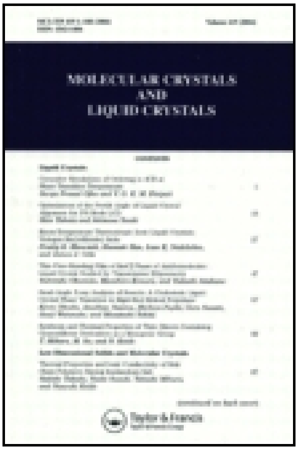

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OPTICAL PROPERTIES OF DOPED TRANS $(CH)_x$

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Abstract A new method of calculation of the imaginary part of the dielectric constant of a one dimensional crystal is presented. This method is applied here to the study of soliton lattices in trans $(CH)_x$.

A great number of theoretical studies have been done on the optical properties of doped polyacetylene[1]. However, most of them make use of the continuum approximation which is only valid in the light doping regime. We have recently determined the optical properties of doped $(CH)_x$, making use of the discrete soliton model[2]. In that work the imaginary part of the dielectric function $\varepsilon_2(\omega)$ was calculated by the standart numerical procedure, where an histogram of $\varepsilon_2(\omega)$ is constructed according to the classic Gilat-Raubenheimer[3] method. However, in that procedure some difficulties are encountered due to the unidimensionality of the problem. The inverse square root singularity at band edges requires a high number of sampling points in k space in order to obtain a good accuracy. A great number of diagonalisation of the hamiltonian matrix is thus needed, which can become prohibitive if their rank is too large because of the large number of bands in the problem at hand.

In this work we propose a new method to determine $\varepsilon_2(\omega)$ which is free from these limitations. The method will be applied here to soliton lattices in $(CH)_x$ whe the unit cell may contain a number of atoms as large as 100. This method which is based on a recursive procedure necessitates only a modelisation of the Huckel type for the hamiltonian. It is thus felt that it can be readily extended to other polymers whose electronic properties are often described by such a Huckel parametrisation.

MODEL - THE SOLITON LATTICE

The hamiltonian describing the soliton lattice is written as :

$$H = \sum_p t_{p,p+1} \left(|p\rangle \langle p+1| + h.c \right)$$

where the transfer integral $t_{p,p+1}$ is a function of the order parameter u_p ,

$$t_{p,p+1} = t_o - \alpha(u_{p+1} - u_p)$$

$$u_p = (-1)^p u_o \prod_{m} \tanh\left(\frac{p - md/2}{\ell}\right) \tanh\left(\frac{p + md/2}{\ell}\right) \qquad (1)$$

and the involved parameters have their usual meanings[2]. The unit cell contains N = 2d (CH) units and the concentration of solitons is $C_S = 2/N$. The electronic structure corresponding to this model consists in occupied valence bands, unoccupied conduction bands and two "soliton bands" in the middle of the gap which are full or empty according to the n or p character of the doping. We will consider for simplicity here the case of n doping.

METHOD

In the dipolar approximation the imaginary part of the dielectric function due to the interband transitions is given as :

$$\varepsilon_2(\omega) = \frac{C}{\omega^2} \sum_{i}^{occ} \sum_{f}^{un} \int dk \, |M_{if}(k)|^2 \, \delta(E_f(k) - E_i(k) - h\omega) \qquad (2)$$

where C is a constant of no importance for us.
However, for our purpose it is convenient to reexpress $\varepsilon_2(\omega)$ as :

$$\varepsilon_2(\omega) = \frac{C}{\omega^2} \sum_{i}^{occ} \sum_{f}^{un} \sum_{k_o} |M_{if}(k_o)|^2 \frac{1}{\left| \frac{\partial}{\partial k} (E_f(k) - E_i(k))_{k_o} \right|} \qquad (3)$$

The sum over k_o in (3) extends over all the reciprocal wave vectors where the transition $E_i(k) \rightarrow E_f(k)$ is direct in the reduced zone scheme and whose corresponding energy difference $E_f(k) - E_i(k)$ is equal to $h\omega$.
We now proceed to determine this sum. For this purpose, let us develop the wave functions, solutions of the Schroedinger equation on the π orbitals $|p>$: $|\psi> = \sum_p C_p(E) \, |p>$ (4)

Defining $\delta_p^{\pm}(E)$ as

$$\frac{C_p(E)}{C_{p \pm 1}(E)} = t_{p\pm1,p} \, \delta^{\pm}(E) \qquad (5)$$

and using (4), (5), it is easily found that the $\delta_p^{\pm}$ verify the following recursive relation

$$\delta_p^\pm (E) = \left[E - |t_{p,p\pm1}|^2 \, \delta_{p\pm1}^\pm (E) \right]^{-1} \qquad (6)$$

the supplementary boundary condition imposed by Bloch theorem, $\delta_p^\pm (E) = \delta_{p+N}^\pm (E)$ is then sufficient to determine the δ_p by a continued fraction expansion. Let us now define

