the size of the unit cell. Thus, although doubling the unit cell does not in itself break cubic symmetry (consider the helium-argon solid introduced above), when doubling is combined with the arrangement of local rotation axes as in $Pa\bar{3}$, cubic symmetry is broken, in a way dependent on the way the local rotation axes are arranged. We emphasize that cubic symmetry is broken by the orientational arrangement, whether or not there is an accompanying lattice distortion. Of course, in principle, there will be a trigonal lattice distortion. The axis of this trigonal distortion is uniquely determined when Fig. 2 is supplemented by a specification of the local rotation axes. This phenomenon of broken symmetry is naturally treated in the context of the Landau theory of continuous phase transitions, in which ordering takes place by condensation into any one of a number of equivalent minima of the free energy. This point of view is the basis for the symmetry analysis discussed in the next section.

III. DIFFRACTION SPECTRA

In the preceding section we discussed possible 2a space groups. Here we calculate powder diffraction spectra for various 2a cubic structures and compare them to existing experimental data. This comparison indicates that these space groups are not to be associated with the best samples of C$_{60}$. This is not surprising, since the observed powder diffraction spectrum of C$_{60}$ agrees so well with that calculated for the $Pa\bar{3}$ structure that any structure suggested for C$_{60}$ must be a small perturbation away from $Pa\bar{3}$.

Accordingly, we will calculate the effect of what appears to us to be the most plausible such weakly perturbed structure, namely the $2a$-$R\bar{3}$ structure, in which we double the number of sublattices, as suggested by van Tendeloo et al.,[10] but assume that half the sublattices have a setting angle $\phi + \Delta\phi$ and the other half a setting angle $\phi - \Delta\phi$, where $\Delta\phi$ is small. As discussed in Sec. IV, this structure may conveniently be regarded as one in which the doubling of the size of the unit cell is due to the condensation of a zone-boundary libron. The two most important ways this structure deviates from $Pa\bar{3}$ are (a) it has a doubled unit cell (when $\Delta\phi$ is nonzero) relative to the undistorted $Pa\bar{3}$ phase and (b) there is a trigonal distortion of the unit cell. The doubling of the unit cell when $\Delta\phi$ is nonzero leads to superlattice reflections whose intensity is of order $(\Delta\phi)^2$. As we shall see,

the fact that these reflections are not observed within the current resolution of the powder diffraction data places an upper bound of at most $2°$ on $\Delta\phi$. This angular distortion, if nonzero, implies that the unit cell is trigonally distorted. This trigonal distortion is conveniently characterized by the deviation $\Delta\alpha$ of the angle α between Bravais lattice vectors from its canonical value, $60°$, for the fcc lattice. Analysis of the powder diffraction data led Heiney[28] to place an upper limit on $\Delta\alpha$ of $0.02°$. As we will see in Sec. IV, α is proportional to $(\Delta\phi)^2$ and would be expected to be small in any event.

We now present results of our calculations of the powder x-ray diffraction spectra. To start, we show a part of the powder diffraction spectrum as a function of the scattering angle which, in accordance with custom, is denoted 2θ. In Fig. 3 we show experimental curves[29] (kindly supplied to us by Cox) for both the orientationally ordered phase [for $T < T_0$, where T_0 is about 250 K (Ref. 1)] and the orientationally disordered phase (for $T > T_0$). Here we only show the results for large scattering angles, since that portion of the spectrum is most sensitive to the orientational order. Indeed, one sees several peaks which are characteristic of the ordered phase. The spectrum calculated to fit the low-temperature data assumes that all molecules are oriented as required by $Pa\bar{3}$ symmetry for a setting angle (in the convention of Ref. 27) $\phi = 24°$. (The fit is not very sensitive to the precise value of ϕ.) The diffraction peaks were assumed to be
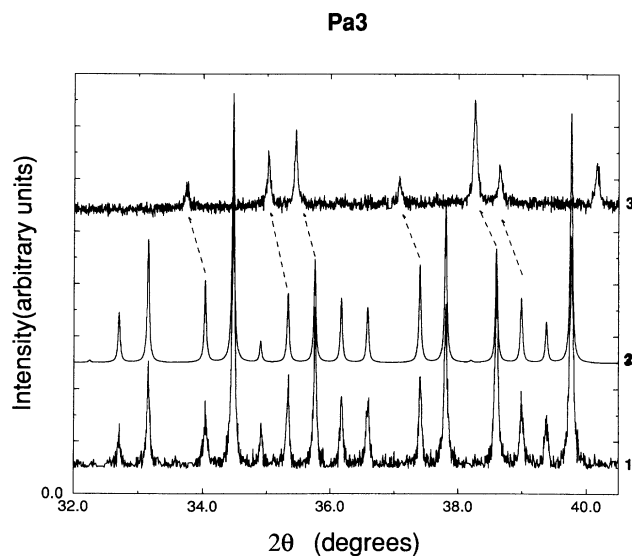
Pa3

FIG. 3. Experimental and theoretical powder diffraction spectra for C$_{60}$. Curve 3 is an experimental spectrum (Ref. 29) in the orientationally disordered phase at $T = 300$ K and curve 1 is an experimental spectrum (with the background subtracted) in the orientationally ordered phases at $T = 17$ K. These data were kindly supplied to us by Cox. Curve 2 is a theoretical fit (Refs. 3 and 4) calculated as discussed in the text, neglecting orientational fluctuations and taking the setting angle to be $\phi = 24°$ in the convention of Ref. 27. Since the lattice constant depends on temperature, the peaks in the disordered phase are shifted relative to their positions at low temperatures as indicated by the dashed lines.

Lorentzian and polarization corrections as described in Ref. 1 were made. Here we did not include fluctuations in the order parameter except insofar as they are included in the Debye-Waller factor. The agreement between calculated and observed spectra is excellent, and can be improved even further by allowing for fluctuations in the order parameter.[1,30]

In Fig. 4 we show a comparison between the various cubic structures discussed in the preceding section (See Table IV) and the experimental data. Note that the $Fm\bar{3}$ structure has no structural parameters (other than the lattice constant, of course) because all molecules are in one or another of the standard orientations. In the $Fd\bar{3}c$ structure we took the single structural parameter (i.e., the setting angle) to be $\phi = 24°$. For the $Fd\bar{3}$ structure we followed the suggestion of Ref. 14 that the setting angles on the two sublattices should differ by 60°.[31] Hence, we took the two setting angles to be 24° and 84°. Although for these space groups we have not optimized the fits with respect to the setting angle(s), these results are characteristic: it is impossible to obtain even qualitative agreement between observed and calculated spectra. (Optimizing $Fd\bar{3}$ with respect to ϕ and ψ leads to $\phi = \psi$, i.e., $Pn\bar{3}$, which does not give a satisfactory fit.[27]) As we mentioned in our earlier summary of these results,[11] these structures are *not* similar to $Pa\bar{3}$. $Fm\bar{3}$ is a generalization of $Pm\bar{3}$ (in that it uses a mixture of the two standard orientations) and the others are generalizations of $Pn\bar{3}$ (in the sense that their local symmetry axes are as in $Pn\bar{3}$). In summary: it seems clear that these alternative cubic structures are not to be associated with solid C_{60}.

