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J. P. Albert [a] & C. Jouanin [a]
[a] Centre d'Etudes D'electronique des solides, Université des Sciences et Techniques du Languedoc, 34060, MONTPELLIER, FRANCE
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SOLITON INTERACTION AND SOLITON LATTICE IN POLYACETYLENE

J.P. ALBERT and C. JOUANIN
Centre d'Etudes d'Electronique des Solides
Université des Sciences et Techniques du Languedoc
34060 MONTPELLIER - FRANCE

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We report here an analysis of the electronic properties of a periodic lattice of solitons in infinite chains of polyacetylene.The method used is a Green's function recursive method which allows an exact determination of the density of states of the system. We have also determined the energy per soliton of this lattice as a function of the concentration of dopants. A semiconductor-metal transition is found to occur at a doping level C $\sim$ 7%.

INTRODUCTION

There has been great recent interest in solitons in polyacetylene since the proposal by Rice[1] and Su, Schrieffer and Heeger[2] (SSH) that neutral and charged solitons will play an important role in the magnetic, optical and electric properties of this substance. Rice and Timonen[3], Lin Liu and Maki[4] and Horovitz[5] studied the properties of a soliton lattice in the continuum limit. Mele and Rice[6] have dealt with the properties of such a lattice in a finite polyacetylene chain. They focused specially on the semi-conductor-metal transition and found that when the effects of disorder, pinning impurities and interchain coupling are taken into account, this transition occurs below 5 % dopant concentration as it is observed experimentaly. In this work, we are

interested with the electronic properties of a regular soliton lattice in an infinite chain of $(CH)_x$. We determine the characteristics of the electronic structure of such a lattice up to a 12.5 % concentration. For each concentration we also obtain the energy per soliton. Within our calculation uncertainties we find a general good agreement between these energies and those obtained by Horovitz in the continuum approximation. Finally, following an argument due to Lin Liu and Maki[4] we obtain a semiconductor-metal transition at a doping level $C \sim 7$ %.

THEORETICAL FORMULATION

Hamiltonian

The infinite $(CH)_x$ chain is described by the SSH hamiltonian[2] :

$$H = \sum_{n,s} (t_{n,n+1} \, c^{+}_{n,s} \, c_{n+1,s} + h.c) + \frac{K}{2} \sum_{n} (u_{n+1}-u_n)^2 + \frac{M}{2} \sum_{n} \dot{u}_n^2 \qquad (1)$$

where

$$t_{n,n+1} = t_o - \alpha (u_{n+1} - u_n)$$

is the transfer integral.
$c^{+}_{n,s}$ ($c_{n,s}$) creates (annihilates) a π electron of spin s on the nth (CH) group and u_n is a configuration coordinate describing the displacement of the nth group along the chain. K and M are respectively the bond stretch spring constant and the CH mass. It is well known that such an infinite chain with one electron per site is unstable in the metallic ($u_n = 0$) configuration and will relax to a ground state described by $u_n = \pm (-1)^n u_o$. In equation (1) we choose the same values for the parameters as SSH, which leads to an equilibrium distortion $u_o = 0.042$ A and an energy gap $2\Delta = 1.4$ eV for the perfectly dimerized chain. Because of the existence of the twofold degenerate ground state an elementary excitation can occur, namely, a soliton which can be described by the variational function.

$$u_n = (-1)^n u_o \tanh \frac{n}{l} \qquad (2)$$

SSH found that $l \sim 7$ leads to the minimum increase of energy of the system, which gives a creation energy for an isolated soliton $E_s \sim 0.42$ eV. Associated with each soliton is a mid-gap localized electronic state. In the neutral soliton this state is singly occupied while the charged soliton corresponds to a doubly or unoccupied state.

The soliton lattice

Let us now consider a doped $(CH)_x$ chain. Within the soliton model, doping proceeds via the formation of charged solitons. We shall consider here the idealized situation where these solitons form a regular periodic lattice and their interactions with the dopants can be neglected. By analogy with (2) we choose to describe the bond alternations along the chain as a product of tanh functions.

$$u_n = (-1)^n u_o \prod_{-\infty}^{+\infty} \tanh\left(\frac{n-m^d/2}{l}\right) \quad \tanh\left(\frac{n+m^d/2}{l}\right) \quad (3)$$

Such a trial function describes an array of solitons centered at $x_s = \pm m \frac{d}{2} a$ where a is the distance between the (CH) groups along the chain. In the following calculations the values of d were selectionned so as the positions of these solitons coïncide with (CH) sites. The lattice thus obtained is schematically drawn in figure 1. Its unit cell is of length 2da and includes 2 solitons. It can be noted that in the limit $d \gg 1$, equation (3) appoaches asymptotically to the exact solution. In this trial function, given a density of solitons $n_s = (d)^{-1}$, the only free parameter is l which is variationaly determined by minimizing the energy of the system.

