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Librational modes in solid C_{60} and doped solid C_{60}

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We present a theoretical study of librational modes in solid C_{60} and doped solid C_{60}. General results are derived by utilizing the space group symmetries of the solids. At the Brillouin-zone center Γ, in solid C_{60} there should be in general five distinct libron frequencies in the simple-cubic phase, and ten in the so-called $2a_0$-fcc phase; in M_3C_{60}, where M=K,Rb, a single libron frequency is expected; in M_6C_{60}, one also expects a single libron frequency. The case of M_3C_{60} is of particular interest since in the first approximation, the potential governing the libron motion contains a single undetermined parameter, and is thus completely determined by a measurement of the libron frequency.

I. INTRODUCTION

Currently the properties of solid C_{60} are of intense general interest. An interesting feature of this molecular solid is that, the C_{60} molecules in the solid can easily rotate due to their approximately spherical shape. It is known[1–3] that at temperatures above the phase transition temperature near 250 K, the C_{60} molecules in solid C_{60} rotate freely, and the solid has a face-centered-cubic (fcc) structure. Below the phase transition temperature, the four C_{60} molecules of a fcc cell of the fcc phase become inequivalent because they no longer rotate freely and have different equilibrium orientations; the structure of the solid becomes simple cubic (sc) with a basis of four molecules sitting on the fcc sites of the sc primitive unit cell. In this sc phase of solid C_{60}, each C_{60} molecule can still librate around its equilibrium orientation, and the presence of such librational motion has manifested itself in experimental data.[4–11] The librons associated with the rotational libration of C_{60} molecules are as basic as the phonons which are associated with the translational vibration of C_{60} molecules, and they are important for understanding the low-temperature specific heat, low-energy Raman and neutron scattering spectra, and other properties of solid C_{60}. The purpose of this paper is to study theoretically the librons in solid C_{60} and in doped solid C_{60}.

II. LIBRONS

First we give a summary of experimental and theoretical efforts in this area. In principle both Raman and neutron scattering experiments are capable of directly detecting librons. In neutron scattering experiments, Neumann *et al.*[4] have observed librons in solid C_{60}. They find a single scattering peak due to librons, and the position of the peak shifts from 16 cm^{-1} to 23 cm^{-1} as the temperature decreases from 250 K to 20 K. Christides *et al.*[5] have observed librons in doped fullerenes K_3C_{60} and Rb_6C_{60}, with libron energies of about 32 cm^{-1} and 48 cm^{-1}, respectively. Pintschovius *et al.*[6] have observed librons in single crystals of solid C_{60}; at 200 K, they find three libron bands around 19, 29, and 37 cm^{-1}, respectively. In the low frequency part of their neutron scattering spectrum of solid C_{60}, Coulombeau *et al.*[7] observed a broad signal with three maxima at 80, 102, and 137 cm^{-1}. In Raman experiments on single crystals of C_{60}, van Loosdrecht *et al.*[8,9] observed peaks of unidentified origin at 56, 81, and 109 cm^{-1}, the latter two in agreement with two of the maxima in the neutron spectrum of Coulombeau *et al.*[7] However, these three peaks are not observed in all spectra, and their presence depends on the spot position on the crystal, thus van Loosdrecht *et al.*[9] suggest these peaks could be due to impurities or defects. van Loosdrecht *et al.*[10] have also performed Raman scattering on single crystals of C_{70}; 11 lattice modes (5 due to phonons and 6 due to librons) are observed in the range of 10–60 cm^{-1}. Beyermann *et al.*[11] have extracted from their specific heat data of solid C_{60} a libron frequency of 40 cm^{-1}. Huant *et al.*[12] have observed peaks at 8.5, 12.8, 17.7, and 21.6 cm^{-1} in their far-infrared transmission spectrum of solid C_{60}, and have suggested that these peaks may be due to librons under the influence of symmetry lowering. We have also recently learned that Horoyski and Thewalt[13] have succeeded in the first conclusive measurement of librons in solid C_{60} by Raman spectroscopy. The resolution of their spectra is much better than neutron scattering spectra. At 77 K their spectra show peaks at 17.9, 20.9, 24.5, 32.6, 41.3, and 49.7 cm^{-1}.

To study librons theoretically, one can take two approaches which complement each other. In the first approach, one uses model potentials for intermolecular interactions, and carries out numerical calculations of libron frequencies. A reasonable and detailed model potential is a prerequisite for this approach. Li, Lu, and Martin (LLM)[14] have used the model potential[15] they proposed to calculate the dispersions of librons in solid C_{60}. Yildirim and Harris[16] have presented a detailed and complete study of librons and phonons in solid C_{60}, and have calculated libron dispersions for two model potentials: one is the LLM potential, and the other is the potential proposed by Sprik, Cheng, and Klein[17] (SCK). They have also presented a group-theoretical analysis of the modes. The authors of the SCK potential have used constant-pressure molecular dynamics to calculate the libron spectral density of solid C_{60}.[17] Cheng and Klein[18]