Finally, to cover other existing suggestions[31] of $2a$ structures, we show in Fig. 5 a fit to the doubled unit
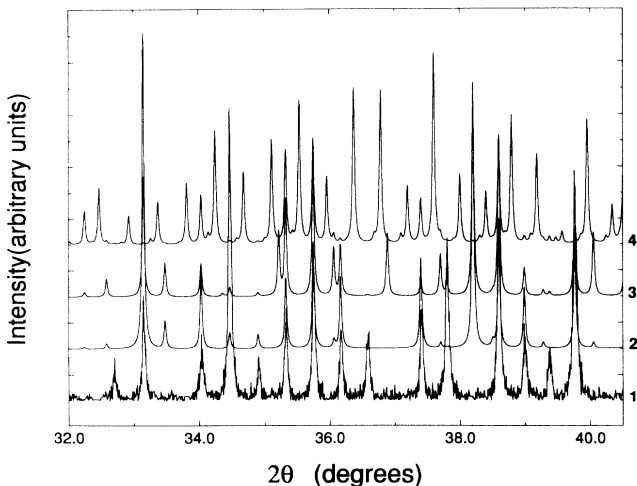

FIG. 4. Calculated powder diffraction spectra for the three allowed cubic $2a$ space groups (See Table IV) compared to the experimental data (1) taken in the orientationally ordered phase at $T = 17$ K (Ref. 29). Curve 2 is for the $Fd\bar{3}c$ structure with setting angle $\phi = 24$ degrees. Curve 3 is for the $Fd\bar{3}$ structure with the two setting angles $\phi = 84°$ and $\psi = 24°$. These angles are given in the convention of Ref. 27. Curve 4 is for the $Fm\bar{3}$ structure.
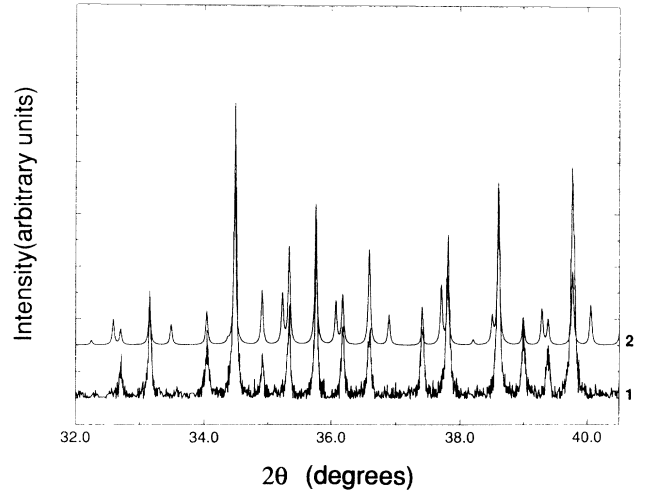

FIG. 5. A comparison of (2), the powder diffraction spectrum calculated for the $2a$-$R\bar{3}$ structure with setting angles 24° and 84°, as seems (Ref. 31) to have been suggested in Ref. 14 to (1), the experimental data (Ref. 29). Although this structure is noncubic, we neglect the trigonal distortion in this calculation.

cell of the type described in Eqs. (17)–(24) based on a $Pa\bar{3}$ arrangement of rotation axes with $\phi_2 - \phi_1 = 60°$, as suggested in Ref. 13. As mentioned in Sec. II F, this structure is not cubic. For the fit shown in Fig. 5 we do not allow any noncubic lattice distortion. Again, one sees that the resulting powder diffraction spectrum calculated for this structure does not agree with the experimental results.

Now we discuss how the diffraction spectrum is perturbed by the trigonal distortion. We start from the Laue condition

$$4Q^2 \sin^2 \theta = (h\mathbf{G}_1 + k\mathbf{G}_2 + l\mathbf{G}_3)^2 , \qquad (32)$$

where $\mathbf{G}_m$ are the basis vectors for the reciprocal lattice, Q is the wave vector of the incident (or scattered) photon, and 2θ is the angle between the incident and scattered photon. Before showing results we make a few general comments assuming perfectly cubic structures. If we assume a fcc lattice of orientationally disordered molecules in which the nearest neighbor separation is $a = a_0/\sqrt{2}$, then we have[32]

$$(aQ/\pi)^2 \sin^2 \theta = H^2 + K^2 + L^2 . \qquad (33)$$

Here we use capital letters to indicate simple cubic indexing. In this case, because the Bravais lattice is actually fcc, reflections only occur when the indices are either all odd integers or all even integers. (This set represents $\frac{1}{4}$ of all possible unrestricted sets of integers.) In the $Pa\bar{3}$ phase, one has reflections (at least when space group limitations are ignored) for all integral values of the indices. These additional superlattice reflections are evident in Fig. 3. When the unit cell is further doubled, we have reflections when either all the indices H, K, and L are odd multiples of half integers or they are all even mul-

tiples of half integers. Thus, in the 2a phase, we expect of order twice as many reflections in reciprocal space as for the $Pa\overline{3}$ phase. We will see these new 2a superlattice reflections in the calculated spectra we present below.

To discuss the trigonal distortion simultaneously with the superlattice reflections of the 2a phase, we wish to write the Laue condition in simple cubic indexing. Within trigonal indexing the Laue condition is[32]

$$(aQ/\pi)^2 \sin^2 \theta = \frac{(h^2 + k^2 + l^2)\sin^2 \alpha + 2(hk + kl + lh)(\cos^2 \alpha - \cos \alpha)}{(1 - 3\cos^2 \alpha + 2\cos^3 \alpha)},$$
(34)

where α is the angle between the basis vectors and a is the lattice constant. For the fcc case $\alpha = 60°$ and $a = a_0/\sqrt{2}$, as before. To convert this expression to simple cubic indexing, we set $h = (K+L)/2$, $k = (H+L)/2$, and $l = (H+K)/2$, in which case we have

$$(aQ/\pi)^2 \sin^2 \theta = \frac{(1 - \cos \alpha)}{(1 - 3\cos^2 \alpha + 2\cos^3 \alpha)}[(H^2 + K^2 + L^2) + 2(HK + KL + LH)(1 - 2\cos \alpha)].$$
(35)

