TWO-BAND ELECTRON–PHONON INTERACTION IN FULLERENE IN THE BOND–CHARGE MODEL

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Abstract. A simplified bond–charge model calculation of the electron–phonon (W_{ep}) and exchange (W_{xc}) coupling constants entering the two-band model for superconductivity in doped C_{60} is presented. The dynamics for the isolated molecule is restricted to the bond stretching modes, and the electronic states near the HOMO–LUMO gap are represented within a four-parameter tight-binding scheme. We have obtained $W_{ep} = 1.2$ meV and $W_{xc} = 39$ meV, which is in reasonable agreement with previous estimations by Kristoffel and Örd (Phys. stat. sol. (b), 1993, **175**, 1, K9–K12; Fullerene Science and Technology, 1994, **2**, 3, 201–212).

Key words: fullerites, superconductivity, electron–phonon interaction, exchange coupling, isotope effect.

1. INTRODUCTION

Recently the class of organic superconductors has been enriched by the discovery of superconductivity in alkali-doped fullerites A_3C_{60} (with A = K or Rb) with a fairly high critical temperature (e.g., $T_c = 33$ K in Rb_3C_{60} [1, 2]). Despite the great effort made to elucidate this new phenomenology, the pairing mechanism for fullerene compounds remains elusive, more or less like the one for cuprate perovskites. Electron–phonon interaction is commonly held responsible for superconductivity in alkali-doped fullerites within the conventional BCS scheme [3, 4], but several objections have been raised to the values and properties of superconducting parameters in favour of alternate or cooperative mechanisms [5–7]. Various arguments, however, indicate that the vibronic coupling, being enhanced by a small mass of carbon atoms, and electron correlations should play a key role in the superconductivity in fullerites.

In previous works Kristoffel and Örd [8, 9] have shown that the two-band model provides a suitable theoretical framework to understand the mechanism of high-T_c superconductivity in the systems with a semiconducting gap, notably in alkali-doped fullerenes. A theoretical analysis shows that, besides the two-band electronic exchange term W_{xc}, a crucial contribution to the coupling mechanism (isotope effect) originates from the two-band electron–phonon interaction W_{ep}.

Although W_{ep} is considerably smaller than W_{xc}, the two mechanisms are shown to cooperate in determining a comparatively high critical temperature [8, 9]. Thus, a thorough knowledge of high-frequency intra-molecular phonon states seems necessary to perform a quantitative calculation of such superconducting properties as the isotope shift and the critical temperature. A very good description of phonon dynamics for both C_{60} and C_{70} has recently been obtained by means of a transferable bond-charge model (BCM) [10, 11]. This model allows for the electronic degrees of freedom associated with the dynamical bond polarizability and the ion–ion interaction mediated by the interposed bond charge. The latter is shown to provide a quantitative value for the electron–phonon interaction W_{ep} required in the two-band theory of superconductivity.

In this paper we present a simplified BCM calculation of electron–phonon and exchange coupling constants, where the dynamics of an isolated C_{60} molecule is restricted to bond stretching modes. Moreover, the electronic states near the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are represented within a four-parameter tight-binding linear-combination-of-molecular-orbital (LCMO) scheme.

2. BOND-CHARGE-MODEL THEORY FOR COUPLING CONSTANTS

We describe the eigenstates of π electrons for an isolated molecule in the LCMO scheme and write the wavefunctions as

$$\psi_\Gamma = \sum_j c_{\Gamma j} \pi_j , \qquad (1)$$

where Γ labels the irreducible representations of the Y_h point group which the eigenstates belong to, as well as their components. The localized π-orbitals $\pi_j = \pi_j(r - r_j)$, are centred at the midpoints of the covalent bonds r_j.

The matrix element of the electron–phonon interaction that we need in our calculation is written as

$$V_{\Gamma\Gamma'}^\gamma = < \psi_\Gamma \left| \frac{\partial H}{\partial A_\gamma} \right| \psi_{\Gamma'} > = \sum_{jj'} c_{\Gamma j}{}^* c_{\Gamma' j'} < \pi_j \left| \frac{\partial H}{\partial A_\gamma} \right| \pi_{j'} > , \qquad (2)$$

where the derivatives of the Hamiltonian H are made with respect to the phonon normal coordinates A_γ. The index γ labels the irreducible representations which classify the C_{60} phonons and their components. If the normal coordinates are written as linear combinations of the atomic displacements u_j $(j=1, 2,..., 60)$

$$A_\gamma = \sum_j e_{\gamma i} \cdot u_i , \tag{3}$$

the electron–phonon interaction can be expressed by a combination of local matrix elements:

$$V_{\Gamma\Gamma'}^\gamma = \sum_{jj'} c_{\Gamma j}{}^* c_{\Gamma'j'} e_{\gamma i} \cdot < \pi_j \left| \frac{\partial H}{\partial u_i} \right| \pi_{j'} > . \tag{4}$$

