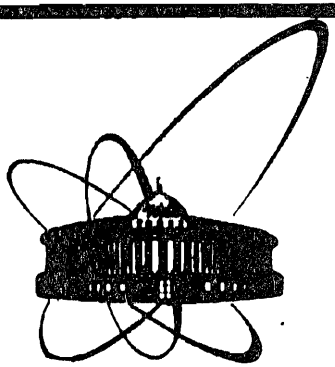

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TRANS-POLYACETYLENE WITHIN THE EXTENDED TIGHT-BINDING PICTURE AND EVIDENCE FOR NEXT-NEAREST NEIGHBOUR HOPPING FROM THE DISPERSION OF INTERBAND TRANSITION EDGES

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Many physical properties of trans-polyacetylene (PA) can qualitatively be explained with considerable success by the well-known Su-Schrieffer-Heeger (SSH)-model [1] and its continuum versions [2,3] . In order to get an improved quantitative description of real PA there are two main lines of generalization. At first, by calculating various quantities one tries to take into account a more realistic electron band structure beyond the simple tight-binding (TB)-picture [4-6] . A more realistic phonon spectrum in connection with the modified electron-phonon-interacting is also of interest [7-9] . Secondly, there are many attempts to include some essential features of the electron-electron-interaction (see, e.g. [10-16]).

The new electron loss data of Fink and Leising [17] for highly oriented nonfibrous PA [18] yield an important physical information on a new level in comparison with the results reported from more or less oriented Shirakawa films which consist of PA-fibres and air inclusions. Thus, a lot of new theoretical concepts can be checked now with high accuracy. In [17] some deviations from our simple RPA-TB-theory for the dielectric function $\epsilon(q,\omega)$ [19] are established. In this letter we want to consider only one from them, namely, the unexpected dispersion of the lower $\pi-\pi^*$-interband transition edge (IBTE) at high transferred momenta $q \geq 1.2\ \text{Å}^{-1}$? Beyond a critical branching point $q_c^{(o-)} = \arccos((1-y)/(1+y))$ ($y = E_g/4t_o \approx 0.14 \div 0.15$ denotes the Peierls gap in units of the whole $\pi-\pi^*$-band width) predicted by our RPA-TB-theory a stronger splitting of the lower IBTE is seen in the imaginary part of the dielectric function obtained fron the loss data (s.figs. 1,2). Due to the nearly 1D-band structure the lower IBTE gives evidence to strong peaks in $\mathrm{Im}\epsilon(q,\omega)$ (square-root-singularities in our RPA-theory). The question being raised in [17] is what kind of the above mentioned effects that are neglected in the SSH-model are responsible for the deviations from the simple RPA-TB-picture. It is the aim of the present paper to show, that the discrepancy disappears if additional hopping processes to next-nearest neighbours are taken into account in a SSH-like model.

Therefore, we start with the Hamiltonian in the site representation

$$H = -\sum_{\ell=1}^{\infty} \sum_{n,s} t_{n+\ell,n} \left(c^{+}_{n+\ell,s} c_{n,s} + \text{h.c.}\right) + \frac{1}{2}\sum_{\ell=1}^{\infty} \sum_{n} K_\ell (u_{n+\ell} - u_n)^2 , \quad (1)$$