Equation (35) has several consequences. First of all, if we have a fcc lattice, then $\cos \alpha = \frac{1}{2}$ and we get the usual result: simple cubic indexing except that the indices must be either all even or all odd. If we have a system with a small trigonal distortion, then $\cos \alpha$ will not be exactly equal to $\frac{1}{2}$, and the term proportional to $(1 - 2\cos \alpha)$

will not vanish. The effect of this term will be to split the peak, which, in the absence of a distortion, has degeneracy between all choices of signs of the indices. The magnitude of this splitting is proportional to $(1 - 2\cos \alpha)$, which, in turn, is related to the trigonal shear strains by $|1 - 2\cos \alpha|/(2\sqrt{3}) = |e_{yx}| = |e_{yz}| = |e_{xz}|$. For general values of H, K, and L, this term gives four possible results for various choices of signs of the indices. For special values of the indices the effect on the powder diffraction spectrum is as follows. For $(H, 0, 0)$ lines this term causes no splitting. For $(H, H, 0)$ lines, this term causes a splitting into two equal intensity components. For (H, H, H) lines, this term splits a line into two components having
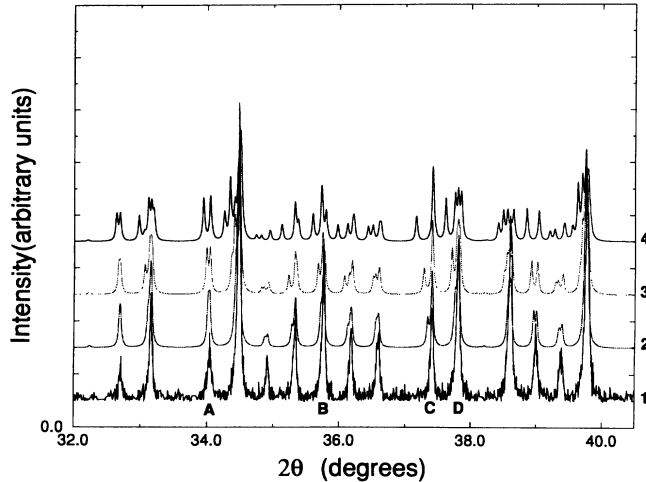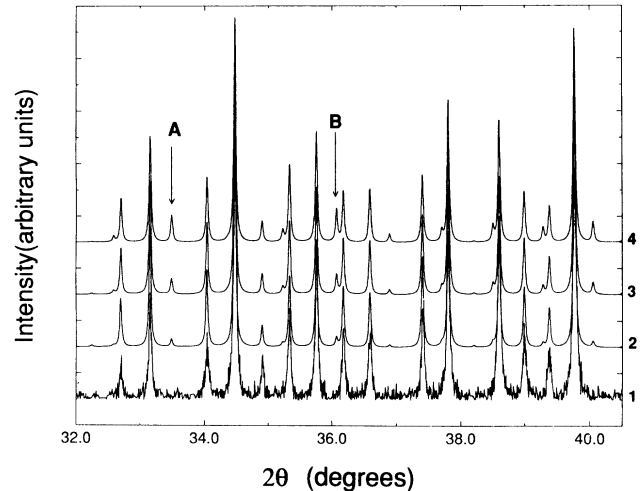

FIG. 6. The effect of a trigonal distortion on the powder diffraction spectrum. The trigonal distortion is characterized by the distortion angle $\Delta\alpha$, as explained in the text. Curve 1 is the data in the orientationally ordered phase at $T = 17$ K (Ref. 29). Curves 2–4 are for distortion angles $\Delta\alpha$ of 0.082°, 0.163°, and 0.327°, respectively. As can be seen from Eq. (35), and as the curves show, the splittings are proportional to $\Delta\alpha$. This figure shows that an upper limit for $\Delta\alpha$ is definitely less than 0.08°. The detailed analysis of Ref. 28 shows that $\Delta\alpha < 0.02°$. The labeled lines are indexed as follows: A has $(H, K, L) = (12, 8, 0)$ and is thus split into two equal intensity components. B has $(H, K, L) = (12, 4, 4)$ and is thus split into three components with intensities in the ratio 1:1:2. C has $(H, K, L) = (8, 8, 8)$ and is thus split into two components with intensities in the ratio 3:1. D is the superposition of $(H, K, L) = (14, 0, 0)$ which is unsplit and $(H, K, L) = (12, 6, 4)$ which is split into four components, one of which coincides with the unsplit line.

FIG. 7. The effect of an angular distortion of the $Pa\overline{3}$ structure in which the two setting angles in the 2a unit cell are taken to be $\phi + \Delta\phi$ and $\phi - \Delta\phi$, where ϕ is the setting angle used to fit the $Pa\overline{3}$ data. Curve 1 is the experimental data (Ref. 29). Curves 2–4 are for $\Delta\phi = 2$, $\Delta\phi = 3$, and $\Delta\phi = 4$ degrees, respectively. We have labeled as A and B the two most prominent 2a superlattice reflections due to the doubling of the unit cell for $\Delta\phi$ nonzero. Note that the integrated intensity of these superlattice reflections is proportional to $(\Delta\phi)^2$. This figure shows that an upper limit for $\Delta\phi$ is definitely less than 2°.

intensities in the ratio 3:1. For (H, H, K) lines, this term splits a line into three components having intensities in the ratio 2:1:1. In Fig. 6 we study the effect of such a trigonal lattice distortion, which, in principle, accompanies the above doubling of the $Pa\bar{3}$ unit cell. To isolate the effect of the lattice distortion we have set $\Delta\phi = 0$. Since we see no splitting of line in the experimental spectrum, we have an experimental upper bound on the distortion angle $\Delta\alpha$, which is defined to be the deviation in the angle between Bravais lattice vectors from the value for a fcc lattice. (See the caption to Fig. 6.)

Next we consider the effect on the powder diffraction spectrum of doubling the $Pa\bar{3}$ unit cell as in Eqs. (17)–(24). Thus we set $\phi_1 = \phi + \Delta\phi$ and $\phi_2 = \phi - \Delta\phi$. In so doing it is helpful to consider separately the effect of the angular distortion $\Delta\phi$ from the effect of the accompanying trigonal lattice distortion. Accordingly, in Fig. 7 we show the effect of doubling the unit cell by taking $\Delta\phi$ to be nonzero, but without allowing any trigonal lattice distortion. In principle, such a doubling of the unit cell leads to superlattice reflections. However, since superlattice reflections are not detectable in the experimental spectrum, we have an experimental upper bound on $\Delta\phi$. A conservative estimate based on Fig. 7 is that $|\Delta\phi|$ is surely less than $2°$.