It is argued that only the π-orbitals j and j', which are neighbours to the ith atom, make a substantial contribution. Thus only a limited number of matrix elements ought to be calculated – a task that many authors have undertaken, using various theories and methods for the electronic structure [6, 7]. Then the coefficients $c_{\Gamma j}$ and $e_{\gamma i}$ can easily be obtained as the eigenvectors of the LCMO electronic structure and of the dynamical matrix, respectively, i.e. the two problems can be solved with semi-empirical models.

Here we consider the dynamical matrix in the framework of the BCM, which has proved very successful for C_{60} [10]. The BCM relies on a simple description of the electron–phonon interaction, providing the coupling between the ionic and electronic degrees of freedom. Actually we show that the electron–phonon matrix elements we need can be approximately expressed in terms of known BCM parameters.

The nonplanar threefold coordination occurring in fullerenes permits the projection of the displacement u_i of each atom i onto its three bonding directions defined by the unit vectors $b_{j(i)}$. Thus the 180 atomic displacement coordinates u_i can be replaced by a new set formed by the 90 bond stretching $s_j b_{j(i)}$ and by 90 longitudinal rigid-bond displacements parallel to the bonds $(\delta r_j) b_{j(i)}$. The choice of the $(s_j, \delta r_j)$ bond coordinates is advantageous because the contribution of each π_j state to the electron–phonon coupling is mostly made by the bond stretching s_j, whereas the rigid-bond displacement δr_j can be assumed to be ineffective. Thus we write:

$$V_{\Gamma\Gamma'}^\gamma = \sum_{jj'j''} c_{\Gamma j}{}^* c_{\Gamma'j'} a_{\gamma j''} < \pi_j \left| \frac{\partial H}{\partial s_{j''}} \right| \pi_{j'} > , \tag{5}$$

where $a_{\gamma j}$ are stretching eigenvectors. Then, in this representation we can keep only the diagonal matrix elements $(j = j')$ involving the same orbital π_j and only the contribution from the jth bond stretching. Due to the Hellman–Feynman theorem, the jth diagonal element $< \pi_j | \partial H / \partial s_j | \pi_j >$ gives the change of the short-range force constant between the two atoms

linked by the jth bond produced by the addition of one π electron. We express such a force change in a linear approximation as $(\partial \Phi'_j / \partial Y_j)c$, where Φ'_j is the first derivative of the short-range ion–ion potential and Y_j is the bond charge. This quantity is easily obtained from the transferable BCM potential recently introduced for fullerenes [11]. In this potential the bond charges Y_j have a known dependence on the interionic distance r_j:

$$Y_j = Y_0 \exp[-c(r_j - r_0)], \qquad (6)$$

where $c = 0.511 \, \overset{\circ}{A}{}^{-1}$ is the charge transfer parameter. The central values $Y_0 = -(8/3)e$ and $r_0 = 1.42 \, \overset{\circ}{A}$ refer to graphite. This enables us to write:

$$< \pi_j \left| \frac{\partial H}{\partial s_j} \right| \pi_j > \approx \frac{\partial \Phi'_j}{\partial Y_j} e = \frac{\partial \Phi'_j}{\partial r_j} e \Big/ \frac{\partial Y_j}{\partial r_j} = -\frac{\Phi''_j e}{c Y_j}, \qquad (7)$$

where the ion–ion short-range force constant Φ'_j is equal to 1453 N/m for short bonds and 1285 N/m for long bonds (see set 1 in [11]). We note that in evaluating the sum in Eq. (5) one may use, for simplicity and with little error, one single average value for Φ''_j, e.g., the central (graphite) value $\Phi''_0 = 1361$ N/m [11]. This gives a uniform value for the electron–phonon matrix elements

$$< \pi_j | \partial H / \partial s_j | \pi_j > \approx 1.0 \times 10^{-7} \text{N} \qquad (8)$$

for all bonds.

