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LETTER TO THE EDITOR

Lattice dynamics of A_3C_{60} fullerides, where the A are alkali-metal elements

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Abstract. We study the external vibrations of the A_3C_{60} fullerides with $F_{m\bar{3}m}$ structure, where the A are alkali-metal elements. It is argued that strong screening occurs in these crystals and the force constants extending to a few shells of neighbours are needed in numerical simulations. By means of the force-constant matrix approach, we have simulated the dispersion curves along three principal symmetry directions.

The recent discoveries of a new method of preparing C_{60} in macroscopic quantity [1] and superconductivity in alkali-metal-doped C_{60} [2, 3] have generated considerable interest in the physical properties of fullerenes and fullerides. It is shown (see [4] and references therein) that, when doped with alkali metals, the FCC C_{60} phase first becomes an ionic compound A_3C_{60} with the same lattice structure, where A is an alkali-metal element (e.g. K, Rb or Cs). Upon further doping, the crystal expands and transforms to an intermediate A_4C_{60} phase with BCT structure and finally to a BCC A_6C_{60} phase. Among these fullerides, only A_3C_{60} is metallic, and this is believed to be the structure of the superconducting phase.

For the superconductivity of the A_3C_{60} fullerides, two different mechanisms have been proposed. The first one [5] suggests that the superconductivity is due to singlet pairing mediated by the electron–electron interactions on the C_{60} balls, while the second one [6–8] suggests that the electron–phonon couplings are responsible for the superconducting ground state. Thus, detailed investigations of the electronic and phonon properties of the A_3C_{60} fullerides would be helpful in judging the superiority of one mechanism to another competing one. For this reason, we study in this article the phonon properties of the A_3C_{60} fullerides.

The crystallographic space group of the A_3C_{60} fullerides is $F_{m\bar{3}m}$ [9]. The A_3C_{60} structure is shown in figure 1, where, for explicitness only the cations A^+ in the primitive cell are illustrated. The anions C_{60}^{3-} are centred at FCC Bravais lattice sites and adopt with equal probability either of two inequivalent orientations, corresponding to two possible ways of lining up the three orthogonal twofold axes of each C_{60} ball with cubic lattice axes, while the cations A^+ are located at octahedral and tetrahedral interstitial sites. Since each cell in the A_3C_{60} structure contains one anion C_{60}^{3-} and three cations A^+ , the computational

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difficulty in setting up the 189×189 dynamical matrix would be excessive. Therefore, it is desirable to look for an approximation that simplifies the setting up of the dynamical matrix. It is known that in a molecular crystal the high-frequency modes are nearly equivalent to the internal modes of the constituent molecules. For the A_3C_{60} fullerenes, one can employ the above approximation and calculate their high-frequency modes by following the procedure for an isolated molecule. As a matter of fact, the electrons transferred to each C_{60} ball upon doping by alkali metals do not change its vibrational spectrum drastically; one can thus use the results obtained for the C_{60} molecule [10–12] to characterize approximately the high-frequency modes of the A_3C_{60} structure. In what follows, we focus only on the external vibrations of the A_3C_{60} fullerenes and assume that each C_{60} ball vibrates as a *rigid* unit which has three translational and three rotational (librational) degrees of freedom. Since each primitive cell has also three interstitial cations A^+ , there are totally twelve translational and three rotational degrees of freedom per cell.

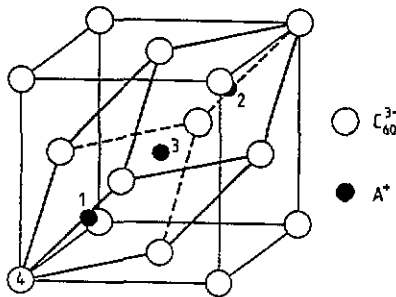


Figure 1. Structure of A_3C_{60} fullerenes, where only the octahedral and tetrahedral interstitial cations A^+ in the primitive cell are illustrated.