IV. SYMMETRY ANALYSIS OF TRIGONAL DISTORTIONS

In this section we give a symmetry analysis of the distortion in angles and center of mass positions that characterize the structure when the $Pa\bar{3}$ unit cell is doubled. Specifically, we consider the $2a$-$R\bar{3}$ structure in which $\phi_1 = \phi_0 + \Delta\phi$ and $\phi_2 = \phi_0 - \Delta\phi$, where ϕ_0 is essentially the angle previously determined for the then-assumed $Pa\bar{3}$ structure. Whatever the microscopic origin and description of these defects, they probably have a small effect on these angles. Therefore, we give an analysis perturbative in $\Delta\phi$. This analysis, which requires a study [given in Appendix A (Ref. 33)] of the libron spectrum at the wave vector of the R point, involves a Landau-like formulation of the energy of the crystal as a function of various generalized coordinates. Since the microscopic origin of a doubling of the unit cell has not been proposed, we introduce a harmonic force constant $k_{\Delta\phi}$ associated with creating nonzero $\Delta\phi$. If we consider the structural phase diagram as a function of the concentration x of these (unknown) defects, it is clear that $k_{\Delta\phi}$ is positive for pure C_{60}. Thus as x is increased this force constant will pass through zero when the $2a$-$R\bar{3}$ phase becomes stable. We now give a phenomenological theory to describe this phase transition. As we shall see in Sec. V, this theory allows a continuous transition for the occurrence of nonzero $\Delta\phi$. So there is a regime where $\Delta\phi$ is arbitrarily small, in which the perturbative analysis is rigorous (assuming the validity of mean field theory). We use this theory to analyze the lower symmetry structure, which, as discussed in Sec. II D, is not cubic, but is described by space group $R\bar{3}$. We discuss the nature of the distortions both in the center-of-mass positions and also in the orientations of the molecules.

It is obvious that a complete microscopic theory of these distortions requires a reliable orientational potential due to whatever defects are responsible for the $2a$-$R\bar{3}$ structure. However, since the microscopic origin of these distortions is presently unknown, there is little hope of soon obtaining such a potential. Accordingly, we assume that the major feature of a successful microscopic orientational potential will be that it gives rise to torques on the molecules in the unit cell to produce the distorted structure, but otherwise the orientational potential is essentially the same as that of pure C_{60}. Therefore, we introduce torques on each molecule which tend to rotate about the local threefold axis. In our development, these torques are introduced phenomenologically. But a true microscopic theory would derive these torques as appropriate derivatives of the intermolecular orientational potential. However, once the appropriate torques are introduced, the remainder of the response may be assumed to be qualitatively that of pure C_{60}. This theory involves a rather complicated analysis of the effects of coupling to various symmetry normal modes. Accordingly, the details of this analysis are given in Appendix B.[33] However, since the physical consequences of these couplings are of some interest, we will summarize them here.

In this theory we consider perturbations of the simple cubic $Pa\bar{3}$ structure using results of the lattice dynamical study of Ref. 21. To obtain the $2a$-$R\bar{3}$ structure, we introduce generalized forces (torques) at the wave vector of the R point: $\mathbf{Q}_0 = \pi(1, 1, 1)/a$. In particular, f_α is a torque (at wave vector $\mathbf{Q}_0$) which is confined to molecules on sublattice α. The torque vector f_α is parallel to the local threefold axis, as defined in Table III, and is thus conjugate to the angular displacement (at wave vector $\mathbf{Q}_0$) of the α sublattice $\Delta\phi_\alpha$. As discussed in Appendix B,[33] the elastic energy in the presence of such torques is given by

$$\Delta E = c_1 \sum_\alpha f_\alpha^2 + \cdots , \qquad (36)$$

where c_1 is an elastic constant analogous to the susceptibility in the case of a magnetic phase transition. Alternatively, since $\Delta\phi$ is proportional to f_α, we may write

$$\Delta E = c_2 \sum_\alpha (\Delta\phi_\alpha)^2 + F_4(\Delta\phi_\alpha) , \qquad (37)$$

where $F_4(\Delta\phi_\alpha)$ denotes contributions which are fourth order in $\Delta\phi_\alpha$. We suppose that the coefficient c_2 in Eq. (37) is zero at the transition where doubling of the unit cell occurs. ($1/c_2$ is analogous to the susceptibility of a magnetic system.) The nature of the phase in which the unit cell is doubled can be determined by an analysis of the fourth-order terms in Eq. (37) that become important when c_2 is negative but small. This analysis will be given in the next section.

So far we have only considered "critical" variables, $\Delta\phi_\alpha$, i.e., those that are unstable at the structural phase transition. However, the angular displacements $\Delta\phi_\alpha$ will couple to other "noncritical" variables (denoted generically X) which remain stable at the structural phase

transition, so that their force constants c_X are nonzero. (In other words, we assume X to be defined so that its equilibrium value in the $Pa\bar{3}$ phase is zero.) Consider now the effect of an interaction energy of the form

$$\Delta E_X = w_\alpha X (\Delta\phi_\alpha)^p + \tfrac{1}{2} c_X X^2 , \qquad (38)$$

where w_α is a coupling constant. Minimization shows that the equilibrium value of X (in the $R\bar{3}$ phase) is now given by

$$X_{eq} = -c_X^{-1} w_\alpha (\Delta\phi_\alpha)^p . \qquad (39)$$

The magnitude of X_{eq} induced by the instability in $\Delta\phi_\alpha$ is determined by the minimum value of p, which, in turn, is determined by symmetry, as is discussed in Appendix B.[33] Contributions to the energy of higher than linear order in X are not relevant for small enough $\Delta\phi_\alpha$, and they are ignored here. Wave vector conservation implies that the only possible wave vectors that can be associated with X are multiples of Q_0: namely, Q_0 and zero, the former with an odd-order multinomial in $\Delta\phi_\alpha$, the latter with an even-order multinomial. Therefore, the noncritical variables that can couple to $\Delta\phi_\alpha$ are (a) Q_0 librons, (b) zero-wave-vector librons, (c) microscopic strains (at zero wave vector, of course), (d) Q_0 phonons, and (e) zero-wave-vector phonons.

However, since both at wave vector zero and at wave vector Q_0 phonons are odd parity modes and librons are even parity modes, these couplings to phonons vanish.

