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Jahn-Teller effect for the negatively charged C_{60} molecule: Analogy with the silicon vacancy

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The isolated neutral C_{60} molecule is characterized by a triply degenerate lowest unoccupied level of t_{1u} symmetry. In the alkali-metal-intercalated C_{60} crystals, this state is partially filled and is thus subject to a Jahn-Teller distortion. To examine the relation between this effect and the superconductivity of these crystals, we first study the stable atomic distortions as a function of the occupancy of the t_{1u} state, stressing the similarity between this problem and the single vacancy in silicon. We then show that the on-ball electron-lattice coupling is not strong enough for C_{60} to behave as a negative-U system. We finally relate the dimensionless electron-phonon coupling constant λ to the magnitude of the Jahn-Teller energies.

An intriguing property of the alkali-metal-intercalated fullerite compounds A_3C_{60} is that they are superconducting with a transition temperature which can exceed 30 K.[1,2] Recent calculations[3-6] have shown that the electronic properties of these materials are dominated by intraball interactions (i.e., within each C_{60} molecule), the interball coupling being more than 1 order of magnitude smaller. Further, alkali-metal intercalation is well described by electron donation to the C_{60} molecule. The first step in understanding the origin of the superconductivity is thus to study the electron-lattice coupling of the isolated negatively charged C_{60} molecule.[7] This coupling is strongly influenced by the fact that its ground state is orbitally degenerate, leading to the existence of a Jahn-Teller effect. The aim of the present work is to examine this Jahn-Teller coupling in some detail and evaluate its role in the superconductivity of the A_3C_{60} compounds. We first determine the possible stable atomic distortions. We then determine the Jahn-Teller energies for C_{60} and calculate the contribution of the Jahn-Teller terms to the dimensionless electron-phonon coupling constant λ. We also show that the Jahn-Teller problem can be cast in the same form as for the single vacancy in silicon. For the relevant case of a half-filled triply degenerate state, we obtain results which differ qualitatively from the current interpretation of the negative vacancy,[8] confirming the recent analysis of Anderson, Ham, and Grossmann.[9]

The electronic structure of negatively charged C_{60} is characterized by the fact that the upper partially filled level is triply degenerate and of t_{1u} symmetry.[3-6] In the A_3C_{60} compounds, this level gives rise to a weakly dispersing band due to the small interball interactions. This band is partially filled with three electrons per C_{60} ball, so that the relevant problem to study is the isolated C_{60} molecule with three electrons in the t_{1u} state. For such a partially filled orbitally degenerate state, there will be a linear coupling to the on-ball distortion modes. These latter can be classified by symmetry. The only modes which couple within the t_{1u} manifold are those contained in the symmetric product $(t_{1u}\times t_{1u})_s$, namely, A_g (nondegenerate fully symmetric modes) and H_g (fivefold-degenerate distortion modes). It turns out that the A_g contribution will be small.

In the following, we shall be concerned mainly with the H_g modes whose amplitude we label $Q_{p,a}$. Here, p is the mode index (there are eight such modes for C_{60}) and $\alpha=\theta,\epsilon,\xi,\eta,\zeta$ is the degeneracy index. In the limit of linear electron-lattice coupling one can treat each fivefold-degenerate set of modes (i.e., each p value) independently. For one such mode, symmetry considerations lead to the following Jahn-Teller coupling 3×3 matrix:

$$V_p=\frac{I_{E_p}}{2}\begin{pmatrix}-Q_{p\theta}+\sqrt{3}Q_{p\epsilon} & 0 & 0\\ 0 & -Q_{p\theta}-\sqrt{3}Q_{p\epsilon} & 0\\ 0 & 0 & 2Q_{p\theta}\end{pmatrix}+I_{T_p}\begin{pmatrix}0 & Q_{p\zeta} & Q_{p\eta}\\ Q_{p\zeta} & 0 & Q_{p\xi}\\ Q_{p\eta} & Q_{p\xi} & 0\end{pmatrix}. \quad (1)$$

We have deliberately chosen the notation to be the same as for the single vacancy in Si,[10] which, in T_d symmetry, corresponds to a T_2 electronic state coupled to modes of E and T symmetry. This can be directly applied to C_{60} by considering that the E and T modes become degenerate, leading to a fivefold-degenerate H_g mode, and imposing one relation between the two electron-lattice parameters, namely, $I_T=\frac{1}{2}\sqrt{3}I_E\equiv I$. This is analogous to the case of p-like electronic states coupling to d-like distortions.

