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INTERACTION OF SELF-LOCALIZED EXCITATIONS WITH C_{60} WEAK DOPANTS IN CONDUCTING POLYMERS.

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Abstract

Weak dopants, like C_{60}, (which have LUMO level within the band gap of conducting polymer (CP)) may provide various types of interactions with self-localized (SL) excitations of CP chain: solitons (S^o, S), polaron/bipolarons (P/BP) or exciton-polarons (Ex), whose electronic levels are also located deeply inside the gap.

In the present paper we analyse some types of interactions: 1) "Chemical reaction" type charge transfer (CT) processes between charged (P/BP, S) and neutral (S^o, Ex) excitations with C_{60} molecules intercallated between chains of CP. We stress the important role of SL states of C_{60} molecule itself: string type polarons ($\bar{Pc}$) and bipolarons BP_C^{2-}) in the stabilisation of this reactions through reorientations of string P_C^- / BP_C^{2-} relatively to CP chains resulting in suppression of backward CT recombination.

2) The C_{60} mediated interchain hoping of electrons is considered within Holstein-Rashba molecular chain polaron approximation, which allows to find exact analytical solutions for two types of local Paround neutral C_{60} dopant: symmetric (SP) and assymetric (AP) in which the extension (radius) and energy of P change compared to free P. The spectrum of local phonons around P (so called IRAV) is found as a function of C_{60} mediated hoping strength γ from which the stability criterions for SP in N=2 and 3 chain case are found. SP states are discussed as intermediates for the interchain hoping of

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1. INTRODUCTION

Photosensitization of photoconductivity of inorganic semiconductors or organic molecular crystals by impurity molecules of dyes absorbed at the surfaces or intercallated into organic solid is a well studied process, widely used in color photography and xerography [1,2]. However in conjugated polymers this phenomena may have new features due to involvement of deeply self trapped q-1-d excitations of chains. It has been suggested earlier that neutral weak dopants (either weak donors $\tilde{D}$ or weak acceptors $\tilde{A}$ with their LUMO or HOMO levels inside the band gap of conducting polymers), can react with self-trapped excitations of polymeric chains[3], changing their properties and population. So the decrease of ESR intensity of polyparaphenylene upon exposure to oxygen, has been interpreted as O_2 -weak dopant assisted transformation of polarons (P) to spinless bipolarons (BP): $P^+ + O_2 \rightarrow BP^{2+} + O_2$ [4]. We have suggested also that such weak dopants may sensitize the photoconductivity of conducting polymers due to the photoinduced charge transfer (CT) from excited D* (or A*) levels to a polymeric chain, or due to dissociation of exciton-polarons (Ex) with CT to $\widetilde{D}$ or $\widetilde{A}$ and accompanied by transformation of Ex to P [5].

Recently we proposed that fullerenes, C_{60} and C_{70} can be used as such weak acceptor dopants in various conducting polymers and in a series of experiments have found quenching of photoluminescence [6,7] and the enhancement of photoconductivity [7,10] due to photoinduced CT between fullerene and CP chains as earlier suggested[3,5]. Photoinduced charge transfer (PCT) from C_{60} to CP has been independently found also in other CP, like MEH-PPV and proved by other methods, like photoinduced absorption (PA), light induced ESR [11] and recently studied by transient time spectroscopy, clarifying rather fast time of foreward PCT process [12,13]. In some polymers, like poly-hexylthiophene, however we have found the changes of optical absorption spectra and,

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cyclic voltamogram, suggesting a partial CT in the ground state (GS), which was not accompanied by increase of dark conductivity and ESR intensity [7]. We also found that increasing the length of a side chain in PAT one may controll the GS CT, i.e. in polyoctadecilthiophene GS CT is not found [9] Earlier it was suggested that twists and bends of PAT chains due to disorder in side chains may rise the bottom of valence band in some parts of POT and make ground state CT energetically favourable if stabilised by self trapping effects in CP and C^{60} and Coulomb attraction [6,7,9]. It has been suggested that close to imperfections of chains created by large C_{60} dopants the GS CT can be stabilised and thus form a coupled state of C_{60}^{-1} monoanion (or polaron on C_{60}, P_C^- [15,16]) with polaron on C_{60}. Recently such C_{60}^{-1} have been found in IR spectra [17], proving that GS CT occurs , however surprisingly IRAV of P^+ in CP chains have not been found. In CP like PPV GS CT does not occur and absence of ESR upon C60 doping of PAT has been interpreted as absence of GS CT [13,14] and the changes in optical absorption will can be clearly observed have been assigned to mixing of GS wave functions of C_{60} and CP [14]. The problem of hybridization at account but we adress some other problems connected with special properties of C_{60} molecules differing it from other weak dopants like O_2 [2] or organic dyes, (like well known dimethyl terephthalate (DMTP) molecule in PVK [1]). This features of C_{60} arise due to its following properties:

1. C_{60} has 2-D π-electrons, which should have strong overlaping with 1-d π electrons of CP chains, with $t_{f-p} \sim 0.1$ - 0.3 eV, which should make CT processes between them, much pronounced. Note that interaction of C_{60} with nonaromatic polymers, do not lead to enhanced photoconductivity [19], and thus supports the important role of π electrons for CT .

2. Due to 2-dimensional geometry the pronounced self-traping effects on C_{60} spheres lead to formation P/BP and self trapped excitons of string type [15-16] which should play important role in CT processes from P/BP and Ex of CP chains and may cause new features in their interactiones.

3. Due to their large size, C_{60}, C_{70} and higher fullerenes should introduce disorder,deforming chains and creating defects; while the CP chains on their turn should deform C_{60} molecules, changing their symmetry (as we have proved by observation of forbiden optical transitions in C_{60} upon intercallation into CP [10].

This new features can influence the CT processes and we discuss below some of this microscopic processes. However at the present stage when no analytical models (like TLM for CP [20]) are available for ST states on C_{60} this analysis can be done only either on the qualitative level or within simple analitically soluble models.