Usually, two approaches are employed to derive the dynamical matrix. In the first approach, phenomenological models are proposed for the interatomic interactions. This approach was recently used to study the lattice dynamics of solid C_{60} [13, 14]. For ionic crystals, the rigid-ion and the shell models are commonly used [15]. The latter reproduces the dispersion curves well but requires more parameters in the model. However, though A_3C_{60} fullerenes are ionic crystals, they are in fact *metallic* and the dimension of each C_{60} ball is *comparable* to the lattice constant. These features imply that *strong screening* exists in the A_3C_{60} fullerenes, as produced by the conduction electrons and the electrons on the C_{60} balls. Furthermore, there are disorders regarding the orientations of the C_{60} balls. Extreme difficulty then arises from incorporating both the electron screening and the orientational disorders into the phenomenological model. Thus, we resort to the second approach often used for metals [16]. In this approach, the general forms of the force-constant matrices are derived by means of the symmetry relation associated with the space group of the crystal. Since there is strong electron screening in the A_3C_{60} fullerenes, the interactions between the *screened* ions are of *short-range* nature. Therefore, in the derivation of the dynamical matrix, we take account of the force constants extending to only few shells of neighbours of each ion in the primitive cell.

From group theory it follows that the force-constant matrix between two atoms satisfies the following symmetry relation [15]:

$$\Phi \begin{pmatrix} g_l & g_{l'} \\ g_\kappa & g_{\kappa'} \end{pmatrix} = \mathbf{R} \Phi \begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix} \mathbf{R}^T. \quad (1)$$

Here (l, κ) denotes atom κ within the l th cell and g is a symmetry operation given by

$$g = \{\mathbf{R}|v(\mathbf{R}) + t(n)\} \quad (2)$$

where \mathbf{R} is the 3×3 orthogonal matrix representation of a proper or improper rotation of the point group of the space group, $v(\mathbf{R})$ is a vector associated with \mathbf{R} which is smaller than any primitive translational vector, and $t(n) = \sum n_i a_i$ with n_i integers. When molecules are regarded as rigid units, the force-constant matrix between two molecules becomes a 6×6 matrix with elements of four types, describing the translation-translation, translation-libration, libration-translation, and libration-libration couplings between these two molecules, and the matrix \mathbf{R} in (1) is replaced by [16]

$$\mathbf{P} = \begin{pmatrix} \mathbf{R} & 0 \\ 0 & \mathbf{R} \det(\mathbf{R}) \end{pmatrix} \quad (3)$$

where \det denotes the determinant of a matrix.

As stated above, to reproduce the dispersion curves of the metallic A_3C_{60} fullerenes well requires the force constants out to certain (but only a few) shells of neighbours. However, to our knowledge, no experimentally observed dissipation curves of the A_3C_{60} fullerenes have been reported till now. Thus, as an example, we consider the force constants as follows. We take account of the adjoining ions of ions 1, 2, and 3 up to the second neighbours, while those of ion 4 are extended to the third neighbours. According to the space group $F_{m\bar{3}m}$ of the A_3C_{60} fullerenes and in terms of the symmetry relation (1), one can derive the force-constant matrices between ion 1 at $\frac{1}{4}(111)$ and its neighbouring ions 2 at $\frac{1}{4}(311)$ and 3 at $\frac{1}{2}(111)$. The explicit expressions for the force-constant matrices are given, respectively, by

$$\Phi(12) = - \begin{pmatrix} \alpha_1 & 0 & 0 \\ 0 & \beta_1 & \delta_1 \\ 0 & \delta_1 & \gamma_1 \end{pmatrix} \quad \Phi(13) = - \begin{pmatrix} \alpha_2 & \beta_2 & \beta_2 \\ \beta_2 & \alpha_2 & \beta_2 \\ \beta_2 & \beta_2 & \alpha_2 \end{pmatrix}. \quad (4)$$

