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Phase transitions and cooperative Jahn-Teller effects in fullerene anions

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Fullerene-based solids are known to undergo a range of structural, orientational, magnetic, and superconducting phase transitions. One important factor in many of these phase transitions is a combination of intramolecular and intermolecular vibronic couplings. The former can be described in terms of an on-site Jahn-Teller effect, while the latter can be described as a cooperative Jahn-Teller effect. We will look at the Jahn-Teller effects applicable to all negatively charged states of fullerene ions to show that, depending on the values of the vibronic coupling strengths, cooperative distortions can result in individual C_{60} molecules being distorted in the same or opposite sense to their nearest neighbors. More complicated phases can also occur under certain coupling conditions, particularly when symmetry-lowering distortions are present. This opens the possibility that new states of fullerene solids could be observed experimentally in the future.

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I. INTRODUCTION

Isolated fullerene molecules have the now well-known icosahedral I_h symmetry of a soccer ball. The interaction between the electrons of the C_{60} molecule and vibrations of the C_{60} nuclei can be quite strong. This is believed to have important consequences for many properties of the fullerenes. The vibronic interactions can locally distort the C_{60} molecule. However, tunnelling between different distorted configurations restores the I_h symmetry for an isolated molecule and thus no static distortion is observed. This is known as the dynamic Jahn-Teller (JT) effect. However, the situation is somewhat different when C_{60} forms a solid. There will then be interactions between C_{60} molecules and/or with other atoms or molecules introduced into the solid lattice. In these polycentric cases, a cooperative JT effect can lock in place the JT distortions of each molecule, resulting in nonzero static distortions. An example of a structure that is likely to result in three-dimensional (3D) ferromagnetic ordering of C_{60} molecules is given in Ref. 1.

Cooperative JT effects are seen in a large number of crystals, such as rare-earth zircons and spinels. In general, it is known that cooperative JT effects can lead to different macroscopic states, as discussed in a number of books and reviews.[2–4] At low temperature, ordering of local distortions may lead to a macroscopic deformation of a crystal. Structural distortions are accompanied by a corresponding ferro, antiferro or ferrimagnetic ordering of the orbit (or pseudospin as it is often called). At higher temperatures, thermal fluctuations destroy the correlations between the distortions leading to a structural phase transition, which can be understood using a simple Ginzburg-Landau approach.[5] Structural orderings are related to real magnetic orderings,[2] leading to the possibility of magnetic phase transitions. It has been suggested that observed changes in magnetic ordering in the antiferromagnetic semiconductor $Cr_{0.5}Mn_{0.5}S$ are related to cooperative JT effects.[6]

Experimentally, it is seen that fullerene solids can exhibit various phase transitions.[7,8] The A_3C_{60} fullerides (where A is an alkali metal) and related compounds exhibit various structural and orientational phase transitions and can be metals or superconductors, while in contrast the A_4C_{60} materials are insulators. Solid C_{60} is diamagnetic; the rhombohedral polymer of C_{60} is usually diamagnetic but under certain conditions can become weakly ferromagnetic.[9] Charge-transfer complexes such as tetrakis (dimethylamino) ethylene (TDAE)-C_{60} can be antiferromagnetic or ferromagnetic.

At high temperatures, fullerene-based solids can form crystals which are translationally ordered but which are usually orientationally disordered.[10,11] As the temperature is decreased, there are one or more phase transitions to a more orientationally ordered phase with lower symmetry crystal structure and long-range orientational order. The transition need not be sharp, but instead there may be a continuous path from the disordered to the ordered phase. Orientational phase transitions can be described in terms of translation-rotation coupling.[12]

Pure crystalline C_{60} has a fcc structure at room temperature with individual C_{60} molecules rotating almost randomly between different orientations. As the temperature is lowered below 261 K, an orientational alignment begins to take place whereby the rotational axis of each molecule starts to become constrained along one of two standard orientations, and the crystal is said to have merohedral disorder. As the temperature is lowered further, the rotations slow[8] and the probability of occupying the configuration with the lower energy increases,[13] although the merohedral still persists even at low temperatures. In doped solids, rotations become hampered by the dopant resulting in merohedral disorder at higher temperatures.[8] The A_3C_{60} fullerides such as K_3C_{60} also exhibit merohedral disorder.[14] K_4C_{60} and Rb_4C_{60} have a body-centered-tetragonal (bct) crystal structure which again has merohedral disorder.[15,16] Cs_4C_{60} has a pure phase in which there is an orthorhombic distortion of a bct lattice, which results in D_{2h} symmetry and complete ordering of the C_{60} molecules at room temperature[17] with an order-disorder transition to a state with two possible anion orientations at 623 K.[18]

Although not all the phase transitions observed in fullerene solids will be related to vibronic coupling, a combination of coupling to high-frequency intramolecular vibra-

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tions and low-frequency intermolecular vibrations is widely cited as a possible mechanism behind a number of the observed effects. This view has been reinforced by calculations which indicate that the fullerene solids involving the molecule C_{36} may have a higher superconducting transition temperature than even the alkali-metal doped C_{60} solids.[19] The C_{36} molecule is much smaller than the C_{60} molecule and so should be more sensitive to vibronic interactions. A model involving a charge-transfer induced intramolecular JT distortion combined with an intermolecular cooperative JT interaction has been used to explain an observed pressure-induced depression in the Curie temperature of TDAE-C_{60}.[1] The A_3C_{60} compounds may be superconductors and the A_4C_{60} insulators because in the former, the alkali-metal atoms sit in symmetric positions, while in the latter the alkali-metal sites are less symmetric. This means that vibronic hopping matrix elements largely cancel in A_3C_{60} but a smaller cancellation occurs in A_4C_{60}. Another explanation is that the ‘‘band’’ gap is widened due to a combination of electron-phonon interactions and electron correlation.[20] A mechanism by which a Mott-Hubbard insulator can be changed into a band insulator through a Jahn-Teller effect has also been suggested.[21] While the explanations may not yet be clear, it is agreed that vibronic coupling is an important feature. It is therefore clearly important to develop a good theoretical understanding of all of the JT effects experienced by C_{60} ions.

A signature of a cooperative JT effect is when there is a nonzero expectation value $\langle Q_\nu \rangle$ for one or more of the collective displacements Q_ν of the vibrationally coupled mode(s). Alternatively, this is equivalent to a nonzero value for the expectation value $\langle \sigma_\nu \rangle$ of the electronic operators σ_ν used to describe the JT interaction. As the strength of the cooperative interaction increases, the value of $\langle \sigma_\nu \rangle$ for (at least) one component ν will increase, tending to a constant for very strong interactions. In this paper, we will investigate the relative values that these expectation values can take in order to explore the range of possible cooperative distortions that could be seen in negatively charged fullerene anions C_{60}^{n-} which are coupled to h_g modes of vibration.[22,23]

II. THE HAMILTONIAN

Fullerene anions are coupled to h_g modes of vibration in what is known as $p^n \otimes h$ JT effects.[23] We will consider i interacting C_{60} molecules. Each molecule experiences an on-site JT effect which can be represented by the Hamiltonian $\mathcal{H}_i$, and a cooperative JT effect with neighboring molecules j that can be represented by the Hamiltonian $\mathcal{H}_{ij}$. As is usual in the cooperative JT effect, we will consider interactions with nearest neighbors only. The total Hamiltonian is thus

$$\mathcal{H} = \sum_i \mathcal{H}_i + \sum_{\langle i,j \rangle} \mathcal{H}_{ij}, \tag{1}$$

where $\langle i,j \rangle$ indicates the sum is taken over nearest neighbors.