We consider several types of recharging reactions: 1) between C_{60} and kink solitons So, and present some preliminary experimental prove from ESR in C_{60} doped polyacetylene derivative. 2) Transformation of P into BP. 3) Formation of BP in C_{60} due to interaction with Ex at long term photoexcitation which may give rise to persistent photoconductivity, observed recently.*) In the last Section the C_{60} mediated interchain hopping of P, is studied within a simple exactly soluble model of δ- coupled molecular chains. We show that there are states of P spread over several chains surrounding C_{60}, and study there stability. Such distributed P can be intermediates in the C_{60} mediated intetrchain hoping of P, the process, which should increase the mobility of P/BP , and hence may contribute to the enhanced photoconductivity in C60-doped polymers, additionally to the effect of increased photogeneration efficiency, which is believed to be the main origin. [8-11]

2. REACTIONS BETWEEN SELF-TRAPPED EXCITATIONS OF CP AND C60

We have discussed recently the reaction of Ex dissociation at the C_{60} dopant:

$$Ex + C_{60} = P^{+} + C_{60}^{-}$$

as one of the origins for photoinduced charge transfer to C_{60} with formation of charged P^{+}s , which contribute to enhanced photoconductivity and photoluminescence quenching,

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in C_{60} doped conducting polymers. At large concentrationes of Pc on C_{60} the reactions

$Ex + P_c^- \longrightarrow P^+ + BP_c^{2-}$, should become possible

leading to formation of bipolarons on C_{60} and additional mobile P+ in CP chains. This reaction should contribute to persistant photoconductivity which we recently observed in CP/C_{60} systems (see this Proceedings). We can not exclude at present the energy transfer processes from Ex to P+ and Pc-:

$Ex + Pc^-$ ------ (Pc-)*,

which should additionaly quench Ex-ic PL and give nonlinear PL quenching at high pumping levels.

2.2. Reactions with solitons.

In polyacetylene-type degenerate ground state polymers, which support kink solitons (So,S+,S-), the rechanging reaction of neutral kinks So with C_{60} becomes possible if the energy separation between that C60 LUMO and mid-gap level of So is larger than Hubbard repulsion of two holes on S+ state:

$S^0 + C60 \longrightarrow S^+ + C60^-$

We have found that in PTMSiPA polyacetylene derivative the spin density decrease with C60 doping (Fig.1, which can be related with the above soliton S^0 (carying spin) transformation into charged spinless S+ .

3. C_{60} - MEDIATED INTERCHAIN HOPING OF P

To consider the questione of C_{60} mediated hoping of Ps we need first to study the spectrum of P in the vicinity of neutral C_{60}. However this task is too dificult for analytical study within TLM model [20], appropriate for P/BP in CPs. It has been shown [20] that molecular polaron of Rashba-Holstein [21-22] model is actually a limiting case of TLM for Pierels type CP in a limit of strong confinement. So it can be used for the analysis of various problems due to possibility to obtain analytical results, e.g. for P/BP interchain

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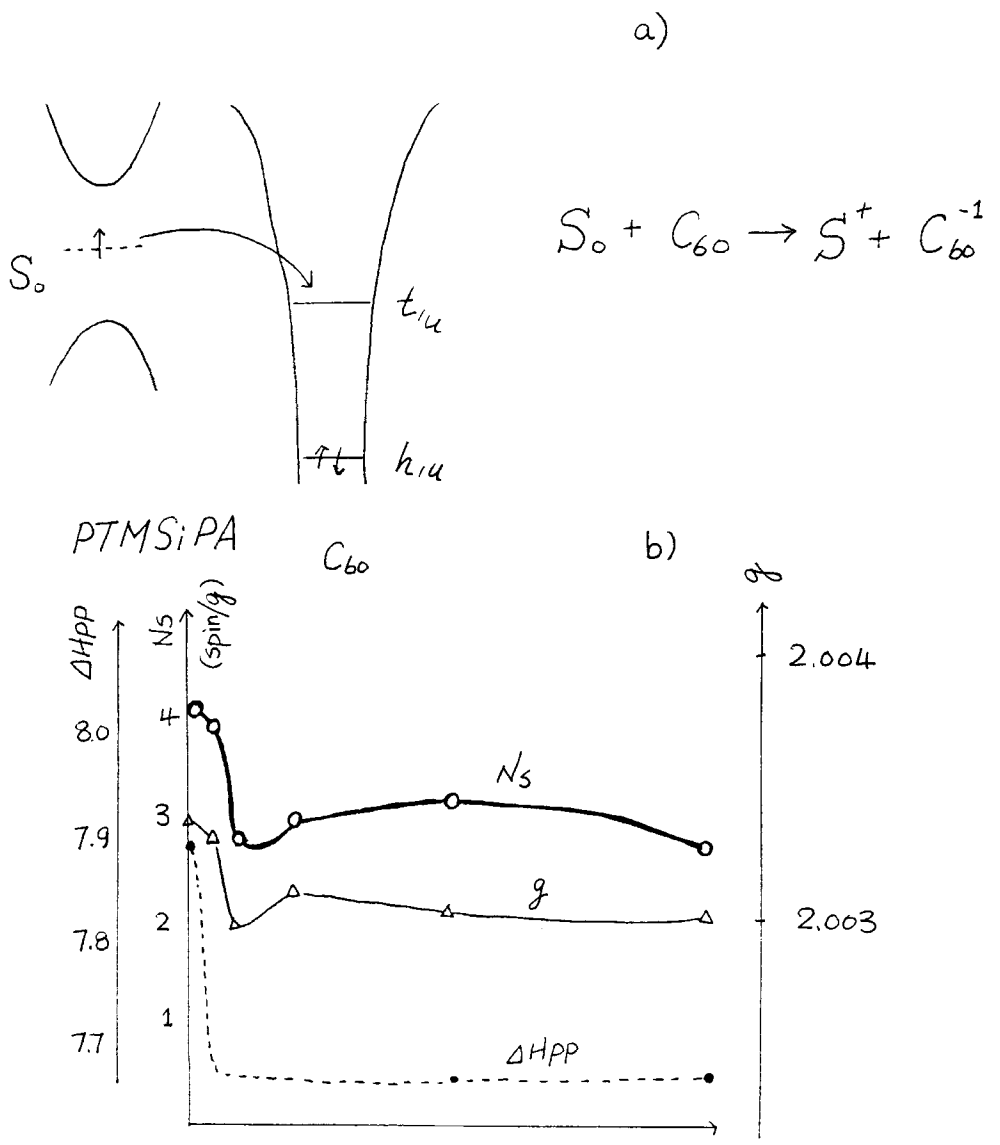