In this way the calculation of the electron–phonon matrix element is virtually solved, being reduced to that of the electronic (LCMO) and phonon (BCM) eigenvectors.

With regard to phonon eigenvectors we want to discuss, at this point, a further simplification which exploits a relatively weak coupling between the dynamics of the s_j and r_j coordinates. Indeed, the C_{60} normal modes exhibit either a dominant stretching or a rigid-bond character, depending on whether they fall in the high- or low-frequency regions of the spectrum, respectively. Such a separation leads to a straightforward, albeit approximate, handling of the problem. The dynamical matrix restricted to only the s_j-coordinates with nearest-neighbour (nn) interaction needs just four parameters and takes the same formal structure as the LCMO matrix when restricted to only one kind of nn $\pi - \pi$ hopping and π-state Coulomb integrals per bond.

In this case both LCMO and BCM matrices have two different diagonal elements, α_p and α_h, due to two distinct bond lengths of C_{60}, and two different nn coupling elements, β_{pp} and β_{ph}, associated with the long–long and long–short nn bond pairs. The best fit of the C_{60} electronic states around the HOMO–LUMO gap [7] and of the high-frequency modes [10] is obtained with the values

$$\alpha_p(\text{LCMO}) = 6.0 \, \text{eV}, \qquad \alpha_p(\text{BCM}) = 2.8 \times 10^4 \, \text{dyne cm}^{-1},$$

$$\alpha_h(\text{LCMO}) = 2.0 \text{ eV}, \quad \alpha_h(\text{BCM}) = 3.4 \times 10^4 \text{ dyne cm}^{-1},$$

$$\beta_{pp}(\text{LCMO}) = -7.4 \text{ eV}, \quad \beta_{pp}(\text{BCM}) = -0.9 \times 10^4 \text{ dyne cm}^{-1},$$

$$\beta_{ph}(\text{LCMO}) = 3.2 \text{ eV}, \quad \beta_{ph}(\text{BCM}) = 0.4 \times 10^4 \text{ dyne cm}^{-1}.$$

The resulting eigenvalues are displayed in the Figure together with the corresponding symmetries, and compared with the calculations by Troullier and Martins (for the C_{60} electronic structure) [12] and with the previous complete BCM calculation (for the phonon structure) [11]. The latter comparison is rather instructive. The stretching modes are distributed over three spectral regions around 1500, 1000, and 600 cm^{-1}, as expected from the complete calculation. The highest region, containing most of the stretching modes responsible for the electron–phonon interaction, nicely reflects the actual phonon density. On the other hand, the lower modes become of less and less stretching character and the correspondence between stretching and full spectra gets worse. As regards the electronic states, apart from a scale factor depending on the fitting of different gaps (we have used an experimental gap of 2.2 eV [13], which is somewhat larger than the one reported in [12], 1.75 eV), there is a good correspondence, except for a discrepancy for the $T_{2u} - G_u$ splitting, which in the present calculation is very large. Also, in this case such discrepancy is not crucial because only the eigenvalues and the eigenvectors for the levels around the gap are used in the calculation.

3. SUPERCONDUCTIVITY PROPERTIES

We can now evaluate the interband electron–phonon and exchange coupling coefficients, W_{ep} and W_{xc}, respectively, which enter a two-band model for high-T_c superconductivity in doped C_{60} [8, 9]. They are expressed as

$$W_{ep} = \frac{1}{M} \left(\frac{2\hbar\Phi_0''}{cY_0} \right)^2 \sum_{\gamma} \frac{1}{E_G^2 - (\hbar\omega_\gamma)^2} \left| \sum_j c_{\Gamma j}{}^* c_{\Gamma' j} a_{\gamma j} \right|^2, \tag{9}$$

$$W_{xc} = e^2 \sum_{jj'}' \frac{1}{|r_j - r_{j'}|} c_{\Gamma j}{}^* c_{\Gamma' j} c_{\Gamma' j'}{}^* c_{\Gamma j'}, \tag{10}$$

where M is the carbon mass and the LUMO–HOMO energy separation, $E_G = E_\Gamma - E_{\Gamma'} = 2.2$ eV, refers to the band centres [13]. Here Γ labels the HOMO and covers the three components of the irreducible representation T_{1u}, while Γ' labels the LUMO and covers the five components of the irreducible representation H_u. Due to the intrinsic isotropy of the isolated molecule, all of the 15 possible HOMO–LUMO state pairs contribute equally to the coupling constants so that the sums over the level multiplicity are implicit in Eqs. (9)–(10).