$\Delta(E) = C_N(E)/C_0(E)$; Δ can be calculated as

$$\Delta(E) = (t_{0,1} \, \delta_1^+ (E)) \, \ldots\ldots \, (t_{N-1,N} \, \delta_N^+ (E)) \qquad (7)$$

and is related to the wave vector k by the Bloch theorem $\Delta(E) = e^{ikNa}$, where a is the distance between two CH units. Writing (7) for energies E_f and $E_i = E_f - h\omega$ we then obtain :

$$\Delta(E_f) \, \Delta^* (E_f - h\omega) = e^{i(k-k')Na}$$

which is in general a complex number. However it will be real and equal to one for the precise energies E_f at which the transition $E_f - E_i$ is a direct interband transition contributing to $\varepsilon_2(\omega)$. Given a frequency ω the sum on the interband transitions contributing to (3) is thus reduced to a sum over the final state energies

verifying : $\Delta(E_f) \, \Delta^* (E_f - h\,\omega) = 1$

Once these energies are determined, it is a simple matter to obtain $\varepsilon_2(\omega)$.

- The dipolar matrix element $P_{if} (k_0)$ is given as :

$$P_{if}(k_0) = \sum_p C_p^* (E_i) \, C_{p\pm1} (E_f) \, \langle p \mid M \mid p\pm1 \rangle$$

where the C_p are determined by (5) and the normalization condition of the wave function

- The last factor in (3) can be transformed easily as :

$$\frac{1}{\left| \frac{\partial}{\partial k} (E_f - E_i) \right|_{k_0}} = \frac{g(E_f) \, g(E_i)}{g(E_f) \pm g(E_i)} \qquad (8)$$

where g(E) is the density of states and is directly related to the imaginary part of the Green's function which is obtained by a recursive procedure.

The ± sign occuring in (8) is to be chosen according to the relative curvatures of the two bands involved in the transition (+ sign corresponds the case of opposite curvatures while - sign corresponds to curvatures of the same sign).

RESULTS

The resulting $\varepsilon_2(\omega)$ for different concentrations of solitons is shown in Fig. 1. It is found that a great number of inverse square root singularities occuring at band edges in the combined density of states are smeared out because of the dipolar matrix element. In fact the smallness of the dipolar matrix elements suppresses a great number of direct possible transitions, in particular the transitions involving symmetric bands with respect to the gap center. The two most important interband transitions labelled 1 and 2 in Fig. 1 occur between the soliton band and the conduction band and the valence and the conduction bands. These two peaks dominate the optical spectra, the weight of the transition 1 increasing with increasing concentration of solitons while that of transition 2 is decreasing with increasing concentrations. We found that this transition practically disappears at a concentration of 8 % of solitons.

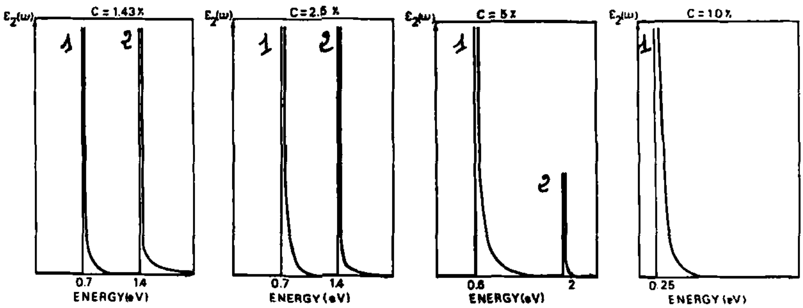

FIGURE 1 Evolution of $\varepsilon_2(\omega)$ with the soliton concentration

CONCLUSION

In this work we have presented a new method to determine theoretically the optical constants of a one dimensional crystal. This method has been applied to soliton lattices in $(CH)_x$ but can be extended easily to treat others polymers. The results obtained are in quantitative agreement with previous calculations and in qualitative agreement with the experimental data.

REFERENCES

1. K. Fesser, A.R. Bishop and D.K. Campbell, Phys. Rev. B 27, 4804, (1983) and references therein.
2. M. Jestin, M. Kabbaj, J.P. Albert and C.Jouanin, J. de Physique C3, 499, (1983).
3. G. Gilat and L.J. Raubenheimer, Phys. Rev. 144, 390, (1966).