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have also used the Lennard-Jones potential to calculate the libron spectral density of solid C_{60} and solid C_{70}; however it is known[17] that this potential does not lead to the correct low-temperature crystal structure for solid C_{60}. The numerical results using the LLM and SCK potentials agree on the libron energy scale of solid C_{60} to be about 15 cm^{-1}.[16] The libron energies vary between 7–24 cm^{-1},[16,17] which appear too low compared to some of the experimental values. Other detailed results are very much dependent on the model potential. For example, for the SCK potential, the lowest energy mode at Γ point is an A_g mode, and there are five distinct libron frequencies, while for the LLM potential the lowest modes at Γ point are accidentally degenerate E_g and T_g modes, with only four distinct libron frequencies. In the second approach, one utilizes the symmetries of the molecules and the crystals to analyze the general properties of the librons. The results are independent of model potentials. This is the main approach in this paper. Some of our results for pure C_{60} are equivalent to some of the results of Yildirim and Harris,[16] which appeared as our work was being completed.

In the study of librons, it is legitimate to assume that fullerene molecules are rigid, because intramolecular vibrations of carbon atoms occur at much higher energies than the energies of the external modes. It is useful to have a comparison between librons and phonons. Here "phonon" refers to the translational motion, and "libron" refers to the rotational motion of molecules. (Some authors use the word "phonon" as a generic name which includes librons.) A difference between phonons and librons is that while there are acoustic phonons, there are no acoustic librons.[19] But like phonons, librons are also in principle collective lattice modes, which means that in general one cannot treat the motion of molecules as independent from each other. This is certainly true in solid C_{60}, where it is known that the orientational ordering is driven by the correlation between pentagons and double bonds of C_{60} molecules: it is energetically favorable to have the configuration in which a pentagon of a C_{60} faces an oppositely charged double bond of a neighboring C_{60}.[20,1] Thus as one C_{60} rotates, one expects the neighboring C_{60} molecules to be affected due to this pentagon-double bond correlation.

A. Simple-cubic solid C_{60}

In sc solid C_{60}, the four molecules of the sc primitive cell, which we label by the index s =1,2,3, and 4, respectively, have the coordinates (0,0,0), $(\frac{1}{2},\frac{1}{2},0)$, $(0,\frac{1}{2},\frac{1}{2})$, and $(\frac{1}{2},0,\frac{1}{2})$. The librational motion of each molecule in the solid is described by the rotational parameters $\theta\left(\begin{smallmatrix}\mathbf{i}\\ s\\ \alpha\end{smallmatrix}\right)$, which represent the (infinitesimal) rotation angles of the molecule about the axis α. Here $\mathbf{i}$ labels the unit cell, and α labels components with respect to the sc crystal axes. The x,y,z components of $\theta\left(\begin{smallmatrix}\mathbf{i}\\ s\\ \alpha\end{smallmatrix}\right)$ form the components of an axial vector. By assumption, when all $\theta\left(\begin{smallmatrix}\mathbf{i}\\ s\\ \alpha\end{smallmatrix}\right)$=0, i.e., all molecules are in their equilibrium orientations, the total librational energy $V(\{\theta\left(\begin{smallmatrix}\mathbf{i}\\ s\\ \alpha\end{smallmatrix}\right)\})$ of the solid reaches a minimum, which we define to be zero. Near this minimum, V can be expanded as

$$V\left(\left\{\theta\begin{pmatrix}\mathbf{i}\\ s\\ \alpha\end{pmatrix}\right\}\right)=\frac{1}{2}\sum_{\substack{\mathbf{i}\,s\,\alpha\\ \mathbf{i}'s'\alpha'}}\Phi\begin{pmatrix}\mathbf{i}&\mathbf{i}'\\ s&s'\\ \alpha&\alpha'\end{pmatrix}\theta\begin{pmatrix}\mathbf{i}\\ s\\ \alpha\end{pmatrix}\theta\begin{pmatrix}\mathbf{i}'\\ s'\\ \alpha'\end{pmatrix}$$
$$+\text{higher order terms.} \qquad (1)$$

The equation of motion for $\theta\left(\begin{smallmatrix}\mathbf{i}\\ s\\ \alpha\end{smallmatrix}\right)$ is given by $Id^2\theta\left(\begin{smallmatrix}\mathbf{i}\\ s\\ \alpha\end{smallmatrix}\right)/dt^2=-\partial V/\partial\theta\left(\begin{smallmatrix}\mathbf{i}\\ s\\ \alpha\end{smallmatrix}\right)$, where $I=1.0\times10^{-43}$ kg m^2 is the isotropic moment of inertia of the C_{60} molecule. Thus in the harmonic approximation where the higher order terms in (1) are neglected, the libron frequencies are solutions of the equation

$$e\begin{pmatrix}s\\ \alpha\end{pmatrix}\omega^2=\sum_{s'\alpha'}D\begin{pmatrix}s&s'\\ \alpha&\alpha'\end{pmatrix};\mathbf{q}\Bigg)e\begin{pmatrix}s'\\ \alpha'\end{pmatrix}, \qquad (2)$$