The calculation of Eqs.(8) and (9) yields the following results:

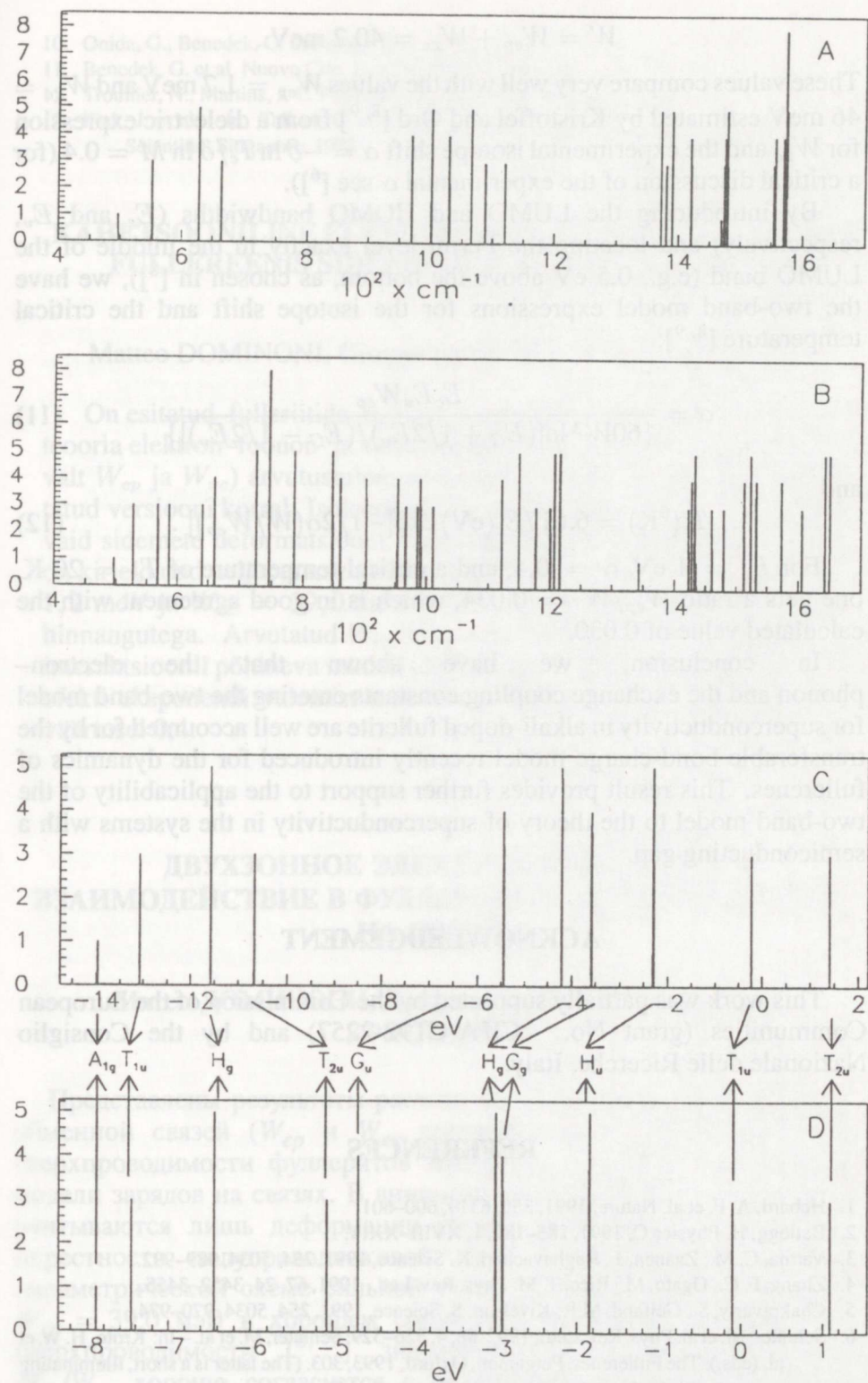$$W_{ep} = 1.2 \text{ meV}, \quad W_{xc} = 39.0 \text{ meV},$$