Figure 1. a) Transformation of neutral S^0 into S^+ due to charge transfer to C_{60} LUMO
b) Experimentally observed change of ESR intensity (Ns), linewidth and g-value as

stability problem [23,24]. Particularly it has been found that exact solutions can be found for δ – type local interchain hoping [24]. Let below use this approach, but, contrary to [24], starting from the discrete model, which will allow us to derive the parameters of chain-C_{60} interaction through parameters of C_{60} molecule.

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3.1. N-coupled chains, main equations.

Consider a model of N molecular chains, with C_{60} impurity between them so that hopping of electrons between chains are not allowed, and the only possible is hoping between HOMO level of C_{60} and one **n** site at each chain (as shown at Fig.2). Then each chain is decribed by following discrete Hamiltonian in a nearest neighbour approximation:

$$H_m = \varepsilon_0 \sum c^+_{nm} c_{nm} - t_{II} \sum_n c^+_{nm} (c_{n+1,m} + c_{n-1,m}) + h.c. - \lambda \sum_n c^+_{nm} c_{nm} u_{nm} \qquad (1)$$

where c^+_{nm} is the creation operator of electron at site n of a chain number m, with energy ε_0 (1) and, hoping transfer integrals t_{II}. Above we take the simplest form of site diagonal electron-phonon interaction with intramolecular displacements u_{nm}, used for phonons, where λ is the coupling constant. The energy of dispersiveless phonons have the form:

$$H_{ph} = U + T, U = \frac{k}{2} \sum_n u^2_{nm}, T = \frac{M}{2} \sum_n u^2_{nm} \qquad (2)$$

where K is the spring constant. If we consider only local hoping T_{nm} from chain site to the level in C_{60} with energy Λ, we get: (b^+_0, b_0 creation, annihilation operators for impurity e^-)

$$H_f + H_{f+m} = \Delta_0 b^+_0 b_0 + \sum_{nm} T_{nm} (b_0 c^+_{nm} + b^+_0 c_{nm}) \delta_{no} \qquad (3)$$

Full Hamiltonian for N- chains coupled with C_{60} molecule is thus:

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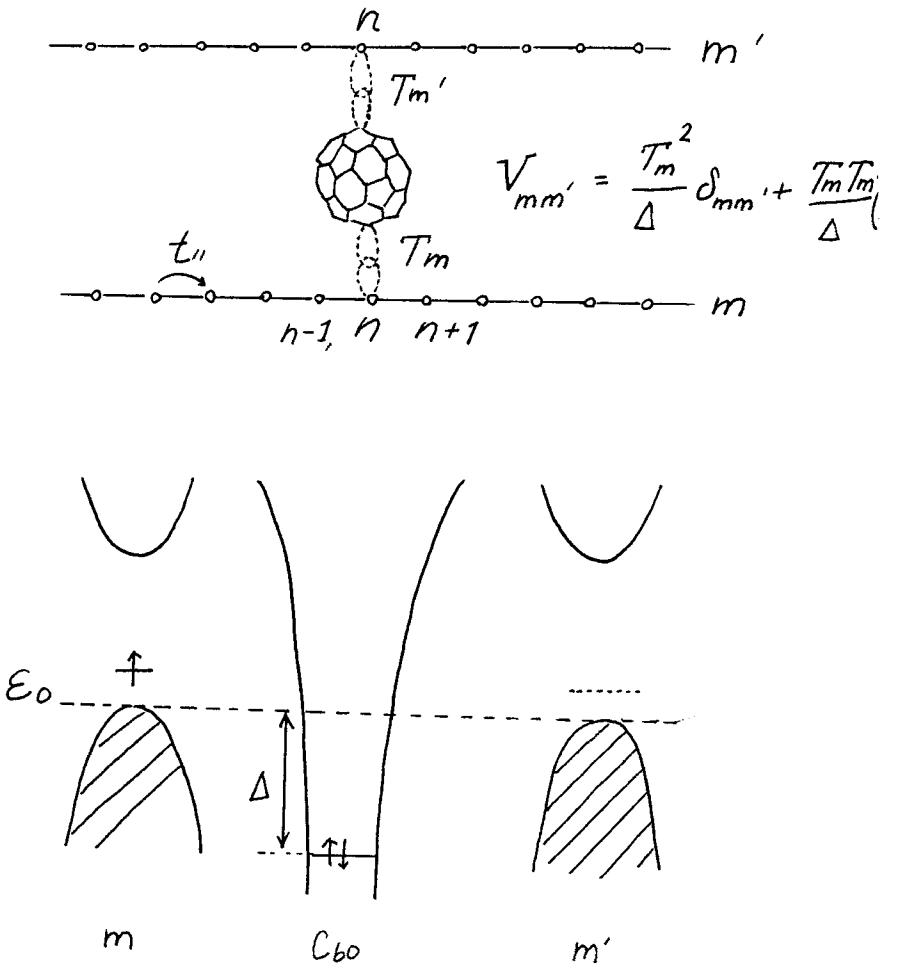

Fig. 2. The model of C_{60}-mediated hoping of a charge at site n, between chains m and m', T_m and $T_{m'}$ the chain-C_{60} transfer integrals, $V_{mm'}$ the resulting interchain hopping potential.