where $e\binom{s}{\alpha}=\sqrt{I}\sum_{\mathbf{i}}\theta\left(\begin{smallmatrix}\mathbf{i}\\ s\\ \alpha\end{smallmatrix}\right)e^{-i\mathbf{q}\cdot\mathbf{R}_\mathbf{i}}$, $D\left(\begin{smallmatrix}s&s'\\ \alpha&\alpha'\end{smallmatrix};\mathbf{q}\right)=\frac{1}{I}\sum_{\mathbf{i}'}\Phi\left(\begin{smallmatrix}\mathbf{i}&\mathbf{i}'\\ s&s'\\ \alpha&\alpha'\end{smallmatrix}\right)e^{-i\mathbf{q}\cdot(\mathbf{R}_\mathbf{i}-\mathbf{R}_{\mathbf{i}'})}$.[21] Since in sc solid C_{60} there are 12 rotational degrees of freedom per primitive unit cell (s takes 4 values and α takes 3 values), Eq. (2) represents a 12-dimensional matrix equation. At general points in wave-vector space, it gives 12 librational modes. Here we are not considering the coupling between librons and phonons, which in principle is present for $\mathbf{q}\neq\mathbf{0}$.

The Brillouin zone center Γ where $\mathbf{q}=\mathbf{0}$ is of special importance, because Raman scattering experiments measure excitations of the Γ point, where the symmetries are given by the point group of the solid. Let us consider the restrictions placed by the point group of solid C_{60} on the form of the real symmetric matrix $D\left(\begin{smallmatrix}s&s'\\ \alpha&\alpha'\end{smallmatrix};\mathbf{0}\right)$ which for brevity we simply write $D\left(\begin{smallmatrix}s&s'\\ \alpha&\alpha'\end{smallmatrix}\right)$. ($s,\alpha$ are row indices, and s',α' are column indices.) The space group of sc solid C_{60} is known[1] to be $Pa\bar{3}$, whose point group is T_h. Among the generators of $Pa\bar{3}$, one is a threefold rotation along the [111] direction at the origin.[22] This rotation causes a cyclic permutation of the x,y,z axes of the s =1 molecule, and also causes a cyclic permutation of the s =2,3,4 molecules at the same time causing a cyclic permutation of the x,y,z axes of each of the three molecules. Since the total librational energy should be invariant under this operation, we must have $D\left(\begin{smallmatrix}1&1\\ x&x\end{smallmatrix}\right)=D\left(\begin{smallmatrix}1&1\\ y&y\end{smallmatrix}\right)$, $D\left(\begin{smallmatrix}1&2\\ x&y\end{smallmatrix}\right)=D\left(\begin{smallmatrix}1&3\\ y&z\end{smallmatrix}\right)$, etc. Another generator of $Pa\bar{3}$ is a twofold screw rotation along the [001] direction at $x=\frac{1}{4}, y=0$. This operation exchanges molecules s =1 and 4, and also s =2 and 3, at the same time the x and y axes of the molecules are inverted. From this we derive $D\left(\begin{smallmatrix}1&1\\ x&x\end{smallmatrix}\right)=D\left(\begin{smallmatrix}4&4\\ x&x\end{smallmatrix}\right)$, $D\left(\begin{smallmatrix}1&1\\ x&z\end{smallmatrix}\right)=-D\left(\begin{smallmatrix}4&4\\ x&z\end{smallmatrix}\right)$, $D\left(\begin{smallmatrix}1&2\\ x&y\end{smallmatrix}\right)=D\left(\begin{smallmatrix}4&3\\ x&y\end{smallmatrix}\right)$, etc. (These relations are useful for checking errors in numerical calculations.) One can show that the form of the matrix $D\left(\begin{smallmatrix}s&s'\\ \alpha&\alpha'\end{smallmatrix}\right)$ is completely determined by considering the relations derived from the above two generators, and there are only 8 independent matrix elements. We parametrize the matrix by the following elements: $u_1=D\left(\begin{smallmatrix}1&1\\ x&x\end{smallmatrix}\right)$, $u_2=D\left(\begin{smallmatrix}1&1\\ x&y\end{smallmatrix}\right)$, $u_3=D\left(\begin{smallmatrix}1&2\\ x&x\end{smallmatrix}\right)$, $u_4=D\left(\begin{smallmatrix}1&2\\ x&y\end{smallmatrix}\right)$, $u_5=D\left(\begin{smallmatrix}1&2\\ x&z\end{smallmatrix}\right)$, $u_6=D\left(\begin{smallmatrix}1&3\\ x&x\end{smallmatrix}\right)$, $u_7=D\left(\begin{smallmatrix}1&3\\ x&z\end{smallmatrix}\right)$, $u_8=D\left(\begin{smallmatrix}1&4\\ x&x\end{smallmatrix}\right)$. Thus, we arrive at the explicit form of the 12×12 symmetric matrix $D\left(\begin{smallmatrix}s&s'\\ \alpha&\alpha'\end{smallmatrix}\right)$ in terms of these 8 parameters,