We start by considering the response of librons at wave vector Q_0 to the instability. In this connection it is convenient to talk in terms of the torque f_α. The response to f_α is of two types. The first type is to cause nonzero values of the Q_0 component of the setting angles $\Delta\phi_\alpha$, so that $\Delta\phi_\alpha = \chi^{-1}\phi_\alpha$, where χ is a type of "susceptibility" evaluated in Appendix B (Ref. 33) in terms of elements of the dynamical matrix. For potentials currently in use, χ is not infinite because, as we have said, these potentials do not predict the kind of instability we are describing. Thus we consider χ to be a phenomenological constant that diverges as the transition to the $2a$-$R\bar{3}$ transition is approached. We refer to this response in $\Delta\phi_\alpha$ as the critical response. The noncritical response is to cause an infinitesimal rotation (assuming f_α to be infinitesimal) of the molecules on sublattice α at wave vector Q_0 about an axis perpendicular to the local rotation axis of the $Pa\bar{3}$ structure. This infinitesimal rotation can be considered to be the sum of rotations $u_{i,\alpha}$ about coordinate axes i (fixed in the crystal), where i assumes the values x, y, and z. The results obtained in Appendix B (Ref. 33) for this response are given in Table V.

The coupling to zero-wave-vector librons leads to angular distortion of the orientations of the molecules as follows. In the $R\bar{3}$ structure, only one of the $[1,1,1]$ directions remains a threefold axis. Suppose this direction is denoted $[1,1,1]$. In the convention of Table III, this means that in the $R\bar{3}$ phase only the first sublattice still has a local threefold axis of symmetry. Thus, in the $R\bar{3}$ structure, molecules on sublattice 2 can be rotated through an angle θ about an axis perpendicular to the previous three-

TABLE V. Asymmetric response $u_{i,\alpha}$, the amplitude of rotation at wave vector Q_0 in sublattice i about the α Cartesian axis. Here $u_{i,\alpha} = (\lambda_{i,\alpha}\lambda + \gamma_{i,\alpha}\gamma + \epsilon_{i,\alpha}\epsilon)/(\sqrt{3}\Delta)$, where λ, γ, and ϵ are force constants of solid C_{60}. [The dynamical matrix is given in Table IX of Appendix A (Ref. 33).] Also, $\Delta = a[(\alpha+2\beta)(\alpha+\lambda-\beta-\gamma-\epsilon) - 2|\lambda - e^{-2\pi i/3}\gamma - e^{2\pi i/3}\epsilon|^2]Ic^2$, where $I = 1.0 \times 10^{-36} \mathrm{gr\,cm^2}$ and c is the velocity of light. For the potential of Ref. 19 the parameters assume the values (in units of cm^{-2}): $\alpha = 7.815$, $\beta = 1.417$, $\epsilon = 0.513$, $\gamma = -1.235$, and $\lambda = -0.315$.

i,α	$\lambda_{i,\alpha}$	$\gamma_{i,\alpha}$	$\epsilon_{i,\alpha}$
$1,x$	$f_D - f_C$	$f_D - f_B$	$f_B - f_C$
$1,y$	$f_C - f_B$	$f_C - f_D$	$f_D - f_B$
$1,z$	$f_B - f_D$	$f_B - f_C$	$f_C - f_D$
$2,x$	$f_C + f_D$	$f_C - f_A$	$f_A + f_D$
$2,y$	$-f_A - f_D$	$-f_C - f_D$	$f_C - f_A$
$2,z$	$f_C - f_A$	$-f_D - f_A$	$f_C + f_D$
$3,x$	$-f_A - f_B$	$-f_B - f_D$	$f_D - f_A$
$3,y$	$f_D - f_A$	$-f_A - f_B$	$f_B + f_D$
$3,z$	$f_D + f_B$	$f_D - f_A$	$f_A + f_B$
$4,x$	$f_B - f_A$	$-f_A - f_C$	$f_C + f_B$
$4,y$	$f_C + f_B$	$f_B - f_A$	$f_A + f_C$
$4,z$	$-f_A - f_C$	$-f_C - f_B$	$f_B - f_A$

fold axis in the $Pa\bar{3}$ structure. Symmetry does not fix the orientation of the axis of this rotation, other than that it is perpendicular to the previous threefold axis. Since the $[1,1,1]$ direction is a threefold axis, sublattices 3 and 4 are reoriented as required by this symmetry given the reorientation of sublattice 2. Also, since the coupling required for this orientational distortion must be quadratic in $\Delta\phi_\alpha$ (in order to conserve wave vector), we can say that in the terminology of Eq. (39), $p = 2$ for this coupling. In other words, the zero-wave-vector reorientation within the unit cell (a) preserves only one of the threefold axes, and (b) involves angular displacements of order $(\Delta\phi_\alpha)^2$.

Finally, we discuss the strain induced by nonzero $\Delta\phi_\alpha$. As in the case we have just discussed, the coupling of macroscopic strains must be quadratic in $\Delta\phi_\alpha$ in order to conserve wave vector. So, the $R\bar{3}$ structure is obtained from the $Pa\bar{3}$ structure by strain components such that

$$|e_{xy}| = |e_{yz}| = |e_{xz}| \sim (\Delta\phi_\alpha)^2 . \qquad (40)$$

The signs of these strains are fixed so that they correspond to elongation (or compression) along that one of the $[1,1,1]$ directions which is preserved as a threefold axis. The magnitude of this shear distortion is quadratic in $\Delta\phi_\alpha$.

V. LANDAU THEORY FOR THE $Pa\bar{3} \to R\bar{3}$ STRUCTURAL PHASE TRANSITION

In this section we discuss the Landau description of the structural phase transition from the $Pa\bar{3}$ to the $R\bar{3}$ phase. We do this by constructing a free energy functional that incorporates fluctuations towards the $R\bar{3}$ structure assuming one is in the $Pa\bar{3}$ phase. This theory does *not*

describe a direct transition from the disordered phase into the $R\bar{3}$ phase.

First we remark that as far as symmetry is concerned, it does not matter whether we talk in terms of displacements or forces conjugate to displacements. Thus, if we wish to express the free energy in terms of angular displacements, we can adopt the results of the preceding section for their allowed form. To quadratic order, we have the result from Appendix B:[33]

$$E = \tfrac{1}{2}a(T - T_c)(\Delta\phi_A^2 + \Delta\phi_B^2 + \Delta\phi_C^2 + \Delta\phi_D^2) . \quad (41)$$

In writing this result, we have replaced the prefactor in this term by the usual coefficient whose vanishing at $T = T_c$ leads to a phase transition at this temperature. (In our interpretation T_c is a function of x such that there is a transition only if the defect concentration is sufficiently large.) The parameter a is an unimportant scale factor. In principle, Eq. (41) should result from the extension of Eq. (37) to nonzero temperatures. However, such an instability cannot be obtained from currently available potentials.[19,20]

Already it is clear that we are dealing with a Landau theory involving a four-component order parameter.