The existence of this Jahn-Teller coupling leads to energy surfaces which can be calculated by adding to the linear terms (1) an elastic term of the form

$$L_p=\tfrac{1}{2}K_{pE}(Q_{p\theta}^2+Q_{p\epsilon}^2)+\tfrac{1}{2}K_{pT}(Q_\xi^2+Q_\eta^2+Q_\zeta^2), \quad (2)$$

with $K_{pE}=K_{pT}\equiv K$ for C_{60}.

To determine the stable distortions one must minimize

the total energy resulting from (1) and (2). This energy takes the form

$$E_{\rm tot}=\sum_{i=1}^{3} n_i\lambda_i(Q_{p\alpha})+L_p(Q_{p\alpha})\,. \tag{3}$$

The λ_i are the eigenvalues of (1) and the n_i are the occupation numbers. The solution to this problem is well known for $n_e=\sum_i n_i$ equal to 1 or 2, i.e., when only the lowest state is filled.[11] Here we want to consider also the case $n_e=3$ which is relevant for A_3C_{60}. For this we have generalized an approach to this problem given by Opik and Pryce[11] for the case $n_e=1$.

We follow exactly the same lines (details can be found in Ref. 10) and summarize here only the main steps in the derivation. We first write the ith normalized eigenfunction of the matrix (1) in the form

$$\psi_i=\sum_m a_{im}\psi_m^0\,, \tag{4}$$

where the ψ_m^0 are the basis states. The eigenvalues λ_i are solutions of

$$\lambda_i a_{im}=\sum_{m'} V_{mm'}a_{im'}\,, \tag{5}$$

the $V_{mm'}$ being the elements of matrix (1). This allows one to express λ_i as

$$\lambda_i=\sum_{m,m'} a_{im}V_{mm'}a_{im'}\,. \tag{6}$$

We insert this last expression into $E_{\rm tot}$ given by Eq. (3) and minimize $E_{\rm tot}$ with respect to the distortion coordinates $Q_{p\alpha}$. Noticing that each λ_i is already an extremum with respect to any variation of the a_{im}, we get the set of equations

$$\frac{\partial E_{\rm tot}}{\partial Q_{p\alpha}}=0=\sum_i n_i\left(\sum_{m,m'} a_{im}\frac{\partial V_{mm'}}{\partial Q_{p\alpha}}a_{im'}\right)+K_{p\alpha}Q_{p\alpha}\,. \tag{7}$$

The $V_{mm'}$ are linear in the lattice coordinates so that their derivatives are numbers. Equation (7) can then be used to express the $Q_{p\alpha}$ in terms of the a_{im}. If we now insert these values of the $Q_{p\alpha}$ into the $V_{mm'}$ of Eq. (5), we get an equation involving only λ_i and the a_{im}. After some manipulations (essentially generalizing those detailed in Ref. 10 for the case $n_e=1$) we get the following set of equations, valid for any level occupancy:

$$a_{jm}\left[\lambda+\frac{I_{E_p}^2}{2K_{E_p}}\sum_i n_i(3a_{im}^2-1)+\frac{2I_{T_p}^2}{K_{T_p}}\left(n_j-\sum_i n_i a_{im}^2\right)\right]=0\,. \tag{8}$$

These equations reduce to the standard Opik and Pryce result for $n_e=1$ or 2 where only the lowest λ_i is occupied. In the present situation, we have $n_i=2$, 1, and 0 for the lowest, intermediate, and upper states. We must analyze all possible solutions of Eq. (8), considering the possibility that either a_{jm} is zero or nonzero. The number of possibilities is larger than those investigated in Ref. 10. However, the result we obtain is surprisingly simple: We find that the only stable distortions are either pure tetragonal (i.e., having only the Q_θ, Q_ε modes being nonzero) or pure trigonal (having only the Q_ξ, Q_η, and Q_ζ modes being nonzero). Which of the two situations is the stable one depends upon the corresponding Jahn-Teller gains in energy. These can be written as $f(n_e)E_p$ for tetragonal distortions and $f(n_e)T_p$ for trigonal modes. The function $f(n_e)$ takes the values 1, 4, and 3 for $n_e=1$ or 5, 2 or 4, and 3, respectively.[12] The units of Jahn-Teller energy are

$$E_p=\frac{I_{E_p}^2}{2K_{E_p}},\quad T_p=\frac{4}{3}\frac{I_{T_p}^2}{2K_{T_p}}\,. \tag{9}$$

Only pure distortions occur (tetragonal for $E_p>T_p$, trigonal for $E_p<T_p$) irrespective of the value taken by n_e. For the vacancy in silicon this result agrees with Watkins' observations of a pure tetragonal distortion for the positive state V^+ ($n_e=1$).[8,10] However, for the negative state V^- ($n_e=3$), it contradicts his simple explanation for the observed mixed (tetragonal + trigonal) distortion since this analysis predicts only pure modes of distortion. Our results confirm the recent conclusions of Anderson, Ham, and Grossmann[9] that more complex effects like multiplet splitting must be included to explain the observed mixed distortion.