$$D(\Gamma)=\begin{pmatrix}
u_1 & u_2 & u_2 & u_3 & u_4 & u_5 & u_6 & -u_5 & u_7 & u_8 & u_7 & -u_4\\
 & u_1 & u_2 & -u_4 & u_8 & u_7 & u_5 & u_3 & u_4 & u_7 & u_6 & -u_5\\
 & & u_1 & -u_5 & u_7 & u_6 & u_7 & -u_4 & u_8 & u_4 & u_5 & u_3\\
 & & & u_1 & -u_2 & -u_2 & u_8 & -u_7 & u_4 & u_6 & u_5 & -u_7\\
 & & & & u_1 & u_2 & -u_7 & u_6 & -u_5 & -u_5 & u_3 & u_4\\
 & & & & & u_1 & -u_4 & u_5 & u_3 & -u_7 & -u_4 & u_8\\
 & & & & & & u_1 & -u_2 & u_2 & u_3 & -u_4 & u_5\\
 & & & & & & & u_1 & -u_2 & u_4 & u_8 & -u_7\\
 & & & & & & & & u_1 & -u_5 & -u_7 & u_6\\
 & & & & & & & & & u_1 & u_2 & -u_2\\
 & & & & & & & & & & u_1 & -u_2\\
 & & & & & & & & & & & u_1
\end{pmatrix}.$$

This matrix is equivalent to Eq. (B34) of Ref. 16, although the ordering of the entries is different. The identification of our parameters with those in Ref. 16 is given by $u_1=\alpha, u_2=\beta, u_3=h, u_4=\delta, u_5=-\lambda, u_6=\epsilon, u_7=\gamma$, and $u_8=\kappa$.

Since the irreducible representations of T_h are either one, two, or three dimensional, the 12-dimensional vector space in which $D\binom{s\ s'}{\alpha\ \alpha'}$ acts must be reducible, and its reduction can be represented by the direct sum $A_g \oplus E_g \oplus 3T_g$. The matrix $D\binom{s\ s'}{\alpha\ \alpha'}$ can thus be block diagonalized accordingly. Since the A_g, E_g, and T_g modes are all allowed by the selection rules for Raman scattering,[23] all the librational modes should be Raman-active. We have also derived 12 eigenvectors belonging to the irreducible representations. The eigenvector for the A_g mode libron is $t_1=(1,1,1,1,-1,-1,-1,1,-1,-1,-1,1)/\sqrt{12}$. (We adopt the ordering of entries such that the 1st to 3rd entries correspond to $s=1, \alpha=x,y,z$, the 4th to 6th entries correspond to $s=2, \alpha=x,y,z$, etc.) From this eigenvector we learn that the A_g mode libron corresponds to rotating the molecule $s=1$ about [111], the molecule $s=2$ about $[1\bar{1}\bar{1}]$, the molecule $s=3$ about $[\bar{1}1\bar{1}]$, and the molecule $s=4$ about $[\bar{1}\bar{1}1]$. As expected, this mode conserves the $Pa\bar{3}$ space group symmetry. Using the 12 eigenvectors as row vectors of a matrix T, we block-diagonalize the matrix $D\binom{s\ s'}{\alpha\ \alpha'}$ into its irreducible form $D'=TD\widetilde{T}$. The other 11 eigenvectors are:

$$\begin{aligned}
t_2 &= (2,-1,-1,2,1,1,-2,-1,1,-2,1,-1)/\sqrt{24},\\
t_3 &= (0,-1,1,0,1,-1,0,-1,-1,0,1,1)/\sqrt{8},\\
t_4 &= (1,0,0,1,0,0,1,0,0,1,0,0)/2,\\
t_5 &= (0,1,0,0,-1,0,0,-1,0,0,1,0)/2,\\
t_6 &= (0,0,1,0,0,-1,0,0,1,0,0,-1)/2,\\
t_7 &= (0,1,0,0,1,0,0,1,0,0,1,0)/2,\\
t_8 &= (0,0,1,0,0,1,0,0,-1,0,0,-1)/2,\\
t_9 &= (1,0,0,-1,0,0,-1,0,0,1,0,0)/2,\\
t_{10} &= (0,0,1,0,0,1,0,0,1,0,0,1)/2,\\
t_{11} &= (1,0,0,-1,0,0,1,0,0,-1,0,0)/2,\\
t_{12} &= (0,1,0,0,1,0,0,-1,0,0,-1,0)/2.
\end{aligned}$$

[The doublet (t_2,t_3) gives a basis for E_g. The triplet (t_4,t_7,t_{10}) gives a basis for T_g, and so do the triplets (t_5,t_8,t_{11}) and (t_6,t_9,t_{12}).] The irreducible matrix D' has the form $A\oplus B\oplus B\oplus C\oplus C\oplus C$, where

$$\begin{aligned}
A &= u_1+2u_2+u_3-2u_4-2u_5-u_6-2u_7-u_8,\\
B &= u_1-u_2+u_3+u_4+u_5-u_6+u_7-u_8,
\end{aligned}$$

and C is a 3×3 symmetric matrix, whose elements are

$$\begin{aligned}
C_{11} &= u_1+u_3+u_6+u_8,\ C_{12}=u_2-u_4+u_5+u_7,\\
C_{13} &= u_2-u_5+u_7+u_4,\ C_{22}=u_1-u_3+u_6-u_8,\\
C_{23} &= u_2+u_5-u_7+u_4,\ C_{33}=u_1-u_3-u_6+u_8.
\end{aligned}$$

Our eigenvectors are equivalent to those in Ref. 16, but our eigenvectors and the resulting 3×3 matrix are simpler.