The form of the on-site JT Hamiltonian $\mathcal{H}_i$ is well known for all the fullerene anions C_{60}^{n-}.[23] We will consider linear coupling to h_g modes of vibration in a JT effect of strength k. It is generally accepted that the Hamiltonian $\mathcal{H}_{ij}$ for interactions between JT centers can be represented phenomenologically by a form quadratic in the Q_ν, or equivalently in the σ_ν, independent of the physical mechanism causing the interaction.[2] For example, the interaction could be direct exchange between orbitally degenerate states, or indirect exchange through an interaction between localized electrons and collectivized electrons of the conduction band.[2] For the case of interacting C_{60} molecules of interest here, we will choose a quadratic form involving the Q_ν. The Hamiltonian will thus be written in the form

$$\mathcal{H}_{ij}(\mathbf{K}(\mathbf{i}-\mathbf{j})) = \mathbf{Q}_\mathbf{i}^\dagger \mathbf{K}(\mathbf{i}-\mathbf{j}) \mathbf{Q}_\mathbf{j} \equiv \sum_{\nu\mu} K_{\nu\mu}(\mathbf{i}-\mathbf{j}) Q_{i\nu} Q_{j\mu}, \tag{2}$$

where $\mathbf{Q}_\mathbf{i}$ is a vector whose components are the collective coordinates Q_ν for molecule i (which will be called $Q_{i\nu}$), and $\mathbf{K}(\mathbf{i}-\mathbf{j})$ is a matrix whose components $K_{\nu\mu}(\mathbf{i}-\mathbf{j})$ represent the strength of the interaction between an intramolecular vibration ν of the C_{60} molecule i and the vibration μ of the molecule j.

It is usual to restrict the modes $Q_{i\nu}$ considered to the JT active modes, as they are expected to be the most important. In our case here, this means the five components of the h_g mode. There are arguments for including other modes in some cases. For example, a cooperative interaction between two molecules may involve a net displacement of the center of mass of each molecule indicating that the translational modes should also be included. However, we will restrict our considerations to the h_g mode, which is the active mode relevant for fullerene anions. We will follow Ref. 24 and use the labels $\mathbf{Q} = \{Q_\theta, Q_\epsilon, Q_4, Q_5, Q_6\}$ to represent the components of this mode, which correspond to the labels $\{Q_1, Q_4, Q_5, Q_2, Q_3\}$, respectively, used in Ref. 23.

The values of the interaction coefficients $K_{\nu\mu}(\mathbf{i}-\mathbf{j})$ are determined by the symmetry of the crystal structure and the physical nature of the cooperative interaction. The coefficients can be positive, corresponding to antiferrodistortive ordering, or negative, which corresponds to ferrodistortive order. In other JT systems, the physical mechanisms that have been considered include direct exchange and superexchange in orbital degeneracy, and indirect exchange through conduction electrons.[2] However, we are not concerned with the nature of the interaction in this paper. We will seek to determine useful information on the nature of the cooperative JT effect and of possible phase transitions keeping these quantities as free parameters. Nevertheless in Sec. VI we will obtain some restrictions, due to symmetry considerations, on the allowed parameters for C_{60} molecules at fcc sites in the two standard orientations of A_3C_{60} fullerides. The results also illustrate how the ideas can be applied in other geometries.

A. Molecular-field approximation

We will now find solutions to the Hamiltonian in Eq. (1). The first step is to decouple the interdependence between the vibrations of neighboring C_{60} molecules i and j. Such a separation is commonly achieved using a molecular-field approximation, and we will use such an approach here. The specific details follow the approach used by Feiner for the $E\otimes e$ system,[25] which follows from original ideas of Englman and Halperin,[26,27] although the situation is considerably more complicated due to the higher dimensions of both the electronic and vibrational systems. The interaction is written in terms of fluctuations $(Q_{i\nu}-\langle Q_{i\nu}\rangle)$ from the average displacements $\langle Q_{i\nu}\rangle$ of the C_{60} molecules. Products of fluctuations in the displacements of different C_{60} molecules are neglected. This ignores dynamic correlations between the vibrational motion of different molecules but preserves correlations between vibrational and electronic motion within a molecule. A more common decoupling procedure is to use a displaced phonon approach in which correlation between vibrational and electronic motion within each molecule would be neglected. This is extremely successful in describing behavior of systems in which the dominant coupling is to acoustic phonons and strain. However, it will not be appropriate in our case where JT interactions within a molecule are important, as it does not allow quantitative connections between the JT effects experienced by isolated C_{60} molecules and cooperative JT effects involving the same molecules.

In our molecular-field approach, $\mathcal{H}$ can be replaced by the molecular-field Hamiltonian

$$\mathcal{H}^{mf}=\sum_i \mathcal{H}_i^{mf}-\sum_{\langle i,j\rangle} E_{ij}^c, \tag{3}$$

where

$$\mathcal{H}_i^{mf}=\mathcal{H}_i-\sum_\nu \lambda_{i\nu}Q_{i\nu},$$

$$E_{ij}^c=\sum_\nu \sum_\mu \langle Q_{i\nu}\rangle\langle Q_{j\mu}\rangle K_{\nu\mu}, \tag{4}$$

with

$$\lambda_{i\nu}=-\sum_{j(i)} \sum_\mu K_{\nu\mu}\langle Q_{j\mu}\rangle, \tag{5}$$

where $j(i)$ is taken to mean all molecules j adjacent to i.

The molecular-field Hamiltonian $\mathcal{H}_i^{mf}$ for molecule i no longer contains explicit reference to the coordinates of the neighboring molecules j, and solutions to the decoupled equations can now be sought.

B. Coordinate transformations

$\mathcal{H}_i^{mf}$ can be made to resemble the JT Hamiltonian $\mathcal{H}_i$ for a vibronic coupling within a C_{60} molecule with linear JT coupling of strength k and subject to a strain in the θ direction of strength w. Solutions to this problem are either already known or can be found (at least in principle). The required on-site JT Hamiltonian for molecule i has the form

$$\mathcal{H}_i(k,w)=\frac{1}{2}\sum_\nu (P_{i\nu}^2+Q_{i\nu}^2)+k\sum_\nu Q_{i\nu}\sigma_{i\nu}-w\sigma_{i\theta} \tag{6}$$

in units in which $\hbar$, the reduced mass of the mode, and the vibrational frequency are taken to be unity. The form of the $\sigma_{i\nu}$ for each of the $p^n\otimes h$ JT problems are given in Refs. 22 and 23.

It should be noted that Chancey and O'Brien use a fivefold z axis throughout their work (e.g., Ref. 23). With this choice, minima in the lowest adiabatic potential-energy surface (APES) of warped systems can be mapped onto corners of an icosahedron. However, Dunn and Bates (e.g., Refs. 24 and 28) use a twofold axis in their work as this gives a symmetric form for the vibronic states. In general, the form of the JT Hamiltonian will be different for the different choices of axes. However, the Hamiltonian $\mathcal{H}_i(k,0)$ in the absence of strain has SO(3) symmetry, which is accidentally higher than the I_h symmetry of the system being modeled. As a consequence of the accidentally higher symmetry, the form of the linear JT Hamiltonian is the same whatever axis is chosen as the z axis. (The form of the Hamiltonian for quadratic or other higher-order terms is different, as is the form of the Hamiltonian describing coupling to an electronic H state used to describe C_{60}^{n+}.) In linear coupling, the only way in which the definition of the choice of axis becomes important is in defining the meanings of the distortions Q_γ. In Refs. 23 and 24, $\{Q_\theta,Q_\epsilon,Q_4,Q_5,Q_6\}$ (or their equivalent) are modes transforming as $\{(3z^2-r^2)/2,\sqrt{3}(x^2-y^2)/2,\sqrt{3}yz,\sqrt{3}zx,\sqrt{3}xy\}$, respectively (like d-orbitals) in terms of the defined axes $\{x,y,z\}$. Thus, for example, in Ref. 24 a Q_θ-type mode represents a distortion along a twofold axis, whereas in Ref. 23 it represents a distortion along a fivefold axis. This distinction will be important in Sec. VI when discussing the form of the cooperative interaction Hamiltonian for C_{60} molecules in specific geometries. An additional complication is that in other papers,[28,29] Q_θ and Q_ϵ are defined to be linear combinations of the Q_θ and Q_ϵ given above. Again, the results obtained for warped systems are simpler with this choice. In this paper, we will follow the definitions in Refs. 23 and 24 as we are concerned with linear coupling only.