However, unlike some previous models,[34] this model for distortions will not lead to a Potts model. The reason the present model is different is because wave-vector conservation ensures that only even powers of order parameters (at the R point) can occur. (Thus, the cubic terms characteristic of ferromagnetic Potts models are missing. However, the present model is similar to an antiferromagnetic Potts model.[35]) Thus, this structural phase transition may be a continuous one, depending on the overall sign of the fourth-order term in the Landau expansion. Since we are not able to give a microscopic evaluation of these terms (remember, no orientational potential is known to predict this transition), we cannot say more than that. Potentially, one could imagine that by applying pressure (or some other noncritical field) one could change the sign of the fourth-order terms, and thereby pass through a tricritical point.

To proceed further, we investigate the form of the fourth-order terms. What we need to do is to form all possible invariants made up of four $\Delta\phi$'s. It is useful to note that the space of multinomials of the $\Delta\phi$'s of degree four induce a representation of the space group $Pa\bar{3}$. An analysis of this type leads to construction of the following invariants:

$$
\begin{aligned}
H_1 &= (\Delta\phi_A^2 + \Delta\phi_B^2 + \Delta\phi_C^2 + \Delta\phi_D^2)^2, \\
H_2 &= \Delta\phi_A^2\Delta\phi_B^2 + \Delta\phi_A^2\Delta\phi_C^2 + \Delta\phi_A^2\Delta\phi_D^2 + \Delta\phi_B^2\Delta\phi_C^2 + \Delta\phi_B^2\Delta\phi_D^2 + \Delta\phi_C^2\Delta\phi_D^2, \\
H_3 &= \Delta\phi_A\Delta\phi_B\Delta\phi_C\Delta\phi_D, \\
H_4 &= \Delta\phi_A^3(\Delta\phi_B + \Delta\phi_C + \Delta\phi_D) + \Delta\phi_B^3(\Delta\phi_D - \Delta\phi_A - \Delta\phi_C) + \Delta\phi_C^3(\Delta\phi_B - \Delta\phi_A - \Delta\phi_D) \\
&\quad + \Delta\phi_D^3(\Delta\phi_C - \Delta\phi_A - \Delta\phi_B), \\
H_5 &= \Delta\phi_A\Delta\phi_B(\Delta\phi_D^2 - \Delta\phi_C^2) + \Delta\phi_A\Delta\phi_C(\Delta\phi_B^2 - \Delta\phi_D^2) + \Delta\phi_A\Delta\phi_D(\Delta\phi_C^2 - \Delta\phi_B^2) \\
&\quad + \Delta\phi_B\Delta\phi_C(\Delta\phi_A^2 - \Delta\phi_D^2) + \Delta\phi_B\Delta\phi_D(\Delta\phi_A^2 - \Delta\phi_C^2) + \Delta\phi_C\Delta\phi_D(\Delta\phi_A^2 - \Delta\phi_B^2) .
\end{aligned}
\quad (42)
$$

Thus, up to fourth order the free energy is of the form

$$F = \tfrac{1}{2}a(T - T_c)\left(\Delta\phi_A^2 + \Delta\phi_B^2 + \Delta\phi_C^2 + \Delta\phi_D^2\right) + \sum_{k=1,5} c_k H_k . \quad (43)$$

Some of the fourth-order terms have a familiar form. In particular, minimizing a potential with only c_1, $c_2 < 0$, and c_3 nonzero does not lead to breaking the symmetry between sublattices. Therefore, H_4 and/or H_5 are essential to produce an $R\bar{3}$ phase. The physical meaning of some of these terms is apparent. For instance, H_1 is the usual fourth-order term for an isotropic (Heisenberg) model. It does not favor any particular direction in the four-dimensional order-parameter space. A term like H_2 leads to an anisotropy that favors ordering along a $(1,1,1,1)$ direction in order-parameter space if $c_2 < 0$, or disfavors it if $c_2 > 0$. In the present case, c_2 must be negative in order to obtain a trigonal distortion for which $\Delta\phi_\alpha^2$ is independent of α. The effect of the term H_3 may be seen as follows. It is clear that the four $[1,1,1]$ directions are equivalent in the sense that any

one of them can be chosen as the threefold axis of the $R\bar{3}$ phase. Neglecting, for the moment, the effect of H_4 and H_5, we see that the sixteen possible choices for the signs of $\Delta\phi_\alpha$ correspond to the four possible choices of the $[1,1,1]$ direction to be a threefold axis. Clearly, for each choice of the $[1,1,1]$ direction, there are four ways to choose the signs of the $\Delta\phi_\alpha$'s. Changing the signs of all $\Delta\phi_\alpha$'s is obviously a symmetry of F and does not affect the selection of the $[1,1,1]$ direction. There thus remain two choices of signs of the $\Delta\phi_\alpha$'s, which, although corresponding to the same choice of $[1,1,1]$ directions, nevertheless correspond to different energies. For instance, choosing $\Delta\phi_2 = \Delta\phi_3 = \Delta\phi_4$ selects the threefold axis to lie along the $[1,1,1]$ direction. We therefore have two signs to discuss, namely, ξ_1, the sign of $\Delta\phi_1$, and ξ_2, the sign of $\Delta\phi_2$. We know that reversing the signs of both ξ_1 and ξ_2 cannot change the energy. However, the relative sign of ξ_1 and ξ_2 is fixed by energetics. In fact, if c_3 in Eq. (43) is positive (negative), the state with $\xi_1\xi_2 < 0$ (> 0) is favored. Analogous considerations hold when other $[1,1,1]$ directions are selected. In Appendix B (Ref. 33) it is shown that one contribution to c_3 comes

from a third-order strain-libron coupling.

The last two invariants may be less familiar. They do not force the order parameter into its highest symmetry direction. Rather, they express the breaking of the equivalence between sublattices. To see that, imagine that c_4 and c_5 are small. Then, since we assume $c_2 < 0$, we may minimize F for each $\Delta\phi_\alpha$ being of the form $|\Delta\phi_\alpha| = 1 + x_\alpha$ and we look for a minimum of F for small x_α. The minimization is carried out in Appendix C.[33] There it is shown that this minimum corresponds to the distorted system, whose symmetry is $R\bar{3}$. Similar statements can be made about the other symmetry-related minima that occur when the signs of an even number of $\Delta\phi$'s are changed. (Only an even number of sign changes leaves H_3 invariant.)