The above results show explicitly that at the center of the Brillouin zone, in general there are five distinct libron frequencies. One is a nondegenerate A_g mode given by $\sqrt{A}$, one is a twofold degenerate E_g mode given by $\sqrt{B}$, and the other three are T_g modes given by the square roots of the three eigenvalues of C, each threefold degenerate. Indeed, the SCK potential does give five distinct libron frequencies at the Γ point. In the LLM potential, the choice of parameter values is such that at Γ there is an accidental degeneracy between an E_g and a T_g mode, resulting in only four distinct libron frequencies.[16] This degeneracy can be lifted by choosing different parameter values.

For numerical calculations one needs explicit model potentials for intermolecular interactions, such as the LLM and the SCK potentials. Both potentials are atomically-pairwise in nature. One can introduce two sets of axes to describe the positions of carbon atoms in solid C_{60}; namely, the crystal axes, and the molecular axes which are fixed on a rotating C_{60} molecule. If R is the coordinate in the crystal axes, and r in the molecular axes, they are related by $R_i=\sum_j \Gamma_{ij}r_j$, where Γ_{ij} are direction cosines. If we denote Λ_{ij} as the equilibrium value of Γ_{ij}, to second order in small rotation θ_i we can express the direction cosine as

$$\Gamma_{ij}=\Lambda_{ij}(1-\tfrac{1}{2}\theta^2)+\sum_{kn}\epsilon_{ink}\Lambda_{nj}\theta_k+\tfrac{1}{2}\theta_i\sum_k\Lambda_{kj}\theta_k. \quad (3)$$

Here $\theta^2=\sum_i\theta_i^2$, and ϵ_{ink} is the Levi-Civita symbol. Note that our small rotation is defined with respect to the crystal axes. If they were defined with respect to the molecular axes as in Ref. 16, Eq. (3) is replaced by

$$\Gamma_{ij}=\Lambda_{ij}(1-\tfrac{1}{2}\theta^2)+\sum_{kn}\epsilon_{njk}\Lambda_{in}\theta_k+\tfrac{1}{2}\theta_j\sum_k\Lambda_{ik}\theta_k. \quad (4)$$

This equation appears simpler than Eq. (4) of Ref. 16, which involves quadruple summations but give the same results as our Eq. (4).

The C_{60} molecule has a set of three mutually perpendicular twofold symmetry axes, which are convenient to be used as the molecular axes. There are two different ways to align this set of molecular axes with the crystal axes, and Harris and Sachidanandam[24] call them orientation 1 and orientation 2. Orientation 2 can be obtained from orientation 1 by a 90° rotation about a [100] direction, but more subtlely, it can also be obtained from orientation 1 by rotating counterclockwise about [111] an angle $\phi_0 = 120^\circ - \cos^{-1}(\frac{1}{4}) = 44.48^\circ$.[24] In orientation 1, coordinates of the carbon atoms are given by the cyclic permutations of the following coordinates:

$$\left[\pm\tau\left(d_1 + \frac{d_2}{2}\right), \pm\frac{d_2}{2}, 0\right],$$

$$\left[\pm\frac{1}{2}(d_1 + d_2), \pm\frac{\tau}{2}d_1, \pm\frac{\tau}{2}(\tau d_1 + d_2)\right],$$

$$\left[\pm\frac{1}{2}(\tau^2 d_1 + d_2), \pm\frac{d_1}{2}, \pm\frac{\tau}{2}(d_1 + d_2)\right].$$

Here τ is the golden mean $(1 + \sqrt{5})/2$, d_1 is the length of single bonds (sides of pentagons), and d_2 is the length of double bonds (shared among hexagons). The bond centers of the 60 single bonds of C_{60} are given by

$$\left[\pm\frac{1}{2}\left(\frac{d_1}{2} + d_2\right), \pm\frac{\tau}{4}d_1, \pm\frac{1}{2}\left(\frac{3\tau + 1}{2}d_1 + \tau d_2\right)\right],$$

$$\left[\pm\frac{1}{2}\left(\frac{2 + \tau}{2}d_1 + d_2\right), \pm\frac{1 + \tau}{4}d_1,\right.$$

$$\left.\pm\frac{1}{2}\left(\frac{2\tau + 1}{2}d_1 + \tau d_2\right)\right],$$

$$\left[0, \pm\frac{\tau}{2}(d_1 + d_2), \pm\frac{1}{2}(\tau^2 d_1 + d_2)\right],$$

and cyclic permutations. The 30 double bond centers are given by

$$\left[\pm\tau\left(d_1 + \frac{d_2}{2}\right), 0, 0\right],$$

$$\left[\pm\frac{\tau}{2}\left(d_1 + \frac{d_2}{2}\right), \pm\frac{\tau^2}{2}\left(d_1 + \frac{d_2}{2}\right), \pm\frac{1}{2}\left(d_1 + \frac{d_2}{2}\right)\right],$$

and cyclic permutations. For orientation 2, noncyclic permutations should be taken.