At this point, $\mathcal{H}_i^{mf}$ does not have the required form $\mathcal{H}_i(k,w)$ due to the additional term $\Sigma_i\lambda_{i\nu}Q_{i\nu}$. However, we can make a canonical transformation to displaced vibrational operators $\hat{Q}_{i\nu}=Q_{i\nu}-\lambda_{i\nu}$ and $\hat{P}_{i\nu}=P_{i\nu}$, so that

$$\mathcal{H}_i^{mf}=\sum_\nu [\tfrac{1}{2}(\hat{P}_{i\nu}^2+\hat{Q}_{i\nu}^2)+k\hat{Q}_{i\nu}\sigma_{i\nu}-d_{i\nu}\sigma_{i\nu}]-E_i^c, \tag{7}$$

where

$$E_i^c=\frac{1}{2}\sum_\nu \lambda_{i\nu}^2 \tag{8}$$

and where

$$d_{i\nu}=-k\lambda_{i\nu} \tag{9}$$

is the molecular field experienced by the pseudospin in the ν direction. $\mathcal{H}_i^{mf}$ now resembles the Hamiltonian for a single molecule with a component of strain in all directions in the coordinate space. We note that if the JT interaction experienced by each molecule i includes a permanent splitting (for example, due to strain in the fullerene solid) of the form $\Sigma_\nu w_{i\nu}\sigma_{i\nu}$, the molecular fields become $d_{i\nu}=w_{i\nu}-k\lambda_{i\nu}$ but the rest of the formalism stays the same. We will return to this point later in Sec. V.

Although the JT problem with a component of strain in all directions in Q space could be solved directly, it is simpler if we make a rotation to coordinates $Q'_{i\nu}$ so that, in the new coordinates, the strain is in one direction only, which we choose to be the θ direction. In the $E\otimes e$ system, where there are only two coordinates, it was easy to see the form this transformation should take.[25] In our case, we need a rotation in five-dimensional coordinate space. The required transformation is given in Ref. 23 in terms of a magnitude Q and four angles, θ, ϕ, γ, and α. This transformation was also used in Ref. 24 to convert from the usual fixed coordinate system to rotating coordinates in which the new θ direction is always perpendicular to the trough, where it was written in the form

$$Q'_\nu=\sum_\mu D_{\mu\nu}(\theta,\phi,\gamma,\alpha)Q_\mu . \tag{10}$$

The corresponding inverse transformation is

$$Q_\nu=\sum_\mu D_{\nu\mu}(\theta,\phi,\gamma,\alpha)Q'_\mu . \tag{11}$$

The same transformation is appropriate here but where the angles take fixed values θ_i, ϕ_i, γ_i, and α_i for molecule i (and similarly for molecule j), rather than being allowed to vary over the whole potential-energy trough. The actual form of the rotation matrix elements $D_{\mu\nu}$, to be called $D^i_{\mu\nu}$ for molecule i, is not important here; all that matters is that such a transformation exists and that it obeys the normalization and orthogonality relations

$$\sum_\beta D^i_{\nu\beta}D^i_{\mu\beta}=\begin{cases}1 & \text{if } \nu=\mu\\ 0 & \text{otherwise.}\end{cases} \tag{12}$$

We apply the transformation in Eq. (11) to the molecular field $d_{i\nu}$, requiring that the resultant field is in the θ direction only and so $d'_{i\nu}=d_i$ for $\nu=\theta$ and zero otherwise, where d_i is the magnitude of the molecular field. Hence $d_{i\nu}=d_iD^i_{\theta\nu}$. (This is equivalent to saying $d_{i\theta}=d_i\cos\phi_i$ and $d_{i\epsilon}=d_i\sin\phi_i$ in the rather simpler $E\otimes e$ system, where there are only two directions to consider.)

In order to preserve the desired form for the Hamiltonian, we must also apply the same transformation to the electronic operators $\sigma_{i\nu}$ to give rotated operators $\sigma'_{i\nu}$. It then follows that

$$\sum_\mu d_{i\mu}\sigma_{i\mu}=d_i\sigma'_{i\theta}, \tag{13}$$

confirming that the molecular field is now in the new θ direction. The form of the Hamiltonian for the remaining terms remains the same as before the rotation, with all quantities simply being replaced by their rotated equivalents.

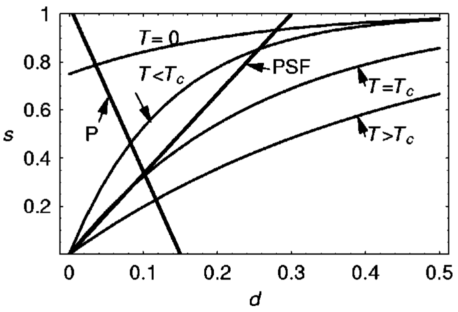

FIG. 1. Schematic representation of the graphical solution of the molecular-field equations for the $E\otimes e$ system (after Ref. 25). The straight lines represent variation of pseudospin $s(k,d,T)$ as a function of field according to Eqs. (18) for different phases, and the curves are values for the pseudospins calculated from knowledge of the energy levels. The points of intersection of the curves and lines give the required solutions. Curves are shown for the critical temperature $T=T_c$ defined in Sec. IV A, and for temperatures above and below this.

The Hamiltonian $\mathcal{H}_i^{mf}$ has now been reduced to a standard form for which the states and energies can, at least in principle, be calculated as a function of k and w for any isolated C_{60}^{n-} anion using analytical or numerical methods.

III. DETERMINATION OF DISTORTIONS

A. Thermal average

The thermal average of any operator $\hat{f}$, at temperature T, can be defined as

$$\langle\hat{f}\rangle=\frac{\sum_n \langle\psi_n|\hat{f}|\psi_n\rangle\exp(-E_n(k,d)/k_BT)}{\sum_n \exp(-E_n(k,d)/k_BT)}, \tag{14}$$

where the ψ_n are taken to be the complete set of (normalized) ground and excited vibronic states of the on-site JT effect of strength k experienced by an isolated C_{60}^{n-} anion subject to a distortion d. The $E_n(k,d)$ are the corresponding energies of the states and k_B is the Boltzmann constant.

In order to calculate nonzero values of distortions, we need to determine averages of the electronic operators $\sigma'_{i\nu}$. We can therefore obtain curves giving $\langle\sigma_{i\nu}\rangle\equiv s(k,d,T)$ as a function of d for any given values of the vibronic coupling strength k and the temperature T, as given in Ref. 25 for the $E\otimes e$ system and illustrated schematically as the curved lines in Fig. 1. Hence using the inverse of Eq. (13), we can find averages of the nonrotated operators $\sigma_{i\nu}$ as a function of k and d. However, we do not know the value of the distorting field d and so this is not sufficient for us to determine values for $\langle\sigma_{i\nu}\rangle$. Fortunately, additional information is available from the quantum mechanics of the operators involved.

B. Commutation condition

As the diagonal matrix elements of the commutator of the momenta $P_{i\nu}$ and $\mathcal{H}$ between eigenstates of $\mathcal{H}$ are zero (where the $P_{i\nu}$ are conjugate to the $Q_{i\nu}$), it follows that

$$\lambda_{i\nu}=\langle Q_{i\nu}\rangle+k\langle\sigma_{i\nu}\rangle. \tag{15}$$

This is equivalent to Eq. (7) of Ref. 25. Equating Eqs. (5) and (15) gives a set of ten coupled equations, five of the form

$$\langle Q_{i\mu}\rangle+k\langle\sigma_{i\mu}\rangle+\sum_{j(i)}\sum_{\nu}K_{\mu\nu}\langle Q_{j\nu}\rangle=0 \tag{16}$$

(for the five values of μ) and another five with the labels i and j interchanged. Now it must always be possible to define new linear combinations of the $\overline{Q}_{i\mu}$ (and equivalent combinations of the $\overline{\sigma}_{i\mu}$) so that each equation only contains reference to one mode and we have five pairs of coupled equations of the form

$$\langle Q_{i\beta}\rangle+k\langle\sigma_{i\beta}\rangle+\sum_{j(i)}K_{\beta}\langle Q_{j\beta}\rangle=0 \tag{17}$$

(and the same with i and j interchanged), where the label β refers to the new linear combinations and the K_β are the roots of the equation $\mathrm{Det}(\mathbf{K})=0$. These equations give extra constraints on the average values of the $Q_{i\beta}$ and the $\sigma_{i\beta}$.