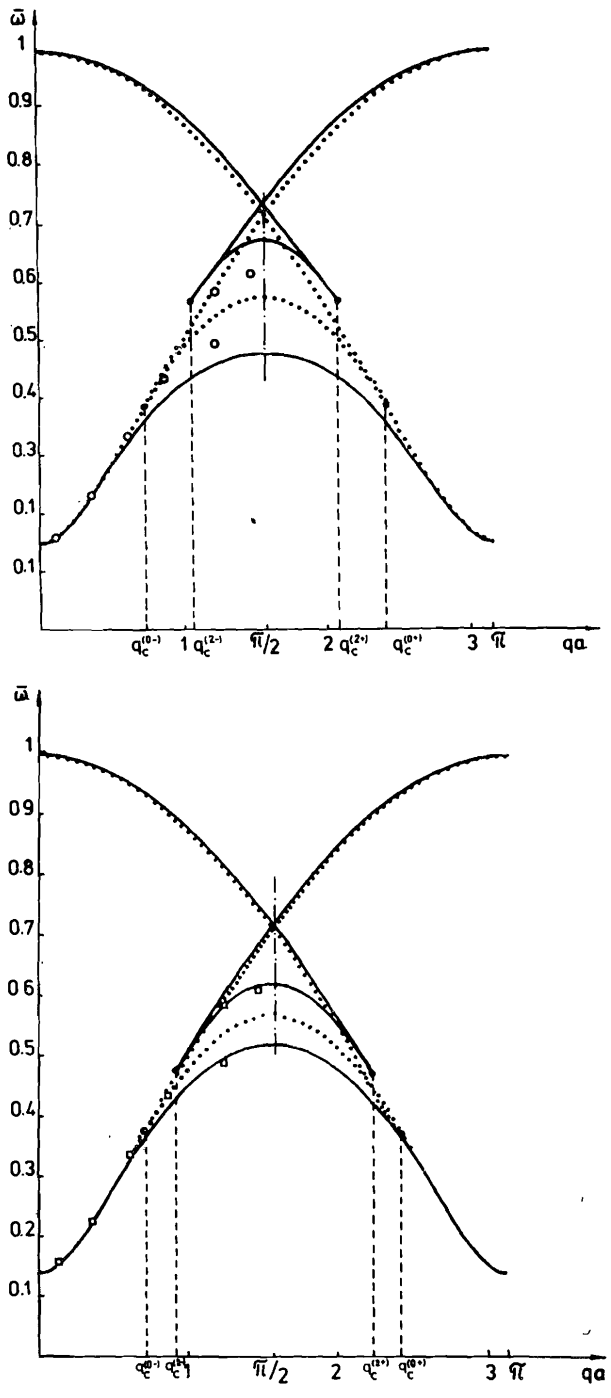

Fig. 1. Absorption region due to interband transitions in the energy-momentum plane. The interband transition edges and singularities of the joint density of states (full lines) for next-nearest neighbour hopping integral $t_2 = \pm 0.1 * t_0$. *The TB-result (i.e.* $t_2 = 0$*) (dotted lines) and the experimental points of /17/ (circels) are shown for comparison. Transitions near the line starting at* $\bar{\omega} = 1$ *and* $q = 0$ *and ending at* $y = 0.15$ *and* $qa = \pi$ *are strongly suppressed by the matrix element* $W(q,k)$ *in eq. (14).*

where both the first terms describe the kinetic energy of the π-electrons and the third term, the change in the elastic energy (σ-binding energy) due to the dimerization pattern $u_n = (-1)^n u$. The hopping integrals can be expanded to first order about the undimerized state:

$$t_{n+\ell,n} = t_\ell - \alpha_\ell (u_{n+\ell} - u_n); \quad \ell = 1, \ldots \tag{2}$$

From the symmetry conserved by the dimerization we have $\alpha_\ell = 0$ for $\ell = 2m$, $m = 1, \ldots$. Usually, the quantity t_1 in eq.(2) is denoted by t_0. The Hamiltonian (1) can easily be rewritten in the k-representation by a Fourier transform

$$H = \sum_k \epsilon_k (c_k^{c+} c_k^c - c_k^{v+} c_k^v) - \epsilon'_k (c_k^{c+} c_k^c + c_k^{v+} c_k^v) + \\ + \bar{\Delta}_k (c_k^{c+} c_k^v + c_k^{v+} c_k^c), \tag{3}$$

where

$$\epsilon_k = \sum_{m=0} 2 t_{2m+1} \cos(2m+1) k a, \tag{4}$$

$$\epsilon'_k = \sum_{m=1} 2 t_{2m} \cos 2mka, \tag{5}$$

$$\bar{\Delta}_k = \sum_{m=0} 4 \alpha_{2m+1} u \sin(2m+1) ka. \tag{6}$$

Fig. 2. The same as in fig. 1 for $t_2 = \pm 0.05 * t_0$ *and* $y = 0.14$. *The experimental data of Fink and Leising /17/ are indicated by squares.*