Coming back to the C_{60} problem, the fact that $I_T=I_E\sqrt{3}/2$ and $K_{E_p}=K_{T_p}\equiv K$ implies that $E_p=T_p$, i.e., that there is an extra degeneracy involving the five distortion coordinates. The origin and consequences of such a degeneracy can be found in the work of O'Brien.[13]

Now that we have the value of the Jahn-Teller energy, which is $f(n_e)E_p$ for the C_{60} molecule, we can answer the question whether it behaves as a positive- or negative-U system. The effective electron-electron interaction U is defined, in terms of total energies $E_{\rm tot}$, as

$$U(n_e)=E_{\rm tot}(n_e+1)+E_{\rm tot}(n_e-1)-2E_{\rm tot}(n_e)\,. \tag{10}$$

This can be decomposed as an electronic contribution $U_{\rm el}$ plus a distortion contribution U_d. The latter is simply given in terms of the $f(n_e)$ and, for $n_e=3$, turns out to be

$$\begin{aligned}U_d&=-[f(4)+f(2)-2f(3)]\sum_p E_p\\&=-2\sum_p E_p\,.\end{aligned} \tag{11}$$

We have calculated this contribution in a tight-binding description for the electronic states and their coupling to the lattice and a Keating model for the vibrational eigenmodes.[14] The results, confirmed by a local-density-approximation (LDA) calculation for some modes, give for U_d a value of -0.05 eV. This is much lower than U_e, which, for the ball, should be of order 0.5 eV. We thus do not expect a negative-U behavior for the isolated C_{60} to arise from the Jahn-Teller effect. There is also a contribution of the A_g symmetric modes to U_d which we found to be too small (-0.02 eV) to modify this conclusion.

Let us finally work out the relation between the Jahn-Teller stabilization energy and the dimensionless electron-phonon coupling constant λ occurring in the theory of superconductivity. We use a standard expression for λ,[15]

$$\lambda=\frac{2}{N(0)}\sum_{p,q}\frac{1}{2K_{p,q}}\sum_{k,k'}|V_{kk'}(p,q)|^2\delta(\epsilon_k)\delta(\epsilon_{k'})\,, \tag{12}$$

where $K_{p,q}$ is the force constant for the pth phonon mode of wave vector q, $V_{kk'}$ is the corresponding electron-phonon matrix element between electronic states of wave vectors k and k'. The δ functions ensure that the sums are restricted to the Fermi surface. $N(0)$ is the total density of states per spin and the sums do not include spin. The electronic states at the Fermi level are essentially built from the three t_{1u} states of the ball and we can write them in the Bloch form

$$\psi(\mathbf{k})=\frac{1}{\sqrt{N}}\sum_{\nu=1}^{3}c_\nu(\mathbf{k})\sum_R e^{ikR}\phi_{\nu,R}\,, \tag{13}$$

where we consider a fcc lattice with one C_{60} ball per unit cell, R defines the cell position, ν runs over the three states per ball, and N is the number of C_{60} balls in the crystal. If we neglect the interball electron-lattice coupling, it is easy to show that $V_{kk'}$ reduces to

$$V_{kk'}=\sum_{\nu,\nu'}C_\nu^*(k)C_{\nu'}(k')\left[\frac{1}{N}\sum_R e^{i(k'-k)R}V_{R,R}^{\nu\nu'}(p,q)\right], \tag{14}$$

where $V_{RR}^{\nu\nu'}$ is the intraball coupling matrix. For the one-phonon mode with wave vector q this term takes the form $(1/\sqrt{N})e^{iqR}V_{00}^{\nu\nu'}$ and when inserted in (14), leads to the condition $k'=k-q$. We thus get

$$V_{k,k-q}=\frac{1}{\sqrt{N}}\sum_{\nu,\nu'}V_{00}^{\nu\nu'}(p)C_\nu^*(k)C_{\nu'}(k-q)\,. \tag{15}$$

We now proceed to calculate λ by inserting this form of $V_{k,k-q}$ into (12) and also considering that the dispersion in the phonon modes can be neglected, i.e., that $K_{p,q}$ is independent of q. We then obtain

$$\lambda=\frac{2}{N(0)}\sum_p\frac{1}{2K_p}\sum_{\substack{k,k-q\\ \nu,\nu'\\ \nu_\lambda,\nu'_\lambda}}\frac{V_{00}^{\nu\nu'}(p)V_{00}^{\nu_\lambda\nu'_\lambda}(p)^*}{N}C_\nu^*(k)C_{\nu_\lambda}(k)C_{\nu'_\lambda}^*(k-q)C_{\nu'}(k-q)\delta(\epsilon_k)\delta(\epsilon_{k-q})\,. \tag{16}$$