C. Bipartite lattices

All the formulas given to this point apply to any crystal lattice structure. The simplest application of the theory occurs for bipartite lattices, such as simple cubic and body-centered cubic lattices. These are lattices which can be divided into two sublattices, a and b, such that the nearest-neighbor to an ion or molecule in one sublattice lies in the other sublattice.

Where the cooperative interaction coefficients are positive and antiparallel distortions are favored, the average values in sublattices a and b will be expected to be different. However, this also accounts for the case where parallel distortions are favored by allowing the average values in the two sublattices to be equal. We will assume that the average distortion and pseudospin in sublattice a are $\overline{Q}_a$ and $\overline{\sigma}_a$ with components $\overline{Q}_{a\beta}$ and $\overline{\sigma}_{a\beta}$, respectively, and similarly for sublattice b. From Eqs. (9), (15), and (17), it thus follows that

$$\overline{Q}_{a\beta}=-\frac{k}{(1-z^2K_\beta^2)}(\overline{\sigma}_{a\beta}-zK_\beta\overline{\sigma}_{b\beta}),$$

$$d_{a\beta}=-g_\beta\overline{\sigma}_{b\beta}+zK_\beta g_\beta\overline{\sigma}_{a\beta}, \tag{18}$$

where $g_\beta=zK_\beta k^2/(1-z^2K_\beta^2)$ and z is the number of nearest neighbors. These are the equivalent of Eqs. (23a,b) and (24a,b), respectively in Ref. 25. It can be shown that these relationships lead to the straight lines in Fig. 1 for the $E\otimes e$ problem.

D. fcc lattices

Unfortunately, the fcc lattice exhibited by many fullerene solids is not bipartite, as two nearest neighbors to a given site can themselves be nearest neighbors. However, it is possible to proceed with a generalized version of molecular-field theory by dividing the fcc lattice into eight sublattices in which no atom interacts with any other atom in its own sublattice (to first order), as shown in Fig. 2.[30] If the sublattices are labeled in the conventional manner as shown in the figure, each atom in sublattice $i=1$–4 has two nearest neighbors in every other sublattice except $i+4$. From Eqs. (9), (15), and (17), we can now obtain the general result

$$\overline{Q}_{1\beta}=\frac{k}{(4K_\beta-1)(12K_\beta+1)}[(1+8K_\beta-24K_\beta^2)\overline{\sigma}_{1\beta}-2K_\beta(\overline{\sigma}_{2\beta}+\overline{\sigma}_{3\beta}+\overline{\sigma}_{4\beta}-12K_\beta\overline{\sigma}_{5\beta}+\overline{\sigma}_{6\beta}+\overline{\sigma}_{7\beta}+\overline{\sigma}_{8\beta})]. \tag{19}$$

Similar results can be obtained for the other $Q_{i\beta}$ by appropriate permutation of the labels.

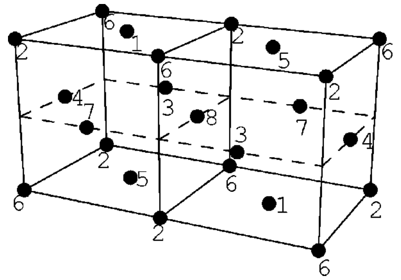

FIG. 2. Division of fcc lattice into eight noninteracting fcc sublattices (after Ref. 30).

IV. SOLUTIONS

The solution(s) for the average pseudospin and corresponding distortion that will occur physically are those which simultaneously satisfy Eqs. (14) and (18). The solutions can be found graphically, as in Fig. 1. Where there is the possibility of more than one phase at a given temperature, the phase that will occur is that for which the free energy per molecule

$$F^{mf}=\left(\sum_i f(k,d,T)-\sum_{\langle i,j\rangle}E_{ij}^c\right)\Big/ N \tag{20}$$

is smallest, where N is the number of molecules and

$$f(k,d,T)=-k_BT\ln\sum_n\exp(-E_n(k,d)/k_BT). \tag{21}$$

A. $E\otimes e$

Before solving the current case, it is useful to summarize the results obtained in Ref. 25 for the $E\otimes e$ system so that we can draw parallels with it. Reference 25 considered the case in which a permanent θ-type splitting of the doublet is present, and wrote the cooperative interaction in the form $\lambda(Q_{a\theta}Q_{b\theta}+Q_{a\epsilon}Q_{b\epsilon})$, i.e., $\lambda=K_{\theta\theta}=K_{\epsilon\epsilon}$ in our notation. A phase with ferrodistortive (F) ordering of the pseudospins (and hence of the distortions) was found when $\lambda<0$; the pseudospins in the two lattices are parallel and are assumed to have the same magnitudes. Three possible phases were

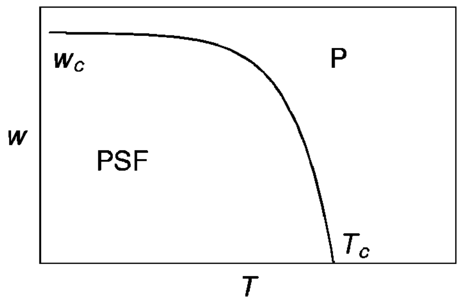

FIG. 3. Schematic phase diagram for the $E\otimes e$ system (after Ref. 25).

found when $\lambda>0$. In the first phase, $\overline{\sigma_{a\epsilon}}=\overline{\sigma_{b\epsilon}}=0$, with the result that the average pseudospins are aligned antiparallel along the θ direction with (in general) different magnitudes. It is termed as an antiferrodistortive (AF) phase in Ref. 25. The equivalent phase is called a ferridistortive phase in Ref. 4. The free energy is

$$F_{AF}^{mf}=\tfrac{1}{2}[f(k,d_a,T)+f(k,d_b,T)]$$
$$-\tfrac{1}{2}g_\theta[\overline{\sigma_a}\,\overline{\sigma_b}-\tfrac{1}{2}z\lambda(\overline{\sigma_a^2}+\overline{\sigma_b^2})]. \qquad (22)$$

The second phase also has $\overline{\sigma_{a\epsilon}}=\overline{\sigma_{b\epsilon}}=0$ but in this case the two pseudospins are aligned parallel along the θ direction and have the same magnitudes $\overline{\sigma_a}=\overline{\sigma_b}=\overline{\sigma}$. This is called a paradistortive (P) phase. The free energy per site is

$$F_P^{mf}=f(k,d,T)-\tfrac{1}{2}g_{\theta+}\overline{\sigma}^2, \qquad (23)$$

where $g_{\beta+}=g_\beta(1-zK_\beta)$. The third phase is called a pseudospin flop (PSF) phase[25] or a spin polyaxial phase.[4] It has equal components of pseudospin in the θ direction, $\overline{\sigma_{a\theta}}=\overline{\sigma_{b\theta}}=w/2g_\theta$, and are mirror images of each other in the ϵ direction, and the free energy is

$$F_{PSF}^{mf}=f(k,d,T)-\tfrac{1}{2}g_{\theta+}\overline{\sigma_\theta}^2+\tfrac{1}{2}g_{\theta-}\overline{\sigma_\epsilon}^2, \qquad (24)$$

where $g_{\beta-}=g_\beta(1+zK_\beta)$.