Finally, we discuss some of the implications of Landau theory. First of all, it gives the usual result for the order parameter, which in this case is the angular distortion

$$\Delta\phi_\alpha \sim (T_c - T)^{1/2} , \quad T < T_c . \tag{44}$$

An immediate consequence of this is that the intensity of the superlattice reflections for the 2a phase will vary like

$$I \propto (\Delta\phi)^2 \sim (T_c - T) , \quad T < T_c . \tag{45}$$

We can use the results of Sec. IV to give the corresponding temperature dependence of the various deformations. Since the trigonal strain ϵ is proportional to to $(\Delta\phi)^2$, we have

$$\epsilon = A(T_c - T) , \quad T < T_c$$
$$= 0 , \quad T > T_c . \tag{46}$$

(This means that $d\epsilon/dT$ is discontinuous as $T = T_c$, so that $d\epsilon/dT|_{T=T_c^-} - d\epsilon/dT|_{T=T_c^+} = A$.) Similar statements can be made about the orientational distortion within the unit cell due to $\mathbf{q} = 0$ librons. There, coupling to the A_g modes also has observable consequences, at least in principle. For instance, the coupling to the A_g strain mode will cause the lattice constant (or better, the density) to have a discontinuity in its derivative with respect to temperature. Likewise, the average setting angle, ϕ, will be continuous at the $Pa\bar{3} \rightarrow R\bar{3}$ transition, but its temperature derivative will be discontinuous. For all these predictions, one must keep in mind that the critical exponents are expected to be modified from the mean-field values by fluctuations.

VI. DISCUSSION AND CONCLUSIONS

We may summarize our principal results as follows.

(1) We identified the possible cubic space groups for C$_{60}$ molecules whose centers form a fcc lattice such that there are eight molecules in the unit cell of dimensions double that of the unit cell for disordered molecules. These 2a space groups are $Fm\bar{3}$ (in which molecules are in the standard orientations), $Fd\bar{3}$, and $Fd\bar{3}c$. In these last two space group the molecules are rotated (starting from their standard orientations) about the local threefold axis, (which are arranged as in $Pn\bar{3}$) half through

an angle ϕ_1, the other half through an angle ϕ_2.

(2) We calculated the powder diffraction spectra from these allowed 2a cubic space groups and obtain results that disagree with previous experimental data. We therefore exclude the above 2a cubic space groups for pure C$_{60}$.

(3) Recent experimental work[16] indicates that the best samples of C$_{60}$ do not show superlattice reflections of such 2a structures. Perhaps the observed[10] superlattice reflections might be explained in terms of some type of defect or impurity.

(4) We consider the case where the volume of the unit cell of the $Pa\bar{3}$ structure (containing four molecules) is doubled in the following way. Start from a structure in which all molecules are centered on fcc lattice sites and are all in standard orientation A of Fig. 1. Then each molecule is rotated about a $[1,1,1]$ direction appropriate to space group $Pa\bar{3}$. Four molecules in the unit cell are rotated through an angle ϕ_1 and four others through an angle ϕ_2. We showed that the resulting structure is no longer cubic (even if the molecules are still restricted to having their centers of mass on a fcc lattice). In this structure only one of the four $(1,1,1)$ directions remains a threefold axis of symmetry, as we show by both simple algebraic and geometrical arguments. This structure is trigonal belonging to space group $R\bar{3}$.

(5) We studied the model in which $\phi_1 = \phi + \Delta\phi$ and $\phi_2 = \phi - \Delta\phi$ with the idea that small $\Delta\phi$ might be induced by defects that can occur[16] in less than perfect samples of C$_{60}$. Since no microscopic models of the intermolecular potential exist that could explain such a structure, we gave a symmetry analysis of the possible distortions away from $Pa\bar{3}$ structure. This analysis indicates that the doubling of the unit cell that occurs for nonzero $\Delta\phi$ is accompanied by a response at zero wave vector that includes a shear strain corresponding to elongation (or compression, depending on the sign of the coupling constant) along the trigonal axis. The magnitude of this trigonal distortion is of order $(\Delta\phi)^2$. Linear coupling to zone-boundary librons is also allowed.

(6) We studied the experimental consequences of a small angular distortion. We calculated powder diffraction spectra as a function of $\Delta\phi$ (see Fig. 7). Optimization of the calculated powder diffraction spectrum (versus experiment) with respect to $\Delta\phi$ yields $\Delta\phi = 0$, i.e., the $Pa\bar{3}$ structure. As expected, the superlattice reflections have an intensity of order $(\Delta\phi)^2$. Since these reflections are not observed experimentally, we infer an upper bound: $|\Delta\phi|$ is certainly less than $2°$. Allowing $\Delta\phi$ to be nonzero breaks cubic symmetry and in general leads to a trigonal lattice distortion. This distortion is characterized by the change in angle $\Delta\alpha$ between lattice vectors relative to the undistorted (fcc) value. We discuss the splittings in the diffraction peaks indexed by (H, K, L) caused by this trigonal lattice distortion. For general values of the indices, each simple cubic peak (for all permutations and signs of the indices) is split into four components in the presence of the trigonal distortion. Since the experimentally observed powder diffraction spectrum shows no such splittings, we see from Fig. 6 that an upper bound on $\Delta\alpha$ is certainly less than $0.08°$. The more

detailed analysis of Ref. 28 gives $|\Delta\alpha| < 0.02°$.

(7) We develop a Landau theory for the assumed $Pa\bar{3} \to R\bar{3}$ structural phase transition which presumably occurs as a function of defect concentration. $R\bar{3}$ ordering is described by an orientational order parameter having four components—one for the angular perturbation $\Delta\phi_\alpha$ of each sublattice α. Because the star of the wave vector associated with doubling the size of the unit cell contains only a single member, there are no cubic terms in the Landau expansion. We find that there are five fourth-order invariants giving rise to an unusual type of "anisotropy" in order-parameter space which leads to trigonal symmetry in the ordered phase that occurs when $\Delta\alpha \neq 0$. Assuming that the fourth-order terms are overall positive, we conclude that the ordering transition is continuous and that the order parameter $|\Delta\phi| \sim (T_c - T)^{1/2}$, where T_c is the temperature of the $Pa\bar{3} \to R\bar{3}$ transition. If ordering into the putative $R\bar{3}$ phase takes place directly from the disordered phase, the ordering transition is then probably discontinuous.

(8) The dependence on temperature (or, equivalently, on defect concentration) of several experimentally accessible quantities can be predicted on the basis of mean field theory. For instance, both the intensity of the $R\bar{3}$ superlattice reflections and also the magnitude of the trigonal strains are of order $T_c - T$ for $T \to T_c^-$. In addition, there are anomalies in the density ρ and the average setting angle ϕ such that $d\rho/dT$ and $d\phi/dT$ are both discontinuous at T_c.

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

[2] R. M. Fleming, T. Siegrist, P. M. March, B. Hessen, A. R. Kortan, D. W. Murphy, R. C. Haddon, R. Tycko, G. Dabbagh, A. M. Mujsce, M. L. Kaplan, and S. M. Zahurak, in *Clusters and Cluster-Assembled Materials*, edited by R. S. Averback, J. Bernholc, and D. L. Nelson, MRS Symposia Proceedings No. 206 (Materials Research Society, Pittsburgh, 1991), p. 691.