Using the fact that $(1/N)\sum_k C_\nu^*(k)C_{\nu'}(k)\delta(\epsilon_k)$ is the partial density of states $n_{\nu\nu'}(0)$ per C_{60} at the Fermi level, this can be rewritten

$$\lambda=\frac{2}{n(0)}\sum_p\frac{1}{2K_p}\sum_{\substack{\nu,\nu'\\ \nu_\lambda,\nu'_\lambda}}V_{00}^{\nu\nu'}(p)V_{00}^{\nu_\lambda\nu'_\lambda}(p)^*n_{\nu\nu_\lambda}(0)n_{\nu'_\lambda\nu'}(0)\,, \tag{17}$$

where $n(0)$ is now the density of states per spin and per C_{60}. For the fcc crystals the local symmetry is such that $n_{\nu\nu'}(0)=\frac{1}{3}n(0)\delta_{\nu\nu'}$, i.e., λ takes the form

$$\lambda=2n(0)\sum_{p,\alpha}\frac{\mathrm{Tr}V_{p\alpha}^2}{18K_p}\,, \tag{18}$$

$V_{p\alpha}$ being the matrix obtained by taking the derivative of (1) with respect to the mode amplitude $Q_{p\alpha}$. From the detailed form of (1), one can express (18) as

$$\lambda=2n(0)\left[\frac{5}{6}\sum_p E_p\right], \tag{19}$$

which directly relates the distortion mode contribution to λ and their total Jahn-Teller energy $3\sum_p E_p$ in the $n_e=3$ situation. Detailed calculations, described in Ref. 14, give a total contribution $\lambda\sim0.6$ with a reasonable density of states of $n(0)\simeq15$ eV^{-1}, which is the correct order of magnitude for explaining the observed values of T_c.

In conclusion, we have studied the Jahn-Teller distortions of the C_{60} molecule as a function of the occupancy of its last filled electronic state. We have derived a general expression, also valid for the vacancy in silicon, showing that only pure distortions are involved. Our calculation leads us to conclude that C_{60} is not a negative-U system. Finally, we have established a sum rule relating the part of λ arising from the distortion modes to the total Jahn-Teller energy.

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[1]K. Tanigaki *et al.*, Nature (London) 352, 222 (1991).

[2]M. J. Rosseinsky *et al.*, Phys. Rev. Lett. **66**, 2830 (1991).

[3]R. C. Haddon, L. E. Brus, and K. Raghavachari, Chem. Phys. Lett. **125**, 459 (1986).

[4]J. H. Weaver, J. L. Martins, T. Komeda, Y. Chen, T. R. Ohno, G. H. Kroll, and N. Troullier, Phys. Rev. Lett. **66**, 1741 (1991).

[5]Q. Zhang, J. Y. Yi, and J. Bernholc, Phys. Rev. Lett. **66**, 2633 (1991).

[6]S. Saito and A. Oshiyama, Phys. Rev. Lett. 66, 2637 (1991).

[7]An independent study of this kind has also been undertaken by C. M. Varma, J. Zaanen, and K. Raghavachari, Science (to be published).

[8]For a review, see G. D. Watkins, in *Deep Centers in Semiconductors,* edited by S. T. Pantelides (Gordon and Breach, New York, 1986), p. 147.

[9]F. G. Anderson, F. S. Ham, and G. Grossman (unpublished).

[10]For details, see J. Bourgoin and M. Lannoo, in *Point Defects in Semiconductors, II. Experimental Aspects,* Springer Series in Solid-State Sciences Vol. 35 (Springer-Verlag, Berlin, 1983).

[11]U. Opik and M. H. Pryce, Proc. R. Soc. London, Ser. A **238**, 425 (1957).

[12]The values of 1 and 4 are easy to understand: putting two electrons in a state drives a distortion which is twice as large as that driven by one electron and which therefore gives an energy 4 times as large. The value of 3 can be obtained only by carrying out the full analysis of Eq. (8). It arises because the third electron not only changes the magnitude of the distortion but also changes its *form,* a point which has been missed in previous studies of this problem.

[13]M. C. O'Brien, J. Phys. C **4**, 2524 (1971).

[14]M. Schlüter, M. Lannoo, M. Needels, G. A. Baraff, and D. Tomanek (unpublished).

[15]P. B. Allen, Phys. Rev. B **6**, 2577 (1972).