The values of $\overline{\sigma}\equiv s$ for the different phases depend linearly on the distortion d. Lines defining the PSF and P phases have been plotted (schematically) in Fig. 1, along with the curves calculated for the thermal average determined from detailed knowledge of the energy levels (as discussed in Sec. III A). Any points of intersection of the curves and lines give the required phases. For high temperatures (e.g., $T>T_c$ on the graph), there is no point of intersection with the PSF line and so only a P phase is possible. However, as the temperature is lowered below the critical temperature T_c (at which the gradient near the origin of the curved line coincides with that of the PSF line), both P and PSF phases become possible. It is found that the PSF phase is thermodynamically stable with respect to the P phase. Thus a structural phase transition from the P phase to the PSF phase can take place. The resulting phases are shown schematically in Fig. 3 as a function of the temperature T and the permanent distortion w.

The actual phase and values of the pseudospins that will be observed is that for which the free energy per molecule is smallest. This shows that the AF phase is always thermodynamically unstable with respect to the PSF phase, as is also the case in a magnetic analog of the same system. This results in a phase diagram with transitions from the PSF phase to the P phase as the temperature increases. In general, the P-PSF phase transition is Ising-like as only the ϵ component of the pseudospin is ordering. However, when the permanent distortion is set to zero, the situation is rather different as there is no longer a preferred direction for the ordering.

B. $\mathbf{C_{60}^{n-}}$

Qualitatively, we know that at finite temperature, the average pseudospin experienced by any isolated JT center will be zero when there is no distortion. In the case of C_{60}, this means that isolated molecules or anions experience local distortions but the JT effect is dynamic with all locally distorted configurations being equally probable. The average pseudospin is only nonzero at zero temperature. For very large distortions, the average pseudospin will tend to a constant, as for the $E\otimes e$ system. Quantitative determination of the energy levels for a given system is a significant undertaking that will not be attempted in this paper. Nevertheless, much useful information on possible allowed phases can still be obtained by consideration of the equations in general terms.

In all of the JT problems applicable to C_{60}^{n-} anions, the form of the interaction in the absence of strain is such that the lowest APES contains a multidimensional trough of minimum-energy points.[23] The motion in the five-dimensional space of the h vibrations is therefore comprised of vibrations in the directions across the trough and rotations in the directions around the trough. (Rotations in this context are often called pseudorotations to distinguish the situation from real rotations of the molecule.) In the cases relevant to C_{60}^{3-}, there are two vibrations and three rotations, whereas for the other C_{60}^{n-} anions there are three vibrations and two rotations. As all points on the trough are equivalent, the average values of the displacements Q_ν, and hence of the σ_ν, are zero for all components ν.

For a θ-type strain $-w\sigma_\theta$ in the JT effect for C_{60}^{3-}, a circle of minimum-energy points will be extracted from the four-dimensional hypersphere of minimum-energy points in the absence of strain, with the center of the circle lying along the strain direction. The values of the angles parametrizing the Q's are also restricted. The circles of minimum-energy points are illustrated schematically in Fig. 4. This means that the averages $\overline{Q_\theta'}$ and $\overline{\sigma_\theta'}$ will be nonzero, but the average values of the other components will still be zero. The curves of s vs d are therefore at least qualitatively similar to those in Fig. 1 for the $E\otimes e$ system. A strain applied in a different direction will result in a similar picture but with the circle of minimum-energy points in a different orientation. In the JT system applicable to C_{60}^{2-}, there is either a circle of minimum-energy points or a single minimum point when any splitting between the ^2P and ^2D terms is neglected, depending upon the sign of the strain term. When the term splitting is included, the situation is not quite so straightforward as

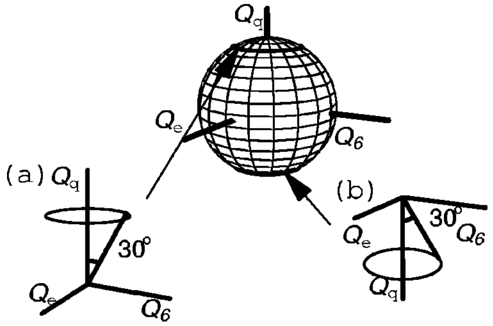

FIG. 4. Representation in the Q_θ-Q_ϵ-Q_6 directions of the minimum-energy points for the JT problem applicable to C_{60}^{3-} in the presence of a θ-type strain. The upper circle [inset (a)] indicates the points that are minima when $w<0$. This has $\theta=0$ and the angle around the circle is $2(\gamma+\phi)$. The lower circle of points [inset (b)] are minima when $w>0$. It has $\theta=\gamma=\pi/2$ and the angle around the circle is 2ϕ.

strain will mix part of higher-energy potential sheets into the ground state. Nevertheless, the average pseudospin will be oriented along the direction of the molecular field in all cases.

1. Bipartite lattices

By comparison with $E\otimes e$, we can now find equivalent solutions for our C_{60}^{n-} anions. We can immediately see that (in the absence of any permanent splitting) one set of solutions occurs when $\bar{\sigma}_{a\beta}$ is nonzero for one of the components β only. If $K_\beta<0$, we obtain a phase equivalent to the F phase of Ref. 25, and if $K_\beta>0$, we obtain a phase equivalent to the AF phase.

Another set of solutions occurs when two of the $\bar{\sigma}_{a\beta}$ are nonzero, say for $\beta=\mu$ and ν. For the requirement for the field and average pseudospin in a sublattice to be collinear, it follows that this phase is only possible if $K_\mu=\pm K_\nu$. When $K_\mu=K_\nu>0$, there is again an AF phase with the pseudospins antiparallel, but with the pseudospins now oriented at an angle in the $\mu-\nu$ plane [Fig. 5(a)]. Such an interaction is certainly possible in a real crystal. For example, in the $E\otimes e$ system an interaction along the body diagonal of a bcc lattice results in an interaction with $K_{\theta\theta}=K_{\epsilon\epsilon}$ and $K_{\theta\epsilon}=K_{\epsilon\theta}=0$.[25] There is also a F phase with $\bar{\sigma}_a=\bar{\sigma}_b$ if $K_\mu=K_\nu<0$ [Fig. 5(b)]. Another interesting possibility can occur if $K_\mu=-K_\nu>0$ (say). In this case, $\bar{\sigma}_a$ and $\bar{\sigma}_b$ make the same angle with the μ axis. This resembles the PSF phase of the $E\otimes e$ system but in which the magnitudes of the two pseudospins need not be the same [Fig. 5(c)]. It is not clear whether any physical mechanism could result in such a coupling, although it must be remembered that the K_β contain both positive and negative combinations from the $K_{\mu\nu}$. Further solutions can be obtained by extending the above ideas for three, four, or all five of the $\bar{\sigma}_{i\beta}$ nonzero, although this places even more restrictions on the coupling constants. Nevertheless, it is possible.

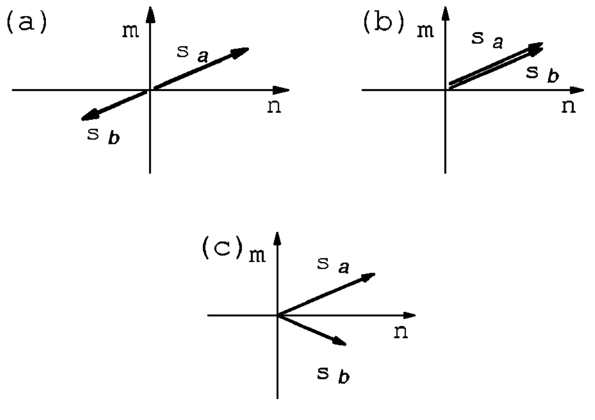

FIG. 5. Possible pseudo spin alignments: (a) antiferrodistortive (AF), (b) ferrodistortive (F), (c) pseudospin flop (PSF).