For ion 1 at $\frac{1}{4}(111)$, there is only translational motion $\mathbf{U}^t(1)$, while ion 4 at (000) has both translation and librational motions $\mathbf{U}^t(4)$ and $\mathbf{U}^l(4)$. In order to derive the force-constant matrix for these two ions, we introduce *pseudo*-librational variable $\mathbf{U}^l(1)$ for ion 1 and obtain

$$\Phi(14) = \begin{pmatrix} \Phi^{tt}(14) & \Phi^{tl}(14) \\ \Phi^{lt}(14) & \Phi^{ll}(14) \end{pmatrix}. \quad (5)$$

In fact, no librational motion exists for ion 1; thus $\Phi^{tl}(14)\mathbf{U}^l(4) + \Phi^{ll}(14)\mathbf{U}^l(4) = 0$. This constraint requires that $\Phi^{tl}(14) = \Phi^{ll}(14) = 0$, since $\mathbf{U}^t(4)$ and $\mathbf{U}^l(4)$ are arbitrary variables that are independent of one another. In addition, the symmetry of the force-constant matrix further yields that $\Phi^{lt}(14) = [\Phi^{tl}(14)]^T = 0$. Thus, when the *pseudo*-librational variable $\mathbf{U}^l(1)$ is ruled out, $\Phi(14)$ is reduced to

$$\Phi(14) = (\Phi^{tt}(14) \ 0) \quad \Phi^{tt}(14) = - \begin{pmatrix} \alpha_3 & \beta_3 & \beta_3 \\ \beta_3 & \alpha_3 & \beta_3 \\ \beta_3 & \beta_3 & \alpha_3 \end{pmatrix}. \quad (6)$$

For the neighbouring ions of ion 2 at $\frac{1}{4}(333)$, the corresponding force-constant matrices have the similar forms. Analogously, the force-constant matrix for ions 3 at $\frac{1}{2}(111)$ and 4 at $\frac{1}{2}(211)$ is

$$\Phi(34) = (\Phi''(34) \ 0) \quad \Phi''(34) = - \begin{pmatrix} \alpha_4 & 0 & 0 \\ 0 & \beta_4 & 0 \\ 0 & 0 & \beta_4 \end{pmatrix} \quad (7)$$

and that between ions 4 at $\frac{1}{2}(211)$ and $\frac{1}{2}(321)$ is given by

$$\Phi(44) = - \begin{pmatrix} \alpha & \gamma & 0 & 0 & 0 & p \\ \gamma & \alpha & 0 & 0 & 0 & p \\ 0 & 0 & \beta & q & q & 0 \\ 0 & 0 & q & a & c & 0 \\ 0 & 0 & q & c & a & 0 \\ p & p & 0 & 0 & 0 & b \end{pmatrix}. \quad (8)$$

As for the force-constant matrices associated with the bonds connecting other neighbouring ions of a given ion in the primitive cell, they can also be derived in terms of the symmetry relation. Finally, following the procedure described in standard solid state physics texts, one can obtain the equation of motion

$$\omega^2 \mathbf{U} = \mathbf{D}(\mathbf{q}) \mathbf{U}. \quad (9)$$

Here, the dynamical matrix is

$$\mathbf{D}(\mathbf{q}) = (\mathbf{m}^{\text{cryst}})^{-1/2} \mathbf{D}_0(\mathbf{q}) (\mathbf{m}^{\text{cryst}})^{-1/2} \quad (10)$$

where

$$\mathbf{m}^{\text{cryst}} = \begin{pmatrix} \mathbf{m}(1) & & & \\ & \mathbf{m}(2) & & \\ & & \mathbf{m}(3) & \\ & & & \mathbf{m}(4) \end{pmatrix} \quad (11)$$

with

$$\mathbf{m}(1) = \mathbf{m}(2) = \mathbf{m}(3) = m_A \mathbf{I} \quad \mathbf{m}(4) = \begin{pmatrix} M \mathbf{I} & 0 \\ 0 & I_0 \end{pmatrix} \quad (12)$$

in which \mathbf{I} is a 3×3 unit matrix, m_A is the mass of an alkali-metal element, and M and I_0 are the mass and the moment of inertia of the C_{60} molecule.