The Hamiltonian (3) is diagonalized in the standard way resulting in

$$H = \sum_k E_k^c n_k^c - E_k^v n_k^v . \qquad (7)$$

The $n_k^{c,v}$ are fermion number operators. The new band energies are defined as

$$E_k^c = -\epsilon_k' + \tilde{E}_k ; \quad E_k^v = -\epsilon_k' - \tilde{E}_k , \qquad (8)$$

$$\tilde{E}_k = (\epsilon_k^2 + \tilde{\Delta}_k^2)^{1/2} . \qquad (9)$$

Generally, the indices c,v mean condition or valence band, respectively. The formulae for the new wave functions exhibit the usual SSH-structure

$$\Psi_k^c = \alpha_k \chi_k^c - i\,\mathrm{sign}(\tilde{\Delta}_k)\beta_k \chi_k^v , \qquad (10)$$

$$\Psi_k^v = \alpha_k \chi_k^v - i\,\mathrm{sign}(\tilde{\Delta}_k)\beta_k \chi_k^c . \qquad (11)$$

Only the diagonalization coefficients are slightly changed

$$\alpha_k = [\frac{1}{2}(1 + \epsilon_k/\tilde{E}_k)]^{1/2} , \qquad (12)$$

$$\beta_k = [\frac{1}{2}(1 - \epsilon_k/\tilde{E}_k)]^{1/2} . \qquad (13)$$

Thereby the $\chi_k^{c,v}$ are expressed by the Wannier functions (s.(3.13) in /1/). The terms with hopping integrals for even number neighbours break the electron-hole symmetry. This is a qualitatively new effect beyond the TB-picture (e.g., as has been mentioned by Kivelson and Wu /5/ the creation energy of opposite charged solitons is splitted due to such terms). The terms with hopping integrals for odd number neighbours determine the gap energy. The main effect is already included in the TB-picture. Therefore, we may restrict ourselves to the consideration of the influence of the next-nearest neighbour-hopping terms only because the small contributions of the higher terms yield no qualitatively new results. Besides, the order of the neglected anharmonic terms in the σ-binding energy is expected to be comparable. For $t_2 < 0$ and $t_m = 0$ for $m \geq 3$ the results of Springborg (eq.(19) in /6/)are involved in eq.(8).

As an application of the above given theory we consider now the imaginary part of the dielectric function (compare eq.(3.11) of /19/) neglecting again local field effects (their influence will be discussed in a subsequent paper):

$$\mathrm{Im}\epsilon(q,\omega) = \frac{c}{(qa)^2}\mathrm{Im}\int_{-\pi/2}^{\pi/2} \frac{dk\,a\,W(q,k)}{\tilde{E}^c(k+q) - \tilde{E}^v(k) - 2\bar{\omega} - i\delta} \xrightarrow{} c = \frac{2e^2a^2}{t_o\Omega_o} \approx 0{,}35\text{–}0{,}45 , \qquad (14)$$

where Ω_o is the volume of the PA-unit cell (in the simplified picture of equivalent chains). The first mentioned number corresponds to the data of /17/ $4t_o$ = 12.8 eV and the second one to the often used value $4t_o$ = 10 eV. Besides, in eq.(15) dimensionless notation has been introduced $\bar{\omega} = \hbar\omega/4t_o$; $\tilde{E}^{c,v} = E^{c,v}/2t_o$. The lower IBTE (and other singularities of $\epsilon(q,\omega)$) is determined by the minimum (extremum) (with respect to k) of the expression

$$\bar{\omega} = \frac{1}{2}(S_{II}(k+q) + S_{II}(k) + \frac{2t_2}{t_o}(\sin^2(k+q)a - \sin^2 ka)), \qquad (15)$$

where $S_{II}(x) = (1-(1-y^2)\sin^2 x)^{1/2}$. The resulting transcendental equation exhibits for $q \leq q_c^{(2-)}$ or $q \geq q_c^{(2+)}$ two real solutions and otherwise four (s. fig. 3). The corresponding interband