It is interesting to note that it has been suggested that bct K_4C_{60} could have either a Jahn-Teller-Mott dynamic state or a staggered distortion in which neighboring C_{60} molecules distort along different directions.[31] Our results show that the only solution in which neighboring sites have different distortions is the PSF phase of Fig. 5, which only occurs if it turns out that the coupling constants for two of the uncoupled modes β are equal in magnitude and opposite in sign.

Depending upon the detailed nature of the interaction and any restrictions on the coupling constants, we now have a series of lines through the origin with positive gradients, each equivalent to the line labeled PSF in Fig. 1. Excluding the origin, each line will intersect at most once with the curve $s(k,d,T)$ calculated from the energy levels for any given temperature. As mentioned before, the phase that will actually occur at that temperature is that for which the free energy F^{mf} is lowest. It is not immediately obvious which line will dominate as F^{mf} contains two parts, one involving $f(k,d,T)$ and the other involving the $\bar{\sigma}$'s.

The dependence of F^{mf} on d can only be found for a given system when the details of the variation of its energy levels with distortion are known. However, we can make some deductions based on the $E\otimes e$ case using the energies given in Ref. 32. These can be used to show that, when there is no permanent distortion, $f(k,d,T)$ decreases as d increases, while the term in the $\bar{\sigma}$'s increases, with the variation in the former being slightly greater in the latter for the parameter ranges considered in that paper. The net result is thus that the free energy will be lowest for the case with the largest value of the intermolecular coupling constant K_β, and the situation with the largest possible value of distortion will dominate. For very high temperatures, the two relevant curves will only intersect at the origin and the only solution is one in which there is no overall distortion. As the temperature decreases, a phase transition to an ordered state becomes possible. We will therefore have a phase diagram equivalent to Fig. 5 but where the PSF phase is now the AF phase and the P phase is a phase with no overall distortion.

2. fcc lattice

The analysis for fcc lattices proceeds in a similar way to above but using the more complicated expression in Eq. (19) for the $Q_{i\beta}$. At first sight, this appears rather complicated as they contain references to $\overline{\sigma_{i\beta}}$ in eight different sublattices. However, as the fcc lattice is translationally invariant, and by analogy to the generalized molecular-field theory of magnetism,[30] we must also impose the condition that either (a) $\overline{\sigma_{i\beta}}=\overline{\sigma_{(i+4)\beta}}$ for all $i=1$–4 or that (b) all $\overline{\sigma_{i\beta}}=-\overline{\sigma_{(i+4)\beta}}$.

When only one of the components of the $\overline{\sigma_{i\beta}}$ is nonzero (so $\overline{\sigma_{i\beta}}=\overline{\sigma_i}$), case (b) leads to the rather simple result $\overline{Q_1}=-k\overline{\sigma_1}$ and $d_1=0$. This is a rather interesting phase in which there is no net molecular field but there is still a nonzero average distortion, with the distortion correlated between neighbors. Case (a) leads to the results

$$\overline{Q_1}=\frac{k}{(4K_\beta-1)(12K_\beta+1)}\times[(1+8K_\beta)\overline{\sigma_1}-4K_\beta(\overline{\sigma_2}+\overline{\sigma_3}+\overline{\sigma_4})],$$

$$d_1=\frac{4k^2K_\beta}{(4K-\beta-1)(12K_\beta+1)}[-12K_\beta\overline{\sigma_1}+\overline{\sigma_2}+\overline{\sigma_3}+\overline{\sigma_4}], \tag{25}$$

and similarly for the other $\overline{Q_i}$. However, for antiferromagnetic ordering these expressions can be simplified further by applying the usual rule that $\Sigma_{i=1}^{8}\overline{\sigma_{i\beta}}=0$, namely, $\overline{\sigma_1}+\overline{\sigma_2}+\overline{\sigma_3}+\overline{\sigma_4}=0$ in our case, so that

$$\overline{Q_1}=\frac{k}{(4K_\beta-1)}\overline{\sigma_1} \quad \text{and} \quad d_1=-\frac{4k^2K_\beta}{(4K_\beta-1)}\overline{\sigma_1}. \tag{26}$$

For ferromagnetic ordering, all the $\overline{\sigma_{i\beta}}$ are usually equal, in which case

$$\overline{Q_1}=-\frac{k}{(12K_\beta+1)}\overline{\sigma_1} \quad \text{and} \quad d_1=-\frac{12k^2K_\beta}{(12K_\beta+1)}\overline{\sigma_1}. \tag{27}$$

However, there are other interesting phases which might occur with different combinations of $\overline{\sigma_i}$ in each sublattice, and also phases in which more than one value of K_β is nonzero (as for the bipartite lattices discussed above). The phase that will prevail in a given system is that for which the free energy is a minimum, which can only be calculated when the exact pattern of energy levels and eigenstates is known. However, this does show that a rich variety of structural phases is certainly possible in fcc fullerene solids.

V. DISCUSSION

From our comparisons with the $E\otimes e$ system, it does not seem likely that phase transitions from one distorted configuration to another can occur. However, the possibility cannot be entirely ruled out for other parameter ranges or in other systems. In particular, it should be noted that the formalism used here applies to all crystal structures. Different lattices (fcc, bcc etc.) will have different relations between the coupling constants $K_{\nu\mu}$. This means that the straight lines representing the phases in the equivalent of Fig. 1 will be in different positions for different lattices. This may play a part in an understanding of the structural phase-transitions observed experimentally in some fullerene solids. Furthermore, the effects of various couplings other than electron-vibration couplings need to be taken into account. For example, it is known that elastic constants can be softened (reduced) as a consequence of translation-rotation coupling to long wavelength phonons if the amount of orientational order changes considerably when the crystal distorts.[12]

It is interesting to note that if it is possible to introduce a permanent distortion into our solid material, such as through ''internal'' strains or by application of a uniaxial stress, an external pressure or magnetic field, then an even wider range of phases become possible. A strain in the β direction is introduced by adding a term w_β to the right-hand side of the expression for d_β in Eq. (18). One solution to the situation with such a strain included occurs when $\overline{\sigma_\beta}$ is the only nonzero pseudospin. This results in AF or P phases if $K_\beta>0$ or a F phase if $K_\beta<0$, just as for $E\otimes e$. However, there are other solutions when more than one of the pseudospin components are nonzero. For example, if $\overline{\sigma_\mu}$ is nonzero (as well as $\overline{\sigma_\beta}$), there is a phase satisfying the equation (from the collinearity condition)

$$\frac{w_\beta-g_\beta\overline{\sigma_{b\beta}}+zK_\beta g_\beta\overline{\sigma_{a\beta}}}{\overline{\sigma_{a\beta}}}=\frac{-g_\mu\overline{\sigma_{b\mu}}+zK_\mu g_\mu\overline{\sigma_{a\mu}}}{\overline{\sigma_{a\mu}}} \tag{28}$$

and the equivalent equation with a and b interchanged. The magnitude and direction of the pseudospin in one sublattice determines the pseudospin in the other lattice, but the magnitudes and directions in the two lattices are different. This introduces extra possible lines in the equivalent of Fig. 1, which could easily result in phase transitions between states with different distortions as the temperature changes.

Any new phases appearing after a stress, pressure, or magnetic field could be observed experimentally by a number of means. A second-order phase transition, such as that between the P and PSF phases, could be observed as an anomaly in the temperature dependence of the specific heat or magnetic susceptibility.[3] Structural changes can be observed in x-ray scattering or by spectroscopic methods. In Raman spectroscopy, extra bands will appear in the spectra of distorted molecules due to the splitting of degenerate modes.[3] Indeed, Raman spectra have already been shown to be sensitive to phase transformations of C_{60} solids subjected to high-pressure and high-temperature (HPHT) treatments,[33] and there is evidence that not all the C_{60} produced by these treatments is polymerized.[34] It should be noted that some solids, including the HPHT fullerite[33] may contain domains of different metastable phases. In these cases, it may be possible to use an external magnetic field to convert the solid into a single domain, which in turn may facilitate experimental measurements.[3]

If any non-negligible quadratic or other higher-order couplings are present, then the pseudospins will tilt away from the ''ideal'' directions predicted in this paper (see Ref. 2, p. 109). The molecular-field approximation can still be made to decouple the mean-field Hamiltonian for molecule i from that for molecule j, as in Sec. II A. However, the canonical transformation used above Eq. (7) to remove the terms in $Q_{i\nu}\lambda_{i\nu}$ from the Hamiltonian does not preserve the form of the higher-order coupling terms. This means that the problem can not be written in terms of the Hamiltonian describing the usual JT effect in an isolated center as it involves extra terms. It may be possible to neglect the extra terms, as they combine the higher-order coupling constant and the cooperative interaction constants. In this case, the problem can be solved as set out in this paper. However, terms which reduce the rotational symmetry may be important when there is no permanent splitting.[25] If this is the case, then it is still possible to proceed using the formalism given in this paper but by solving a different problem for the on-site JT effect.