$$H = \sum_m (H_m + H_{ph} + H_f + H_{f+m}) \tag{4}$$

To find the main equations for polarons, let search for the minimum of the adiabatic potential E = H - $\sum_m$T, with respect to c^+_{nm} and b^+_0 and u_{nm} variables, which are viewed as c-numbers at account of normalization. One arrives to the following set of equations:

$$-t_{II}(c_{n+1,m} + c_{n-1,m}) - \lambda c_{nm} u_{nm} + T_{nm} b_0 \delta_{n0} = (\varepsilon - \varepsilon_0) c_{nm} \tag{5-a}$$

$$\Lambda_0 + \sum_{nm} T_{nm} c_{nm} \delta_{no} = \varepsilon b_0 \tag{5-b}$$

$$k u_{nm} - \lambda c^+_{nm} c_{nm} = 0 \tag{5-c}$$

Eliminating from (5) u_{nm} and b^+_0 one gets the following set for c_{nm}:

$$-t_{II}(c_{n+1,m} + c_{n-1,m}) - 2g(c^+_{nm} c_{nm}) c_{nm} - \sum_{m`} V_{mm`}(\varepsilon) c_{nm`} = (\varepsilon - \varepsilon_0) c_{nm} \tag{6}$$

where g = λ^2 / 2K is the small polaron energy gain, or effective e-ph coupling, and the definition for $V_{mm`}(\varepsilon)$, the effective energy of the electron hoping from chain m to chain m` across the C_{60} impurity is as following: $V_{mm`}(\varepsilon) = \frac{T_m T_{m`}}{\varepsilon - \Lambda_0}$. Generally speaking it depends on the energy of the electron in the system ε. Let assume for convenience that ε_0 = 0, i.e. shift the origin. For the states of polaron which are fare in energy from the HOMO (or LUMO) levels of C_{60}, i.e. for $\varepsilon << \Lambda_0$, we can neglect the dependence of Vmm` on ε, which corresponds effectively to the sort of perturbation theory for the C_{60}-chain transfer interaction, we get:

$$V_{mm`} \cong V_{mm`} = -\delta_{mm`} \frac{T^2_m}{\Lambda_0} - (1 - \delta_{mm`}) \frac{T_m T_{m`}}{\Lambda_0} \tag{7}$$

which accounts that hoping integral from chain m to fullerene: T_m may be different than hoping from m` to $C_{60}$, $T_{m`}$, due e.g. to different separations (C_{60} closer to one of

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chains) and does not necessarily require $T_m T_{m'} < T_m^2$ as supposed in [24]. It worths mentioning that at $\varepsilon \sim \Delta_0$ the structure of polarons at resonance conditions with the C_{60} level should be examined beyond approximation (7) which requires more rigorous analysis. The discrete set of egs. (6) has been studied recently [26] by numerie computational method.

Asuming $t_{||} >> g$, which corresponds to the formation of large radius polarons in a single chain case [21-22], with the extension $l_p = 2t_{||}/ g$, we can transfer from a discrete set of equations (6) to continual ones by substitution :

$$c_{nm} \xrightarrow{x>>a} \Phi_m(x), \delta_{no} \xrightarrow{x>>a} \delta(x), na \longrightarrow x,$$

where a is the lattice constant. One then arrives to a set of coupled nonlinear Scrodinger equations of the type:

$$(-t_{II}\partial^2 / \partial x^2 - 2g|\Phi(x)|^2)\Phi(x) - \sum_{m'}^{N} V_{mm'}\delta(x)\Phi_{m'}(x) = \varepsilon\Phi(x) \qquad (8)$$

The set of equations (8) can be solved exactly following the method of [24]. Below we will analise cases of N=2 (for which we point the new solution, that is missed in [24], but which is important for the examine of dynamic stability problem,) and the new case of N=3 chains and study the question of the dynamic stability of the different types of polarons, i.e. of the correspondence between mathematical formal solutions of (8) and physically allowed equilibrium states,since this questione is important for the study of various physical processes, and interchain mobility in particular.

We recall shortly that at absence of interchain hopping term the NSE gives a solitonic polaron solution [21-22]:

$$\Phi_0(x) = \sqrt{\mu / 2}Sech\,\mu x, \mu = g / 2t_{II}, \varepsilon = -t_{II}\mu^2 = -g^2 / (4t_{II}); E = -E_0 = -t_{II}\mu^2 / 3 \qquad (9)$$

where μ measures the inverse spatial extension of P, ε is its electronic energy level (below conduction band for P-, or above the top of the valence band as in our actual case for P+ .), while E is the ground state energy, which for our case of coupled chains can be

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expressed as:

$$E = \varepsilon + \frac{1}{4g}\sum_{m=1}^{N}\int_{-\infty}^{\infty}\Delta_m(x)^2\,dx, \qquad \Delta_m(x) = 2g|\Phi_m(x)|^2 \tag{10}$$

where function Δ(x) represents the displacement field of P in each chain, and second term in (10) describes the elastic energy of deformation and is derived from discrete U in (2). It has been shown thet at x= 0,the lowest "solitonic" solutions of the set (8), centered at x=0 can be found in the form:

$$\Phi_m(x) = \frac{k}{\sqrt{2\mu}}Sech[k(x+x_m), for \quad x>0 \tag{11-a}$$

$$\Phi_m(x) = \frac{k}{\sqrt{2\mu}}Sech[k(x-x_m), for \quad x<0 \tag{11-b}$$

Let analyse now P solutions in special cases of two and three chains:

When N=2, three types of P solutions exist: two symmetric ones: SP^+, SP^- and one antisymmetric AP, two of which SP^+ and AP have been found in [24]. We point here to a third one, called SP^- (odd solution) for which

$$\Phi_1(x) = -\Phi_2(x), k/\mu = 1/2, x_1 = x_2 = 0, E/E_0 = -1/4, \tag{12}$$

and thus do not depend on $\gamma = V_{nn'}/g$. We will use all solutions later to analise the question of local polaron-phonon modes:

3.2 Three chains

Let now analise in more detail the case of three chins, as more realistic for a 3-D structure of CPs. Integrating eq. (8) over the infnitesimal interval containing the origin x=0, we obtain:

$$(\Phi_m'(-0) - \Phi_m'(+0))t_{II} = V\sum_{m=1}^{3}\Phi_{m'}(0) \quad (\Phi_m'(-0) - \Phi_m'(+0))t_{II} = V\sum_{m=1}^{N=3}\Phi_{m'}(0) \tag{13}$$

which leads after substituting eq (11) to (13) to

$$\tanh(kx)Sech(kx) = \gamma\frac{\mu}{k}\sum_{m=1}^{3}Sech(kx), m = 1,2,3 \tag{14}$$

while from the normalization condition $\sum_{m=1}^{N}\int_{-\infty}^{\infty}|\Phi_m(x)|^2\,dx = 1$, applied to wave function

of (11) gives: $$\sum_{m=1}^{3}(1-\tanh(kx_m)=\mu/k \qquad (15)$$

Following the method of [24] we can find the following solutions [25] of the set (8) at N=3:

1) Polaron solution (SP) symmetric over all three chains at $\gamma = 0$, for wich we get:

$$\frac{k}{\mu}=\frac{1}{3}+3\gamma, \qquad x_m=\frac{1}{k}\arctan h(\frac{9\gamma}{1+9\gamma}), \qquad E/E_0=-\frac{1}{9}-3\gamma-27\gamma^2 \qquad (16)$$

2) Polaronic solution symmetric over two chains (SP_2),at $\gamma = 0$, with

$$\tanh(kx_1)=1, \qquad \tanh(kx_2)=\tanh(kx_3)=0 \qquad (17)$$

3) P-solution concentrated mainly on one chain AP, for which at $\gamma = 0$, one havs:

$$\tanh(kx_1)=0, \qquad \tanh(kx_2)=\tanh(kx_3)=1 \qquad (18)$$

The last two solutions can be analised by finding the numeric solution of the set of eqs.:

$$\tanh(kx)Sech(kx)=\gamma\frac{\mu}{k}(Sech(kx)+2Sech(ky))$$

$$\tanh(ky)Sech(ky)=\gamma\frac{\mu}{k}(Sech(kx)+2Sech(ky) \qquad (19)$$

$$\tanh(kx)+\tanh(ky)=3-\frac{\mu}{k}$$

Above we have denoted $x_1 = x$, $x_2 = x_3 = y$, The full energy of the system is given by:

$$\frac{E}{E_0}=-\left(\frac{k}{\mu}\right)^3(3-\tanh^3(kx)-2\tanh^3(ky) \qquad (20)$$

Fig.3 shows the dependence of full energy E/E_0 on the C_{60}-intermediated coupling potential γ for both cases N=2 and N=3. At $\gamma=0$ the state which is favourable energetically, and stable is always AP (P is located mainly on one chain). With increase of γ the energy of both AP and SP states decrease meaning that polaron is coupled to C_{60} by interchain exchange interactions, and SP gets closer to AP and at $\gamma = \gamma_c$, ($\gamma_c^{(2)} = 0.603$, $\gamma_c^{(3)} = 0.3$) the energies coincide and above γ_c only SP exist as a stable polaronic state, which is uniformly spread over chains surrounding C_{60}. Its size becomes several times larger ($\sim \mu/k$). Note that in N=3 case SP_2 and AP energies coincide at $\gamma_{c1} = 0.304$ and both disappear. So above $\gamma_c^{(3)} = 0.3$ only SP becomes favourable and the only existing state. Naturally $\gamma_c^{(3)} < \gamma_c^{(2)}$, meaning that the tendency of spreading of P around C_{60} impurity increases with larger number of chains coupled with C_{60}.

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It is clear however that at γ=0 the SP is an unphysical solution, althouh formally it exist as solution of (8) it should not correspond to a minimum of the adiabatic potential and should correspond to decaying nonequilibrium.state Only above some $\gamma_S < \gamma_C$ it may become metastable. The question of γ_S can be studied examining the spectrum of local vibrations bound to SP [23]: the apearence of soft mode Ω<0 in this spectrum will indicate the dynamical instability below γ_S[23].

2.3 Spectrum of local phonons at SP polaron and problem of dynamical stability of SP.

To answer the question which states of P (16)- (18) are classicaly stable i.e. correspond to minima of the W{Δ}:

$$W(\Delta) = \int_{-\infty}^{\infty} \left[\frac{1}{4g} \Delta(x)^2 + \Phi^*(x) \left(-t_{II} \frac{\partial^2}{\partial x^2} - \Delta(x) \right) \Phi(x) \right] dx \qquad (21)$$

it isnecessary to find and examine the spectrum of local lattice vibrations around SP and AP. For one-chain P (at γ=0) such spectrum, known as MSW-modes [27,28] lies below the bare phonon frequency ω, converging to it. For P in the system of chains coupled by regular interchain hoping $t_\perp$ at every site, such spectrum may have a soft mode [23] indicating instability of P. We will follow the metod of [23,27] below. Consider a small displacement $\delta_m(x,t)$ around the static P deformation field Δ_{mo} (x). This displacement can be viewed as the perturbaton for electronic hamiltonian, which will generally speaking mix vibrations of different chains due to e-ph interaction, and lead to the Lagranjian for the lattice vibrations:

$$L = \sum_{m=1}^{N} \left[\frac{1}{4g} \int_{-\infty}^{\infty} \left(\frac{1}{\omega^2} \dot{\delta}_m^2 - \delta_m^2 \right) - \delta E_m^{(2)} \right] \quad \text{where} \quad \delta E_m^{(2)} = -\frac{\left| < \phi_{n\alpha}^m \left| \delta_m \right| \phi_{0S}^1 > \right|}{\varepsilon_{n\alpha} - \varepsilon_{0S}} \qquad (22)$$

is the addition to the ground state energy in the second order of perturbaton theory. The electronic wave function Φ is taken in N-component spinor representation, with $\phi_{n\alpha}^m$, being its componet at m-th chain, and the index n corresponds to eigenfunctions of the Schrodinger eq:

$$H_\alpha \phi^n_{n\alpha} = \varepsilon_{n\alpha}\phi^n_{n\alpha}, \quad \text{with} \quad H_\alpha = -t_{II}\frac{\partial^2}{\partial x^2} - 2g\left|\phi^n_{0S}\right|^2 \tag{23}$$

where the index $\alpha = S,\ldots.$,goes over N ortogonal spinors for every N.