To obtain the $Pa\bar{3}$ equilibrium orientations in solid C_{60}, one starts with all C_{60} molecules in orientation 1, or all in orientation 2, then rotates by an angle ϕ the molecule at (0,0,0) about [111], the molecule at $(\frac{1}{2}, \frac{1}{2}, 0)$ about $[1\bar{1}\bar{1}]$, the molecule at $(0, \frac{1}{2}, \frac{1}{2})$ about $[\bar{1}1\bar{1}]$, and the molecule at $(\frac{1}{2}, 0, \frac{1}{2})$ about $[\bar{1}\bar{1}1]$. It is important to note that both the sense of rotation and the magnitude of ϕ are different for orientation 1 and orientation 2. For orientation 1, ϕ_1 is a *counterclockwise* rotation, of about 23° for the LLM potential; for orientation 2, ϕ_2 is a *clockwise* rotation, of about 21° for the LLM potential. These two angles and ϕ_0 defined earlier are related by[25]

$$\phi_1 = \phi_0 - \phi_2 = 44.48^\circ - \phi_2. \tag{5}$$

When comparing theoretical and experimental values of ϕ, it is necessary to specify whether it is ϕ_1 or ϕ_2. We note that the experimental value 22° in Ref. 20 is ϕ_2, but the experimental value 26° in Ref. 1 is ϕ_1, which translates to $\phi_2 = 18.48^\circ$. The theoretical value 21.3° in Ref. 15 is ϕ_2.

B. $2a_0$-fcc solid C_{60}

Recently, Van Tendeloo *et al.* have found a different phase of solid C_{60} at temperatures below the sc phase.[26] They have proposed that in this phase, the four sublattices in the sc phase double into eight sublattices, resulting in a fcc lattice with a doubled lattice constant. They call this phase the $2a_0$-fcc phase. Further experiments by Groenen *et al.*[27] confirmed this phase, by showing that the molecules on the primed sublattices differ from those on unprimed sublattices by a 60° rotation in the [111] directions. The fcc cell with primed and unprimed sublattices is shown in Fig. 3 of Ref. 27. The space group of this $2a_0$-fcc phase has been proposed to be $Fd\bar{3}$.[9] We note that recently the nature of this phase has been questioned by other researchers.[28] Here we assume that the suggestions of Refs. 26 and 27 are correct.

In this phase the molecules on opposite sides of the original simple-cubic primitive cell are no longer equivalent. The eight inequivalent molecules of the $2a_0$-fcc phase are given by the molecules labeled s=1–4 in the sc phase plus molecules at (0,0,1), $(\frac{1}{2},\frac{1}{2},1)$, $(1,\frac{1}{2},\frac{1}{2})$, and $(\frac{1}{2},1,\frac{1}{2})$ in terms of the units of the original sc cell, and we label them by $s = 5, 6, 7, 8$, respectively. Our molecules s =1–8 correspond to the molecules labeled by Groenen *et al.*[27] as A, D, C, B, A', D', C', B', respectively. The identification of the crystal structure in Fig. 3 of Ref. 27 with space group $Fd\bar{3}$ is made easier if we use the origin choice 2 in the International Tables.[22] In this choice the origin can be identified with the site of the A molecule. To conform to the symmetry requirements of $Fd\bar{3}$, we find that starting from all molecules in orientation 1, the molecules A, A' ($s = 1, 5$) should rotate about [111], D, D' ($s = 2, 6$) about $[\bar{1}\bar{1}1]$, C, C' ($s = 3, 7$) about $[1\bar{1}\bar{1}]$, and B, B' ($s = 4, 8$) about $[\bar{1}1\bar{1}]$. The rotation angle for molecules on unprimed sublattices is labeled by ϕ_1, and on primed sublattices by ϕ_1'. Note that the rotation directions are different from those in the sc phase.

The librational vector space for the $2a_0$-fcc phase is 24 dimensional. For space group $Fd\bar{3}$, at Γ this librational space is represented by $2A_g \oplus 2E_g \oplus 6T_g$. Therefore 10 distinct libron frequencies are expected at Γ. It turns out that under the operations of the point group, molecules on primed and unprimed sublattices do not mix, as a result the 24 eigenvectors we have found have the following simple form: 12 of them are given by adjoining a 12-dimensional null vector behind the 12-dimensional vectors listed below,

$$e_1 = (1,1,1,-1,-1,1,1,-1,-1,-1,1,-1)/\sqrt{12},$$
$$e_2 = (2,-1,-1,-2,1,-1,2,1,1,-2,-1,1)/\sqrt{24},$$
$$e_3 = (0,-1,1,0,1,1,0,1,-1,0,-1,-1)/\sqrt{8},$$
$$e_4 = (1,0,0,1,0,0,1,0,0,1,0,0)/2,$$
$$e_5 = (0,1,0,0,1,0,0,-1,0,0,-1,0)/2,$$
$$e_6 = (0,0,1,0,0,-1,0,0,-1,0,0,1)/2,$$
$$e_7 = (0,1,0,0,1,0,0,1,0,0,1,0)/2,$$
$$e_8 = (0,0,1,0,0,-1,0,0,1,0,0,-1)/2,$$
$$e_9 = (1,0,0,1,0,0,-1,0,0,-1,0,0)/2,$$
$$e_{10} = (0,0,1,0,0,1,0,0,1,0,0,1)/2,$$
$$e_{11} = (1,0,0,-1,0,0,-1,0,0,1,0,0)/2,$$
$$e_{12} = (0,1,0,0,-1,0,0,1,0,0,-1,0)/2,$$