It should be noted that several other factors may need to be taken into account before our idealized theoretical calculations can be applied to real C_{60} systems. There is a T_{1g} state only slightly higher in energy than the T_{1u} ground state of the C_{60}^{n-} systems. Therefore pseudo-JT effects coupling to this level also may be significant.[35,36] Also, there are several vibrational modes of each symmetry type, all of which will be JT coupled, although in some circumstances, it is possible to formulate the problem in terms of coupling to a single effective mode.

VI. APPLICATION TO fcc C_{60}

We will now illustrate how the general mathematics developed above can be used in situations that apply to C_{60} molecules at fcc lattice sites. The A_3C_{60} alkali-metal doped fullerides are likely to be the most interesting examples here, although this geometry also include pristine solid C_{60} at high temperatures, for example. The A_3C_{60} fullerides are amongst the most widely studied fullerene compounds due to their relatively high-temperature superconductivity. It is generally accepted that coupling to intramolecular h_g phonon modes plays an important part in driving the superconductivity,[7] along with intermolecular coupling between C_{60} molecules. The superconducting transition temperature is approximately independent of the alkali-metal-atom mass, which indicates that coupling to the vibrational modes of the alkali-metal atoms is not important. The strength of the intramolecular JT coupling is believed to be in the intermediate regime, which is the most difficult to treat theoretically. In particular, the conventional Migdal-Eliashberg theory of electron-phonon driven superconductivity is not valid,[7,37,38] and a JT theory in the nonadiabatic regime that correctly introduces zero-point energies is required to properly determine pair binding energies. Hence the theory presented here is likely to be of interest for these materials. In addition, the superconducting transition temperature of K_3C_{60} shows a very large decrease with increasing pressure,[39] which as mentioned above may be a signature of a cooperative JT effect.

The A_3C_{60} materials form a fcc structure. Over a wide range of temperatures, the individual C_{60} molecules take one of two standard orientations (with a possible orientational phase transition at high temperatures[40]). The C_{60} molecules are each oriented with eight of their 20 hexagonal faces along cubic ⟨111⟩ directions, but have two possible positions of the pentagonal faces related by a 90° rotation about the ⟨100⟩ direction.[14] The orientations can be alternatively visualized in terms of two icosahedra, as shown schematically in Fig. 6. From this, after analyzing the allowed symmetry operations it can be seen that a pair of adjacent molecules in the *same* orientation have a local symmetry of C_{2h}, whereas a pair of *different* orientations have a local C_{2v} symmetry.

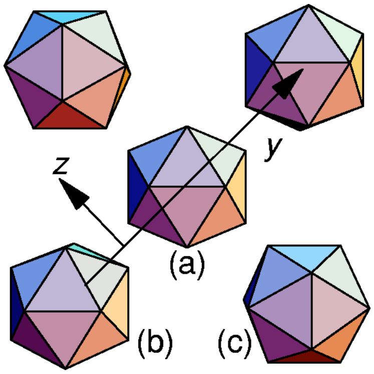

FIG. 6. A view of a face of a fcc crystal with icosahedra representing C_{60} molecules in their two standard orientations. Icosahedra (a) and (b) are in the same orientation so have a local C_{2h} symmetry whereas (a) and (c) have different orientations and hence this pair has C_{2v} symmetry. Also shown are the y and z axes relevant to the local C_{2h} symmetry of the (a)–(b) pair. The x axis is out of the page.

By reference to standard group theory texts (e.g., Ref. 41), we can find that in C_{2h} symmetry, x^2, y^2, z^2, and xy all transform as A_g, whereas yz and zx transform as B_g, where, in order to satisfy the convention that the two reflections are in the xz and yz planes, the y axis is taken to be the axis joining the two molecules, the z axis is perpendicular to this along the body diagonal of the cubic lattice and the x axis is along a cubic axis. The y and z axes are illustrated in Fig. 6. However, these axes are different to those used to label an icosahedron. If we define C_2 axes for the icosahedron (see discussion in Sec. II B) and label them $\{x_2,y_2,z_2\}$, then

$$\{x_2,y_2,z_2\}\equiv\{(y-z)/\sqrt{2},(y+z)/\sqrt{2},x\}. \tag{29}$$

With this correspondence, $\{Q_\theta,Q\epsilon,Q_4,Q_5,Q_6\}$ transform as

$$\left\{\frac{1}{2}(3x^2-r^2),-\sqrt{3}yz,\sqrt{\frac{3}{2}}(xy+zx),\right.$$
$$\left.\sqrt{\frac{3}{2}}(xy\text{-}zx),\frac{\sqrt{3}}{2}(y^2-z^2)\right\}.$$

in terms of the axes used for C_{2h} symmetry. Thus Q_θ, Q_6, and $Q_p\equiv(Q_4+Q_5)/\sqrt{2}$ transform as A_g, while $Q_m\equiv(Q_4-Q_5)/\sqrt{2}$ and Q_ϵ transform as B_g. It is therefore more convenient to express the matrix of interaction coefficients in terms of basis vectors $\mathbf{Q}=\{Q_\theta,Q_6,Q_p,Q_m,Q_\epsilon\}$ rather than the original $\{Q_\theta,Q_\epsilon,Q_4,Q_5,Q_6\}$. As the overall symmetry of each term allowed in the Hamiltonian $\mathcal{H}_{ij}(\mathbf{K})$ must be A_g, the form of the matrix of interaction coefficients for two same-orientation C_{60} molecules in this new basis takes the block-diagonal form

$$\mathbf{K}=\begin{pmatrix} K_{\theta\theta} & K_{\theta 6} & K_{\theta p} & 0 & 0 \\ K_{\theta 6} & K_{66} & K_{6p} & 0 & 0 \\ K_{\theta p} & K_{6p} & K_{pp} & 0 & 0 \\ 0 & 0 & 0 & K_{mm} & K_{\epsilon m} \\ 0 & 0 & 0 & K_{\epsilon m} & K_{\epsilon\epsilon} \end{pmatrix}. \qquad (30)$$

Thus 25 independent coefficients have been reduced to 9.

The relation between the C_{2v} coordinate system and the I_h coordinate system with a twofold z axis is not unique, as there are many possible C_2 axes in an icosahedron. For example, in Eq. (29), the directions of the axes could be reversed and/or, as x, y, and z are *all* twofold axes, the labels $\{x,y,z\}$ could be cyclically permuted. The choice made here is that which gives the simplest results. It corresponds to a particular orientation of the z axis of each of the C_{60} molecules in an interacting pair. Choices with the labels permuted will result in a Hamiltonian involving more complicated combinations of the Q_γ's, such as $\frac{1}{2}Q_\theta+\sqrt{3}/2Q_\epsilon$ rather than simply Q_θ. This combination transforms as $\frac{1}{2}(3x^2-r^2)$, so is equivalent to a θ-type distortion but along the x axis rather than the z axis.