From the Lagranjian (22) we arrive to the equation for the lattice eigenfrequencies Ω:

$$\xi \bullet \delta_m(x) = 4g\sum_{n,\alpha}\frac{\left\{\phi^1_{0S}\phi^n_{n\alpha}\right\}\sum' < \phi^{m'}_{n\alpha}|\delta_{m'}(x)|\phi^1_{0S} >}{\varepsilon_{n\alpha} - \varepsilon_{0S}}, \tag{24}$$

where $\xi = 1 - \frac{\Omega^2}{\omega^2}$,

while prime means that the term with n=0, α=S should be ommited.

For N=2 there are two orthogonal solutions of eq.( ): 1) Symmetric one with $\Phi_S = \begin{pmatrix}\Phi_s \\ \Phi_s\end{pmatrix}$,

where:

$$\phi_s = \frac{k_s}{\sqrt{2\mu}}, Sech(k_s(x \pm x_s)), k_s = \mu(\frac{1}{2} + 2\gamma), x_s = \frac{1}{k}\arctan h\left\{\frac{4\gamma}{1+4\gamma}\right\}, \varepsilon_{0S} = -t_{II}\mu\left\{\frac{1}{2} + 2\gamma\right\}^2 \tag{25}$$

and 2) Asymmetric one $\Phi_A = \begin{pmatrix}\Phi_A \\ -\Phi_A\end{pmatrix}$, with

$$\phi_A = \frac{k_A}{\sqrt{2\mu}} Sech(k_A x), k_A = \frac{\mu}{2}, \varepsilon_{0A} = -\frac{t_{II}\mu^2}{4} \tag{26}$$

Defining the normal displacements $\eta_1 = \delta_1 + \delta_2, \eta_2 = \delta_1 - \delta_2$, we get separate equatons for each:

$$\eta_1(x) = \frac{8g}{\xi_1}\sum_n \frac{\left\{\phi_{0S}\phi_{nS}\right\} < \phi_{nS}|\eta_1(x)|\phi_{0S} >}{\varepsilon_{nS} - \varepsilon_{0S}}, \text{ and } \eta_2(x) = \frac{8g}{\xi_2}\sum_n \frac{\left\{\phi_{0S}\phi_{nA}\right\} < \phi_{nA}|\eta_2(x)|\phi_{0S} >}{\varepsilon_{nA} - \varepsilon_{0S}} \tag{27}$$

First of this equatins is same as the one for MSW-modes and thus has the same specrum of local phonons Ω_{1k}, which does not depend on the C_{60} mediated coupling γ.

Consider the second of eq. (27) for η_2. Operating both sides by the operator $H_\Lambda - \varepsilon_{0S}$, and taking account the completeness of the set ϕ_{nA} we arrive, after simple transformations to the following associated Legendre equations: (here z=μx,)

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$$\left[-\frac{\partial^2}{\partial z^2}-2\left(\frac{1/4}{Ch^2\frac{z}{2}}+\frac{2}{\xi_2}\frac{(1/2+2\gamma)}{Ch^2\left(\frac{1}{2}+2\gamma\right)(z\pm z_1)}\right)+\left(\frac{1}{2}+2\gamma\right)^2\right]\frac{\eta_2}{\phi_{0S}}=0 \qquad (28)$$

For each value of the γ parameter there exist a spectrum of the ξ_{2k} and correspondingly of Ω_{2k}, (k= 1,2,3,....)which gives the finite everywhere solutions of eq. (28). The numerical solutions of (28) are shown in Table 1., from which one can see that at $\gamma < \gamma_S = 0.19$, $\xi_{20} > 1$ and corespondingly $E = \varepsilon + \frac{1}{4g}\sum_{m=1}^{N}\int_{-\infty}^{\infty}\Lambda_m(x)^2 dx$, $\Delta_m(x) = 2g|\Phi_m(x)|^2 20$ becomes imaginary. This means that the perturbation η_2 exponentially increase with time at this small γ values, meaning that displacement field δ_1 increases, while δ_2 decreases, pushing the electronic density from chain 1 to chain 2. In other words at $\gamma<\gamma_S$ the SP becomes dynamically unstable, and transforms into AP, even though the formal solution SP still exist.

For N=3 the orthogonal set of Φ corresponds to Φs of (23) with: $\varepsilon_{0s} = -t_{II}\mu^2\left(\frac{1}{3}+3\gamma\right)^2$

and also to $\Phi_2 = \begin{pmatrix} 0 \\ \phi_2 \\ -\phi_2 \end{pmatrix}$, $\phi_2 = \frac{k_2}{\sqrt{2\mu}}Sech(k_2 x), k_2 = \frac{\mu}{2}, \varepsilon_{02} = -t_{II}\frac{\mu^2}{4}$

and $\Phi_3 = \begin{pmatrix} 2\phi_3 \\ -\phi_3 \\ -\phi_3 \end{pmatrix}$, $\phi_3 = \frac{k_3}{\sqrt{2\mu}}Sech(k_3 x), k_2 = \frac{\mu}{6}, \varepsilon_{02} = -t_{II}\frac{\mu^2}{36}$

In this case the equation for the normal modes around SP polaron can be derived in the form [ ]:

$$\left[-\frac{\partial^2}{\partial z^2}-2\left(\frac{1/4}{Ch^2\frac{z}{2}}+\frac{2}{\xi_2}\frac{(1/3+3\gamma)}{Ch^2\left(\frac{1}{3}+3\gamma\right)(z\pm z_S)}\right)+\left(\frac{1}{3}+3\gamma\right)^2\right]\frac{\eta_2}{\phi_{0S}}=0 \qquad (29)$$

Solutions of which are given in Table 2. It can be seen that at $\gamma < \gamma_S^{(3)} = 0.12$, the $SP^{(3)}$ looses the stability. Naturally the value of $\gamma_S^{(3)}$ is smaller than $\gamma_S^{(2)}$.