and the other 12 by adjoining in the reversed order. We can use the 24-dimensional eigenvectors as the row vectors of a matrix T, and reduce the dynamical matrix $D(\Gamma)$ into its irreducible form $D'(\Gamma) = TD(\Gamma)\widetilde{T}$. Since T is block diagonal, only the matrix elements within the two 12×12 blocks $D_1(\Gamma)$ and $D_2(\Gamma)$ along the diagonal of $D(\Gamma)$ affect the libron frequencies at Γ. We find $D_1(\Gamma)$ has the form

$$D_1(\Gamma) = \begin{pmatrix}
u_1 & u_2 & u_2 & u_3 & u_4 & u_5 & u_6 & -u_5 & u_7 & u_8 & -u_7 & u_4 \\
 & u_1 & u_2 & u_4 & u_8 & -u_7 & u_5 & u_3 & u_4 & u_7 & u_6 & -u_5 \\
 & & u_1 & -u_5 & u_7 & u_6 & -u_7 & u_4 & u_8 & u_4 & u_5 & u_3 \\
 & & & u_1 & u_2 & -u_2 & u_8 & -u_7 & -u_4 & u_6 & -u_5 & -u_7 \\
 & & & & u_1 & -u_2 & u_7 & u_6 & u_5 & u_5 & u_3 & -u_4 \\
 & & & & & u_1 & -u_4 & -u_5 & u_3 & u_7 & -u_4 & u_8 \\
 & & & & & & u_1 & -u_2 & -u_2 & u_3 & -u_4 & -u_5 \\
 & & & & & & & u_1 & u_2 & -u_4 & u_8 & -u_7 \\
 & & & & & & & & u_1 & u_5 & u_7 & u_6 \\
 & & & & & & & & & u_1 & -u_2 & u_2 \\
 & & & & & & & & & & u_1 & -u_2 \\
 & & & & & & & & & & & u_1
\end{pmatrix}.$$

$D_2(\Gamma)$ has the same form as $D_1(\Gamma)$, with u_i replaced by u'_i. We note that $D_1(\Gamma)$ differ from the $D(\Gamma)$ for the sc phase only in the signs of u_i, but not in the locations of u_i. The matrix $D'_1(\Gamma)$ has the form $A \oplus B \oplus B \oplus C \oplus C \oplus C$, where

$$A = u_1 + 2u_2 - u_3 - 2u_4 + 2u_5 + u_6 - 2u_7 - u_8,$$
$$B = u_1 - u_2 - u_3 + u_4 - u_5 + u_6 + u_7 - u_8,$$

and C is a 3×3 symmetric matrix with elements

$$C_{11} = u_1 + u_3 + u_6 + u_8,\ C_{12} = u_2 + u_4 + u_5 + u_7,$$
$$C_{13} = u_2 - u_5 - u_7 + u_4,\ C_{22} = u_1 - u_3 - u_6 + u_8,$$
$$C_{23} = u_2 - u_5 + u_7 - u_4,\ C_{33} = u_1 + u_3 - u_6 - u_8.$$

In Fig. 1 we plot the potential energy per C_{60} molecule as a function of ϕ_1, with $\phi'_1 = \phi_1$, for both the SCK and the LLM potentials. The minimum at $\phi_1=0$ is degenerate with the one at $\phi_1=\phi_0=44.48°$. This is because the energy for all molecules in orientation 1 is the same as the energy for all molecules in orientation 2. In Fig. 2 we fix $\phi_1=0$, and plot the potential energy as a function of ϕ'_1. For the SCK potential, we find a global minimum at $\phi'_1=0$, and a local minimum at $\phi'_1=64°$. For the LLM potential, we find a global minimum at $\phi'_1=71°$, and a local minimum at $\phi'_1=108°$. These global minimum energies are higher than those for the $Pa\overline{3}$ structure. Therefore both the SCK and LLM potentials do not predict $Fd\overline{3}$ as the ground state structure. Numerical calculations of libron frequencies need to await a model potential which predicts an $Fd\overline{3}$ ground state.

C. Doped solid C_{60}

Superconducting compounds K_3C_{60} and Rb_3C_{60} have the same $Fm\overline{3}m$ crystal structure, with point group O_h.[29,30] At Γ point the librational vector space for these compounds is represented by T_{1g}. Therefore for these compounds we expect a single libron peak at Γ. Neutron scattering experiments on K_3C_{60} at 12 K have measured a single sharp libron peak at 4 meV.[5]

Compounds M_6C_{60}, M=K,Rb,Cs are isostructural with cubic space group $Im\overline{3}$, point group T_h.[30,31] At Γ point the librational vector space is represented by T_g, hence a single libron frequency is also expected. Neutron experiments[5] have measured a single libron peak for Rb_6C_{60}, but the peak is much broader than K_3C_{60}.