For two differently oriented molecules, a similar analysis can be carried out but for C_{2v} symmetry. This shows that (again with a two-fold z-axis) Q_θ and Q_6 transform as A_1, Q_ϵ as B_2, Q_p as A_2, and Q_m as B_1. This leads to the same matrix as Eq. (30) above (and with the same basis for $\mathbf{Q}$) but with $K_{\theta p}=K_{6p}=K_{\epsilon m}=0$, i.e., there are only six independent nonzero coefficients in this case. The fact that the matrix is so similar in both symmetries is consistent with the experimental observation that both standard orientations are observed, which implies that both must have similar energies.

With the coupling constants restricted as in Eq. (30), the coupled equations to be solved take the form of four coupled equations,

$$\bar{Q}_{a\epsilon}+k\bar{\sigma}_{a\epsilon}+z[K_{\epsilon\epsilon}\bar{Q}_{b\epsilon}+K_{\epsilon m}\bar{Q}_{bm}]=0,$$

$$\bar{Q}_{am}+k\bar{\sigma}_{am}+z[K_{\epsilon m}\bar{Q}_{b\epsilon}+K_{mm}\bar{Q}_{bm}]=0 \qquad (31)$$

(including the same with a and b interchanged) and a set of six equations

$$\bar{Q}_{a\theta}+k\bar{\sigma}_{a\theta}+z[K_{\theta\theta}\bar{Q}_{b\theta}+K_{\theta p}\bar{Q}_{bp}+K_{\theta 6}\bar{Q}_{b6}]=0,$$

$$\bar{Q}_{ap}+k\bar{\sigma}_{ap}+z[K_{\theta p}\bar{Q}_{b\theta}+K_{pp}\bar{Q}_{bp}+K_{6p}\bar{Q}_{b6}]=0,$$

$$\bar{Q}_{a6}+k\bar{\sigma}_{a6}+z[K_{\theta 6}\bar{Q}_{b\theta}+K_{6p}\bar{Q}_{bp}+K_{66}\bar{Q}_{b6}]=0. \qquad (32)$$

The first set of equations can be decoupled by defining two combinations β of the $Q_{i\epsilon}$ and Q_{im} ($i=a$ or b) such that

$$\bar{Q}_{i\beta}=[K_{\epsilon m}\bar{Q}_{i\epsilon}+(K_\beta-K_{\epsilon\epsilon})\bar{Q}_{im}]/\sqrt{K_{\epsilon m}^2+(K_\beta-K_{\epsilon\epsilon})^2}, \qquad (33)$$

where

$$K_\beta=\tfrac{1}{2}[(K_{\epsilon\epsilon}+K_{mm})\pm\sqrt{(K_{\epsilon\epsilon}-K_{mm})^2+4K_{\epsilon m}^2}]. \qquad (34)$$

The second set of equations is decoupled by defining new combinations of $\bar{Q}_{i\theta}$, $\bar{Q}_{i6}$, and $\bar{Q}_{ip}$. The three new coupling constants K_β are the roots of the equation

$$\begin{vmatrix} (K_{\theta\theta}-K_\beta) & K_{\theta 6} & K_{\theta p} \\ K_{\theta 6} & (K_{66}-K_\beta) & K_{6p} \\ K_{\theta p} & K_{6p} & (K_{pp}-K_\beta) \end{vmatrix}=0. \qquad (35)$$

If axes $\{x_5,y_5,z_5\}$ are defined for the icosahedron such that z_5 is a fivefold axis and y_5 is a twofold axis (to be equivalent to the definitions used in Ref. 23), the mathematics is rather more complicated. The equivalence between these axes and the directions $\{x,y,z\}$ used for C_{2v} and C_{2h} symmetry (which is again not unique) can be defined to be

$$\{x_5,y_5,z_5\}\equiv\left\{\frac{1}{\sqrt{2(2+\phi)}}(\phi^{-1}y+\phi^2 z),x,\right.$$

$$\left.\frac{1}{\sqrt{2(2+\phi)}}(\phi^2 y-\phi^{-1}z)\right\}, \qquad (36)$$

where $\phi=(1+\sqrt{5})/2$ the golden mean. These relationships can be used to show that if we choose a basis

$$\mathbf{Q}=\begin{pmatrix} \dfrac{1}{2}Q_\theta+\dfrac{\sqrt{3}}{2}Q_\epsilon \\ \dfrac{1}{\sqrt{5}}[\sqrt{3}Q_\theta-Q_\epsilon+Q_5] \\ \dfrac{1}{\sqrt{2(2+\phi)}}[\phi^2 Q_4+\phi^{-1}Q_6] \\ \dfrac{1}{\sqrt{2(2+\phi)}}[-\phi^{-1}Q_4+\phi^2 Q_6] \\ \dfrac{1}{2\sqrt{5}}[-\sqrt{3}Q_\theta+Q_\epsilon+4Q_5] \end{pmatrix}$$

then the form of the matrix of interaction coefficients in Eq. (30) will remain the same. (The five components in the new basis transform as $\{A_g,A_g,A_g,B_g,B_g\}$ in C_{2h} symmetry and $\{A_1,A_1,A_2,B_1,B_2\}$ in C_{2v} symmetry.) It should be noted that, unlike $\{x_2,y_2,z_2\}$, the labels $\{x_5,y_5,z_5\}$ cannot be permuted as they are not equivalent to each other.

A similar method to that discussed in this section can be applied to other systems with different symmetries. This will result in different restrictions on the coupling constants.

VII. CONCLUSIONS

We have analyzed, from a general point of view, the possible cooperative JT effects that could be seen in solids containing negatively charged fullerene ions in which the form of the interaction between fullerene molecules can be represented by a form quadratic in either the collective displacements or pseudospin operators. This is a general form of interaction that can be used phenomenologically to represent a number of different physical interaction mechanisms.[2] It may be that there are some important effects in real fullerene solids that cannot be represented by a Hamiltonian of this form. However, the results given here serve as a starting point for helping to understand possible cooperative effects in such materials.

The analysis presented shows that at high temperatures, although the C_{60} molecules vibrate, they will not exhibit any permanent distortion. As the temperature is lowered, the solids may undergo a phase transition in which local distortions of the C_{60} molecules become locked in place by a cooperative JT effect. It also suggests that cooperative JT effects may play a role in structural phase transitions, such as the fcc to simple cubic phase transition observed in pure solid C_{60}. In addition, it predicts that it may be possible to create new and interesting phases if it is possible to generate structures in which there is a permanent distortion. This could be achieved either through internally generated ‘‘strains’’ or by application of an external field.

The formalism developed in this paper applies to molecules or ions which are linearly coupled to icosahedral *h*-type vibrations. The details are given for systems coupled to states derived from a *T* electronic term. This covers the JT effects experienced by all negatively charged fullerene ions when higher-order terms can be neglected. In all of these cases, the lowest APES consists of a trough of minimum-energy points, which gave the result that a strain in a given direction will result in a net distortion in that direction. Positively charged fullerene ions couple to states derived from an electronic *H* term. In the $H \otimes h$ system applicable to one hole, the lowest APES contains distinct wells rather than a trough. Very little work has been carried out that is applicable to higher positive dopings, but the same is expected to be true for these systems as well. The effect of a strain in these systems is not so straightforward. However, the principles of the method are otherwise the same.

In this paper, possible phases have been determined in terms of coupling constants characterizing cooperative JT effects between nearest-neighbor C_{60} molecules. We have shown that useful information on the allowed phases can be obtained without detailed knowledge of these coupling constants or of the on-site JT effects experienced by isolated C_{60} molecules. In the future, models giving the energy levels for specific systems will yield more detailed information on possible phases by allowing the free energy of different states to be calculated, especially now that the energies of different allowed configurational terms has been determined,[42] which is different to the usual Hund’s rule ordering.[23] Recent developments in the JT theory of single centers (including advances in numerical computing) and ready availability of computer algebra systems means such calculations are now feasible. If detailed knowledge of the coupling constants becomes available at a later date, then the results in this paper will allow more quantitative information on possible phase transitions to be obtained, including the temperatures at which phase transitions will take place.

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