Fig. 1. The stretching vibrational frequencies (expressed in wavenumbers; A) and the electronic levels (C) of C_{60} calculated with a four-parameter stretching BCM and a four-parameter LCMO tight-binding model, respectively. The present approximated levels are compared with the vibrational levels calculated by Onida and Benedek (B; [10]) and the π electronic levels by Troullier and Martins (D; [12]), respectively. Note that there are 90 stretching vibrational modes (A) as compared to the 180 modes of the whole spectrum (B; here 37 modes below 496 cm^{-1} are not shown).

$$W = W_{ep} + W_{xc} = 40.2 \text{ meV} .$$

These values compare very well with the values $W_{ep} = 1.7$ meV and $W_{xc} = 46$ meV estimated by Kristoffel and Örd [8, 9] from a dielectric expression for W_{xc} and the experimental isotope shift $\alpha = -\partial \ln T_c / \partial \ln M = 0.4$ (for a critical discussion of the experimental α see [6]).

By introducing the LUMO and HOMO bandwidths (E_c and E_v, respectively) and locating the Fermi level exactly in the middle of the LUMO band (e.g., 0.5 eV above the bottom, as chosen in [8]), we have the two-band model expressions for the isotope shift and the critical temperature [8, 9]:

$$\alpha = \frac{E_c E_v W_{ep}}{\{60W^3 \ln[(E_G + 1/2E_v)/(E_G - 1/2E_v)]\}} \quad (11)$$

and

$$T_c(^0\text{K}) = 6.617 E_c(\text{eV}) \exp[-1/2\alpha(W/W_{ep})] . \quad (12)$$

For $E_c = 1$ eV, $\alpha = 0.4$, and a critical temperature of $T_c = 20$ K, one gets a ratio $W_{ep}/W = 0.034$, which is in good agreement with the calculated value of 0.030.

In conclusion, we have shown that the electron–phonon and the exchange coupling constants entering the two-band model for superconductivity in alkali-doped fullerite are well accounted for by the transferable bond-charge model recently introduced for the dynamics of fullerenes. This result provides further support to the applicability of the two-band model to the theory of superconductivity in the systems with a semiconducting gap.

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KAHETSOONILINE ELEKTRON–FOONON-INTERAKTSIOON FULLEREENIS SIDEMEL ASUVA LAENGU MUDELIS

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On esitatud fulleriitide A_3C_{60} (A = K; Rb) ülijuhtivuse kahetsoonilise teooria elektron–foonon- ja vahetusinteraktsiooni seosekonstantide (vastavalt W_{ep} ja W_{xc}) arvutustulemused sidemel asuva laengu mudeli lihtsustatud versiooni korral. Isoleeritud C_{60} molekuli dünaamikas on arvestatud vaid sidemete deformatsiooni, elektronseisundeid pooljuhtpilu naabruses on kirjeldatud neljaparameetrilises tugeva seose skeemis. Tulemus $W_{ep} = 1,2$ meV ja $W_{xc} = 39,0$ meV on kooskõlas ülijuhtivuse alase töö [8, 9] hinnangutega. Arvutatud W_{ep}/W_{xc} suhe on kooskõlas tsoonidevahelisel interaktsioonil põhineva mudeli ülijuhtivuse siirdetemperatuuri ja isotoopefekti eksponendi valemist määratud suhtega viimase eksperimentaalsel väärtusel 0,4.

ДВУХЗОННОЕ ЭЛЕКТРОН-ФОНОННОЕ ВЗАИМОДЕЙСТВИЕ В ФУЛЛЕРЕНЕ В МОДЕЛИ ЗАРЯДОВ НА СВЯЗЯХ

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Представлены результаты расчета констант электрон-фононной и обменной связей (W_{ep} и W_{xc} соответственно) двухзонной схемы сверхпроводимости фуллеритов A_3C_{60} (A = K, Rb) в упрощенной модели зарядов на связях. В динамике изолированной молекулы C_{60} учитываются лишь деформации связей, электронные состояния в окрестности полупроводниковой щели описываются в четырех-параметрической схеме сильной связи. Получено $W_{ep} = 1,2$ мэВ и $W_{xc} = 39,0$ мэВ в хорошем согласии с оцененными в работе по сверхпроводимости [8, 9] значениями. Вычисленное отношение W_{ep}/W_{xc} хорошо согласуется с найденным на основании формул схемы межзонной связи для температуры сверхпроводящего перехода и показателя изотопического эффекта при экспериментальном значении последнего 0,4.