Unlike in the case of C_{60}-C_{60} interactions where microscopic LLM and SCK potentials have been proposed,

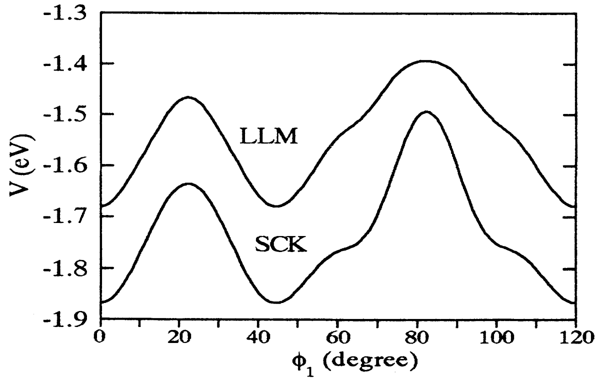

FIG. 1. Potential energy per C_{60} molecule as a function of $\phi_1 = \phi'_1$. For the SCK potential, we use the parameters ϵ = 1.293 meV, σ_{CC} = 3.4 Å, σ_{CD} = 3.5 Å, σ_{DD} = 3.6 Å, $q_D = -0.35e$. For the LLM potential, we use the parameters ϵ = 2.964 meV, σ = 3.407 Å, $q_D = -0.54e$. The lattice constant is 14.041 Å.

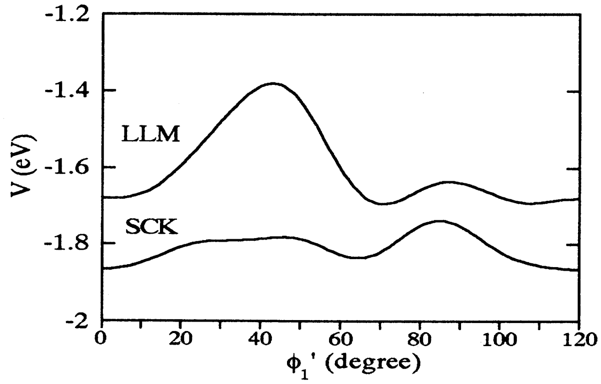

FIG. 2. Potential energy per C_{60} molecule as a function of ϕ_1' with $\phi_1 = 0$.

no microscopic model potentials have been proposed to describe M-C_{60} interactions, where M=K,Rb, or Cs. On the other hand, a phenomenological model potential derived from symmetry considerations only has been proposed by Walker[32] for the M-C_{60} interaction, where M can be any spherical ion. This anisotropic potential for the M-C_{60} interaction is given by

$$V(\mathbf{\Omega}) = aY_0(\mathbf{\Omega}), \tag{6}$$

where $\mathbf{\Omega}$ are Euler angles describing the orientation of C_{60}, a is a parameter which is a function of the center-to-center M-C_{60} distance, and Y_0 is an invariant of the icosahedral double group. The explicit form of Y_0 is given in Ref. 32. The minimum of Eq. (6) corresponds to the M ion located on a threefold symmetry axis of C_{60}, provided $a > 0$.

In M_3C_{60}, the nearest neighbors of a C_{60} are the eight M ions at tetrahedral sites along the cubic [111] directions. The C_{60} has its twofold axes aligned with the cubic edges, so that the locations of the eight nearest-neighbor ions correspond to minima of Eq. (6). Since the eight M ions have the same distance from the center of the C_{60}, the application of Eq. (6) to M_3C_{60} is especially simple: with the assumption that the interactions of a C_{60} with other molecules and ions are dominated by the interactions with the eight nearest-neighbor ions, we have a one-parameter model potential for these compounds, and the parameter can be determined by the measured libron frequency. Using (6) and considering nearest-neighbor M-C_{60} interactions only, we have calculated the libron frequency for M_3C_{60} to be $1.721\sqrt{a/I}$. For K_3C_{60}, the measured libron frequency[5] of 4 meV allows us to determine the parameter a for K_3C_{60} to be $a/I = 5.4\ \mathrm{meV}^2/\hbar^2$. For the other doped solid C_{60} compounds, the application of Eq. (6) is not as simple, because there are more than one M-C_{60} distance for M ions in the immediate neighborhood of a C_{60} molecule.

In conclusion, we have carried out a theoretical study of librons in solid C_{60} and doped solid C_{60}. General results fully consistent with the space-group symmetries of the solids have been derived. At the Brillouin-zone center, we find that in general, there should be five distinct libron frequencies in sc solid C_{60}, ten in $2a_0$-fcc solid C_{60}, one in M_3C_{60}, and one in M_6C_{60}. For M_3C_{60}, in the first approximation the model potential proposed by Walker[32] for the M-C_{60} interaction contains a single parameter. This parameter can be determined by comparing the measured libron frequency with our calculated libron frequency.

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