It is clear now that there is a wide range of C_{60} mediated coupling strength: $\gamma_S<$

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Table 1. The spectrum $\xi_{2k} = 1 - \frac{\Omega_{2k}^2(\gamma)}{\omega}$ for local modes of 2 chain-SP polaron diffrent values of γ. Below $\gamma_S = 0{,}19$ the mode $\Omega_{20}(\gamma)$ becomes negative

k \ γ	0.01	0.17	0.19	0.24	0.32	0.4
0	33.4	1.26	1.03	0.70	0.45	0.31
1	0.89	0.22	0.19	0.14	0.09	0.06
2	0.36	0.10	0.09	0.07	0.04	0.03
3	0.20	0.06	0.05	0.04	0.03	0.02

Table 2. The spectorum $\xi_{3k} = 1 - \frac{\Omega_{3k}^2(\gamma)}{\omega^2}$ for local phenon modes around 3-chain SP-symmetrie polaron at different γ. Below $\gamma_S = 0{,}12$; $\Omega_{30}(\gamma) < 0$, meaning instability.

k \ γ	0.01	0.12	0.17	0.24	0.32	0.40
0	-2.88	1.04	0.49	0.22	0.12	0.08
1	0.94	0.13	0.08	0.04	0.03	0.02
2	0.34	0.06	0.04	0.03	0.02	0.01
3	0.19	0.03	0.02	0.01	0.006	0.003

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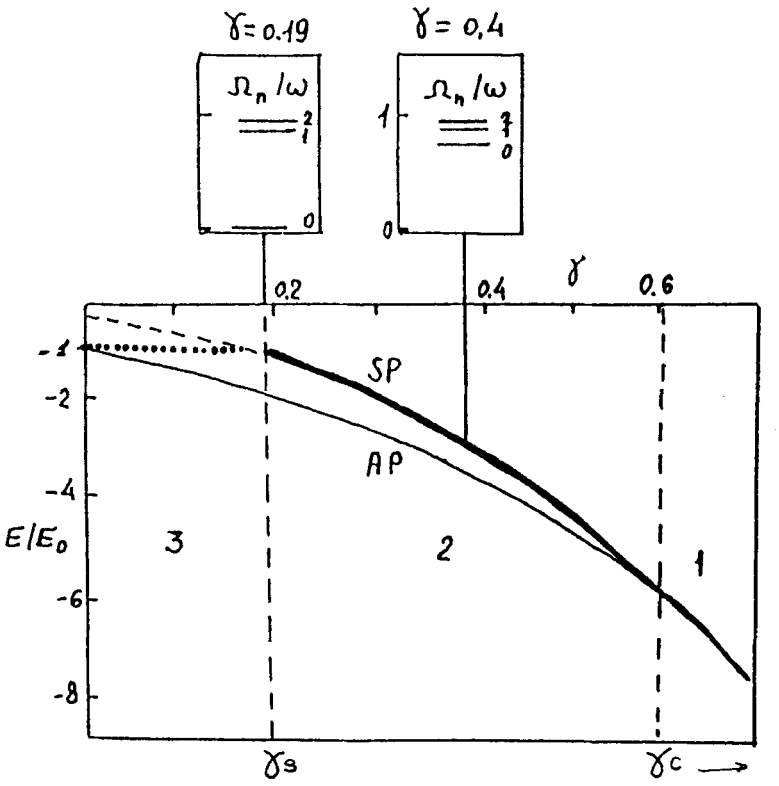

Fig 3. a) The energy E/E_0 of various polaronic states as function of γ; in $N = 2$ case: in region 1 ($\gamma > \gamma_c$) symmetric polaron SP is the only solution in 2 ($\gamma_s < \gamma < \gamma_c$) AP has lower energy, but SP is a metastable state coexisting with AP in 3 ($\gamma < \gamma_s$) SP becomes unstable due to a soft mode $\Omega_{02} \leq 0$. Insets show local modes.

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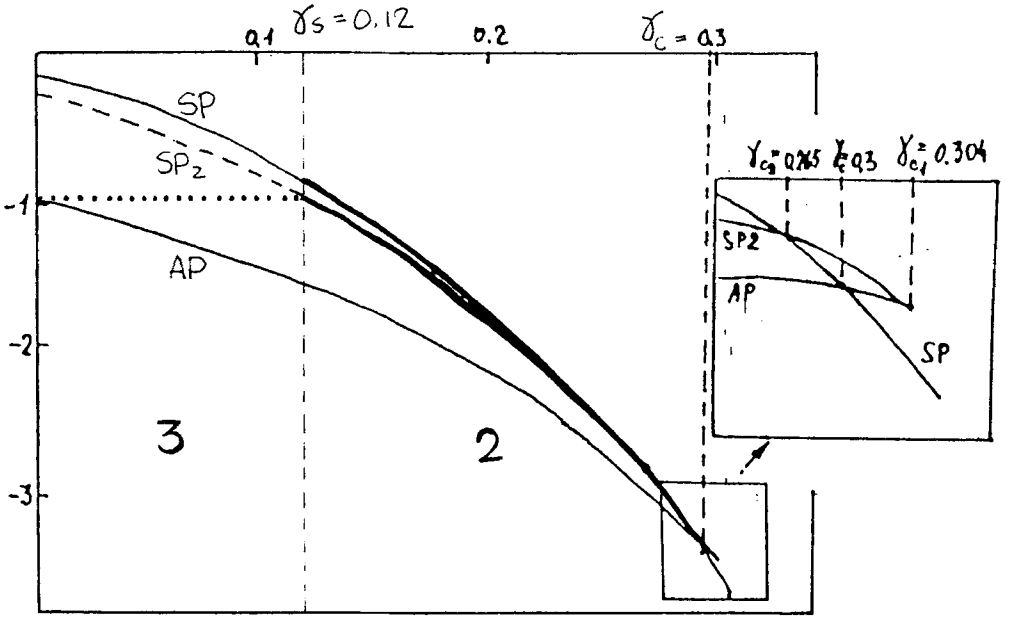