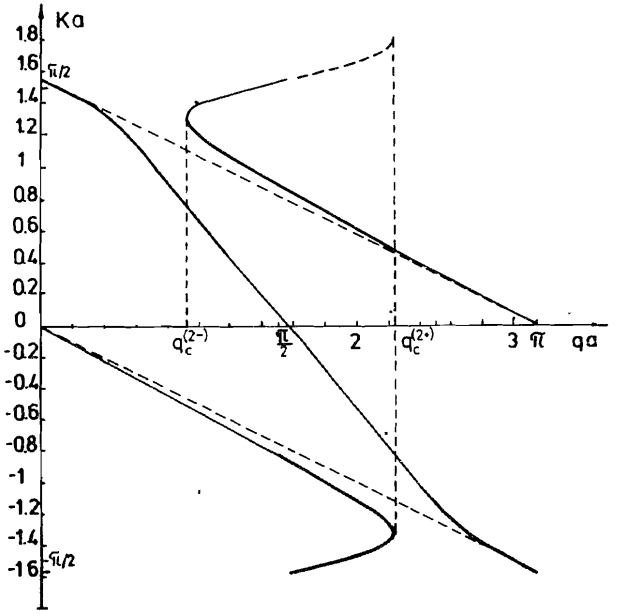

Fig.3. The solutions of the transcendental eqaution $\partial\bar{\omega}(q,k)/\partial k|_{k=0}$ *with* $\bar{\omega}$ *from eq.(15) versus momentum for* $t_2 = -0.05 * t_o$ *and* $y = 0.14$. *The branching points* $q_c^{(2\pm)}$ *which occur in fig.2 are shown too.*

transition region in the $\bar{\omega} - q$ plane is shown in figs.1 and 2 using different ratios t_2/t_o . The branching points $q_c^{(2-)}$ and $q_c^{(2+)}$ are shifted now to the interior region. The interband transition region is slightly broadened in comparison with the TB-case. The largest deviation occurs at $qa = \pi/2$. Thus, the lower TB-line is "splitted" at this point by $\bar{\omega} = 0.5(1+y \pm 2t_2/t_o)$. Note that the modified "butterfly-like" absorption region is independent of the sign of t_2 . For $|t_2|/t_o \approx 0.05$ almost all available at present experimental points lie on the calculated curves. This optimal value is nearly one half of the ratio calculated by Springborg within a LMTO-procedure [6] . By comparing eq.(8) with the 3D-pseudopotential band structure of Grant and Batra [20] , it is unclear to what extent the next-nearest neighbour hopping alone or hybridizations with other bands and/or finite interchain coupling (that results also in an electron-hole symmetric breaking) are responsible for the observed enhanced splitting. Also the discrepancy of our estimate of t_2 with the result of Springborg may be connected with the same effects. Furthermore, the magnitude of t_2 depends crucially on the long range tails of the Wannier functions where oscillations are expected. Therefore, under pressure the splitting energy may be changed considerably. Finally keeping in mind, that the above-mentioned splitting of the creation energy for opposite charged solitons ($\lesssim 0.1$ eV) depends on the Coulomb interaction too [5] , the obtained ratio t_2/t_o should be of interest for the estimate of the former quantity. The photoproduction of neutral versus charged solitons depends also critically on the value of $|t_2|/t_o$ [21].

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Дрекслер Ш.Л., Хайнер Е., Осипов В.А. E17-86-390

Описание транс-полиацетилена в расширенной модели сильной связи и указание на наличие перекрытия вторых соседей на основе дисперсии края межзонного поглощения

Исследовано дополнительное влияние интегралов перекрытия неближайших соседей в модели типа ШШХ. Недавно обнаруженное повышенное расщепление пиков поглощения, обусловленное межзонными $\pi-\pi^*$ переходами /полученное из новых данных по неупругому рассеянию электронов Финком и Лайзингом [17] /, может быть обьяснено на основе разумной величины интеграла перекрывания между вторыми соседями $|t_2| \approx 0{,}05\, t_0$.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

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Drechsler S.L., Heiner E., Osipov V.A. E17-86-390

Trans-Polyacetylene within the Extended Tight-Binding Picture and Evidence for Next-Nearest Neighbour Hopping from the Dispersion of Interband Transition Edges

The influence of additional non-nearest neighbour hopping processes is investigated in a SSH-like model. The enhanced splitting of absorption peaks due to $\pi-\pi^*$ interband transitions (deduced from new electron loss data of Fink and Leising [17]) can be explained by a reasonable value of the next-nearest neighbour hopping integral $|t_2| \approx 0.05\, t_0$.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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