In figure 2 the dispersion curves along three principal symmetry directions are simulated for an A_3C_{60} fulleride with $F_{m\bar{3}m}$ structure, where the parameters are chosen to be $(\alpha_1, \beta_1, \gamma_1, \delta_1)/m_A = (1, 0.2, 0.15, 0.1)$, $(\alpha_2, \beta_2)/m_A = (1.2, 1.1)$, $(\alpha_3, \beta_3)/\sqrt{m_A M} = (0.6, 0.5)$, $(\alpha_4, \beta_4)/\sqrt{m_A M} = (0.4, 0.05)$, $(\alpha, \beta, \gamma)/M = (0.15, 0.02, 0.11)$, $(a, b, c)/I_0 = (0.09, 0.01, 0.06)$, and $(p, q)/\sqrt{M I_0} = (0.03, 0.01)$ (in units of α_1/m_A). Because no experimentally observed dispersion curves are available for the A_3C_{60} fullerides, the choice of the parameters seems to be more or less artificial. However, the simulation is still meaningful, since the intrinsic character of the dispersion curves for the A_3C_{60} structure is irrelevant to the values of the parameters. From figure 2 one can see that at the Γ point the

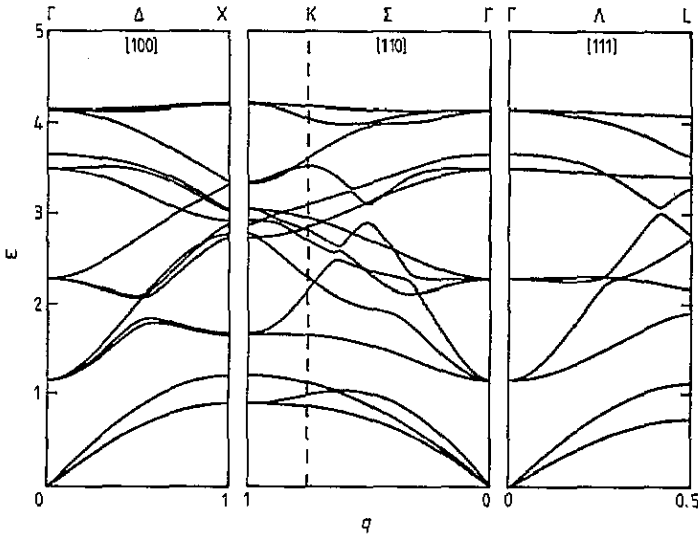


Figure 2. Simulated dispersion curves for an A_3C_{60} fulleride with $F_{m\bar{3}m}$ structure, where ω is in units of $(\alpha_1/m_A)^{1/2}$.

phonon spectrum is highly degenerate, while the degeneracy is completely removed at the K point and the spectrum is less degenerate at the L and X points. For the directions Δ , Σ and Λ the situation is similar. It can be seen that the spectrum is less degenerate along the Σ direction than that along Δ and Λ directions. Moreover, one can also see that at the top of the dispersion curves, there is a curve that is rather flat. We found that this flat feature remains when the parameters vary. This observation indicates that the mode associated with this dispersion curve can be sufficiently well approximated as an Einstein oscillator.

In summary, the force-constant matrix approach was used to study the external vibrations of the A_3C_{60} fullerenes. It was argued that in these crystals there is strong screening produced by the conduction electrons and the electrons on the C_{60} balls. Thus, only the force constants extending to few shells of neighbours are needed to simulate the dispersion curves. Since the force-constant matrix approach is based on the group-theory formalism, it reveals the intrinsic features of the A_3C_{60} fullerenes with $F_{m\bar{3}m}$ structure and can be used to test the proposed phenomenological models.

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