Fig 3. b) The energy E/E_0 of $N=3$ chain system as function of γ. Dotted line shows the energy of free one-chain polaron P ($E/E_0 = -1$). SP is metastable at $\gamma_s < \gamma < \gamma_c$, coexisting with AP, and becomes the only possible solution above $\gamma_{c1} = 0.304$, when AP and SP_2 both disappear. At $\gamma_{c2} = 0.265$. SP becomes lower in energy compared to SP_2

$\gamma < \gamma_c$ in which the SP state is existing as a metastable state, which has larger energy than AP, but can exist as a equilibrium excitation, i.e. can be created by light or what is important for the problem of mobility, can be an intermediate state in the interchain hoping process, which is shown schematically at Fig.4. P_1 traveling along chain 1 meets the segment of chain close to C_{60}, in which at $\gamma > \gamma_s$ it can be transformed into SP, with which it is nearly resonant at $\gamma \sim \gamma_s$, (as one can see from Fig.3). So P_1 transforms to SP, and spreads over chains surrounding C_{60}. Since this state is metastable it can transfrom (by tunneling through the barrier which separates them, or by thermal excitation over it) into either AP or P_2, with lower energy on chain 2, (if e.g. external electric field is applied normally across the chains). To become free AP need another transformation into P_2 which again needs either electric field, or thermal excitation, but the microscopics of this processes is beyond our consideration. What is important from present analysisis, that the existance of the intermediate state should strongly enhance all the hopping processes.

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REFERENCES:

1. K.Okamoto, et.al., Bull.Chem.Soc.Jpn.,46 (1973) 2613, M.Yokoyama, et.al., ibid., 49(1976)1538

2. Bassler et.al., Phys.Stat.Sol., (1991)

3. A.A.Zakhidov, Impurities of Weak Donors and Acceptors in Conducting Polymers,

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:31 18 February 2013

Proc. Int. Conf. ELORMA-87, Moscow, 1987,p 256

4. P.K.Khabibullaev A.A.Zakhidov I.I.Khairullin, P.E.Butlers , Materials Science, Vol XIV, (35) 1987

5. A.A.Zakhidov, Synth.Met.,41-43, 3393 (1991).

6. S. Morita, A.A. Zakhidov and K. Yoshino, Solid State Commun., 82, 249 (1992),

7. S.Morita, A.A.Zakhidov, T.Kawai, H.Araki and K.Yoshino, Jpn.J.Appl.Phys., 31, L890 (1992).

8. K. Yoshino, X.H. Yin, S. Morita, T. Kawai and A.A. Zakhidov, Chem. Express, 7, 817 (1992), also in Solid State Commun., 85, 85 (1993).

9. K. Yoshino, X.H. Yin, K. Muro, S. Kiyomatsu, S. Morita, A.A. Zakhidov, T. Noguchi and T. Ohnishi, Jpn. J. Appl. Phys., 32, L357 (1993).

10. S. Morita, S. Kiyomatsu, M. Fukuda, A.A. Zakhidov, K. Yoshino, K. Kikuchi and Y. Achiba, Jpn.J.Appl.Phys., 32, L1173(1993).

11. K.Yoshino, S.Hayashi,G.Ishii and Y.Inuishi, Jpn.J.Appl.Phys., 22, L376 (1983).

12. N.S. Sariciftci, D. Braun, C. Zhang, V. Srdranov, A.J. Heeger and F. Wudl, Appl. Phys. Lett., 62, 585 (1993), and also Science

13.L.Smilovitz, N.S.Sariciftci,R.Wu C.Gettinger,A.J.Heeger and F.Wudl, Phys.Rev.B 47 (1993) 13 835

14.C.H.Lee,G.Yu,D.Moses,K.Pakbaz,C.Zhang, N.S.Sariciftci, A.J.Heeger and F.Wudl., Phys.Rev., B 48 (1993)

15.K.Harigaya, J. Phys.Soc.Jap.

16.Lieber, Phys.Rev. B

17.S.Luzzati, C.Botta,A.A.Zakhidov and K.Yoshino, (this Proceedings)

18.C.S.Kuo,F.G.Wakim, S.K.Sengupta, and S.K.Tripathy, Sol.St.Comm., 87 (1993) 115

19.Y.Wang, R.West and Chien-Hua Yuan, J.Am.Chem.Soc., 115 (1993) 3844

20.D.K.Campbell, A.R.Bishop & K.Fesser, Phys.Rev.B26 (1982) 6862

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:31 18 February 2013

21.E.I.Rashba, Optica i Spectroscopia 2 (1957) 75,88

22.T.Holstein, Ann.Phys.,8 (1959) 325, also see Mol.Cryst.Liq.Cryst.,77 (1981) 235

23.Yu.N.Gartstein and A.A. Zakhidov, Sol.St.Comm.,60(1986)105, 62(1987)213

24. M.Seimiya and Y.Onodera, J.Phys.Soc.Jpn., 58(1989) 1676

25.A.A.Zakhidov and I.M.Merhasin, Preprint of Inst.Spectroscopy, Moscow, Troitsk, Russia, 1990, pp. 1-22

26.H.A.Mizes and E.M.Conwell, Phys.Rev.Lett. 70 (1993)1505

27.A.A.Zakhidov, K.Tanaka, A.Ito, M.Okada and T.Yamabe, Synth.Metals (submitted)

28.V.I.Mel'nikov, Zh.Exp.Teor.Fiz. (Rus) 72 (1977) 2345

29.P. B.Shaw & G.Whitefield, Phys.Rev.B17 (1978) 1495

Downloaded by [Tomsk State University of Control Systems and Radio] at 12:31 18 February 2013