[3] R. Sachidanandam and A. B. Harris, Phys. Rev. Lett. **67**, 1467 (1991).

[4] P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley, A. M. Smith III, and D. E. Cox, Phys. Rev. Lett. **67**, 1468 (1991).

[5] W. I. F. David, R. M. Ibberson, J. C. Matthewman, K. Prassides, J. J. S. Dennis, J. P. Hare, H. W. Kroto, R. Taylor, and D. R. M. Walton, Nature **353**, 147 (1991).

[6] S. Liu, Y. Lu, M. M. Kappes, and J. A. Ibers, Science **254**, 408 (1991).

[7] W. I. F. David, R. M. Ibberson, T. J. S. Dennis, J. P. Hare, and K. Prassides, Europhys. Lett. **18**, 225 (1992).

[8] X. D. Shi, A. R. Kortan, J. M. Williams, A. M. Kini, B. M. Savall, and P. M. Chaikin, Phys. Rev. Lett. **68**, 827 (1992).

[9] F. Gugenberger, R. Heid, C. Meingast, P. Adelmann, M. Braun, H. Wuhl, M. Haluska, and H. Kuzmany, Phys. Rev. Lett. **69**, 3774 (1992).

[10] G. Van Tendeloo, S. Amelinckx, M. A. Verheijen, P. H. M. van Loosdrecht, and G. Meijer, Phys. Rev. Lett. **69**, 1005 (1992).

[11] A. B. Harris and R. Sachidanandam, Phys. Rev. Lett. **70**, 102 (1993).

[12] R. Moret, S. Ravy, and J.-M. Godard, J. Phys. I **2**, 1699 (1992).

[13] P. H. M. van Loosdrecht, P. J. M. van Bantum, M. A. Verheijen, and G. Meijer, Chem. Phys. Lett. **198**, 587 (1992).

[14] E. J. J. Groenen, O. G. Poluektov, M. Matsushita, J. Schmidt, and J. H. van der Waals, Chem. Phys. Lett. **197**, 314 (1992).

[15] R. Moret, S. Ravy, and J.-M. Godard, J. Phys. I **3**, 1085 (1993).

[16] J. E. Fischer, D. E. Luzzi, K. Kniaz, A. R. McGhie, D. A. Ricketts-Foot, W. R. Romanow, G. B. M. Vaughan, P. A. Heiney, R. M. Strongin, D. Li, A. L. Smith, R. M. Strongin, M. A. Cichy, L. Brard, and A. B. Smith III, Phys. Rev. B **47**, 14 614 (1993).

[17] A. B. Harris, O. G. Mouritsen, and A. J. Berlinsky, Can. J. Phys. **62**, 915 (1984).

[18] H. You, S. C. Fain, Jr., S. Satija, and L. Passell, Phys. Rev. Lett. **56**, 244 (1986).

[19] J. P. Lu, X.-P. Li, and R. M. Martin, Phys. Rev. Lett. **68**, 1551 (1992).

[20] M. Sprik, A. Cheng, and M. L. Klein, J. Phys. Chem. **96**, 2027 (1992).

[21] T. Yildirim and A. B. Harris, Phys. Rev. B **46**, 7878 (1992).

[22] X.-P. Li, J. P. Lu, and R. M. Martin, Phys. Rev. B **46**, 4301 (1992).

[23] T. Yildirim (unpublished).

[24] W. Que and M. B. Walker, Phys. Rev. B **48**, 13 104 (1993).

[25] Note that as a function of direction, $(X^2 + Y^2 + Z^2)^2 + A(X^4 + Y^4 + Z^4)$ is minimal along a (1,1,1) direction if A is positive and is minimal along a (1,0,0) direction if A is negative.

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

[27] A. B. Harris and R. Sachidanandam, Phys. Rev. B **46**, 4944 (1992).

[28] P. A. Heiney, J. Phys. Chem. Solids **53**, 1333 (1992).

[29] D. E. Cox, P. A. Heiney, G. B. M. Vaughan, J. E. Fischer, N. Coustel, J. P. McCauley, Jr., and A. B. Smith III (unpublished). X-ray powder diffraction data was previously presented in Ref. 28.

[30] P. C. Chow, X. Jiang, G. Reiter, P. Wochner, S. C. Moss, J. D. Axe, J. C. Hanson, R. K. McMullan, R. L. Meng, and

C. W. Chu, Phys. Rev. Lett. **69**, 2943 (1992).

[31] There seems to be some confusion about the nature of the 2a phases suggested by various authors. For instance, in Ref. 14 reference is made to evidence that rotations about local (1,1,1) directions in the $Pa\bar{3}$ may be 22° or 82° (Ref. 5) [R. Hu, T. Egami, F. Li, and J. S. Lannin, Phys. Rev. B **45**, 9517 (1992)], to support their suggested structure with two setting angles differing by 60°. Together with the presentation of their Fig. 3, it seems clear that Ref. 14 assumes (incorrectly) that the $Pa\bar{3}$ arrangement of threefold local axes holds for the 2a fcc structure as well. In Ref. 13 it is similarly stated that the molecules are rotated about the $\langle 111 \rangle$ directions, "just as in the sc phase." Furthermore, in their Table I which gives the factor group analysis, it should be noted that they incorrectly identify the fcc (orientationally disordered) phase as T_h^3 ($Fm\bar{3}$), rather than the correct O_h^5 ($Fm\bar{3}m$) space group. Similarly, Ref. 10 assumes the $Pa\bar{3}$ arrangement of rotation axes.

[32] B. D. Cullity, *Elements of X-Ray Diffraction*, 2nd ed. (Addison-Wesley, Reading, MA, 1978).

[33] Since the Appendixes are of a technical nature, they have been deposited in the Physics Auxiliary Publication Service of AIP. See AIP document no. PAPS PRBMD-50-2622-21 for 21 pages of Appendixes A, giving a detailed group-theoretical analysis of the libron amplitudes at the R point; B, in which coupling to noncritical variables is analyzed; and C, in which minimization of Eq. (43) is analyzed. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 500 Sunnyside Blvd., Woodbury, New York 10017-2999. The price is $1.50 for a microfiche, or $5.00 for a photocopy. Airmail additional.

[34] A. Aharony, K. A. Muller, and W. Berlinger, Phys. Rev. Lett. **38**, 33 (1977).

[35] See J. R. Banavar, G. S. Grest, and D. Jasnow, Phys. Rev. B **25**, 4639 (1982), and references therein.