Energy and density of states of the system

Because of its periodicity, it is only necessary to minimize the energy corresponding to a unit cell of the infinite lattice. This energy can be written as :

$$E = E_e + E_l \quad (4)$$

The electronic energy is given by :

$$E_e = \int_{-\infty}^{EF} \varepsilon N(\varepsilon)\, d\varepsilon \quad (5)$$

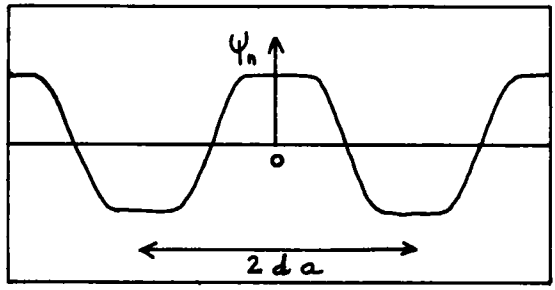

FIGURE 1 Form of the order parameter $\psi_n = (1)^n u_n$ for the soliton lattice

Where E_F is the Fermi energy and $N(\varepsilon)$ is the electronic density of states. E_1 corresponds to the remaining static terms in equation (1) and involves a simple summation of elastic terms over the 2d sites in the unit cell. The electronic density of states has been evaluated by a Green-function technique specially suited to the study of such tight-binding one dimensional systems[7].

$N(\varepsilon)$ is written as :

$$N(\varepsilon) = -\frac{2}{\pi} \sum_n \text{Im } G_{nn}(\varepsilon) \tag{6}$$

Where the summation goes over the sites in the unit cell and G_{nn} is the diagonal element of the Green function of the system :

$$G(\varepsilon) = (\varepsilon - H_e)^{-1} \tag{7}$$

H_e is the electronic part of H given by (1)

It may be shown that these diagonal elements can be exactly expressed as :

$$G_{nn}(\varepsilon) = (\varepsilon - |t_{n,n+1}|^2 \delta^+_{n+1} - |t_{n,n-1}|^2 \delta^-_{n-1})^{-1} \tag{8}$$

where the $\delta^{\pm}_n$ verify the relations :

$$\delta^{\pm}_n = (\varepsilon - |t_{n,n+1}|^2 \delta^{\pm}_{n\pm1})^{-1} \tag{9}$$

Thus, once a starting $\delta^{\pm}_n$ is determined by a boundary condition imposed by the problem, the rest of the δ's

can be computed using this recursion relation. In our case, the periodicity of the soliton lattice is 2d and so the boundary condition is simply.

$$G_{nn}(\epsilon) = G_{n+2d,n+2d}(\epsilon) \tag{10}$$

which gives the following condition on the δ's :

$$\delta^{\pm}_{nn}(\epsilon) = \delta^{\pm}_{n+2d,n+2d}(\epsilon) \tag{11}$$

Equations (11), (9), (8), (6) then allow the determination of $N(\epsilon)$. As it has been already said, the width of the solitons was then minimized in order to seek the minimum value E_m of the total energy. The energy per soliton at the concentration $n_s = (d)^{-1}$ is then given by :

$$E_s(n_s) = \frac{1}{2}(E_m - E_o)$$

where E_o is the energy corresponding to 2d (CH) units of the perfectly dimerized chain.

RESULTS

Energy spectrum and density of states

The numerical calculations were done for several densities of charged solitons extending from 1.25% to 12.5%. The energy spectrum for such lattices is schematically drawn in figure (2) in an extended zone scheme. The corresponding densities of states are drawn in figure (3).

Because of the new periodicity 2da of the lattice, two gaps are opening at wave vectors $q = \frac{\pi}{2a} - \frac{\pi}{2da}$. According to the type of doping (donors or acceptors) the Fermi level lies in one or in the other of these gaps. The lower valence band is completely full with (2d-2) electrons per unit cell while the conduction band is empty. Between these two bands the "soliton" band has 4 states per unit cell and is either completely empty (acceptor doping) or full (donor doping) However, as this band is symmetrical with respect to the energy zero it does not contribute to the evaluation of the total energy. In figure 4 we have reported the behavior of the half

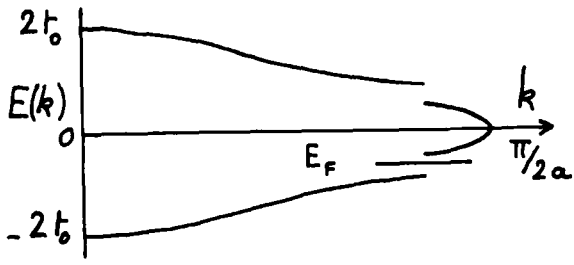

FIGURE 2 Electronic band structure of the charged soliton lattice in the extended zone scheme. The Fermi energy is indicated by a vertical bar (case of acceptor doping).

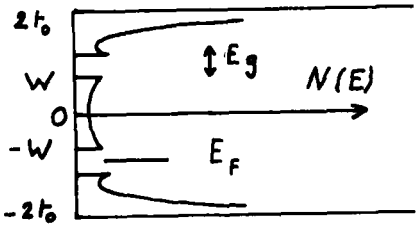

FIGURE 3 Electronic density of states of the charged soliton lattice. The Fermi energy is indicated by a vertical bar (case of acceptor doping).

width W of this band and of the gap Eg between this band and the conduction or valence one with respect to the concentration of solitons.

These curves were drawn for a fixed value of l namely l = 7 which is the isolated soliton width, and for that value of l which was found to minimize the total energy. The influence of the relaxation of the soliton is thus clearly shown. These results show that until a doping level of about 2,5 % the soliton lattice has the same electronic characteristics W = 0, Eg = 0.7 eV as that of isolated solitons. This is in fact quite natural as up to this doping level the solitons are too far apart to interact significantly. Then the half width of

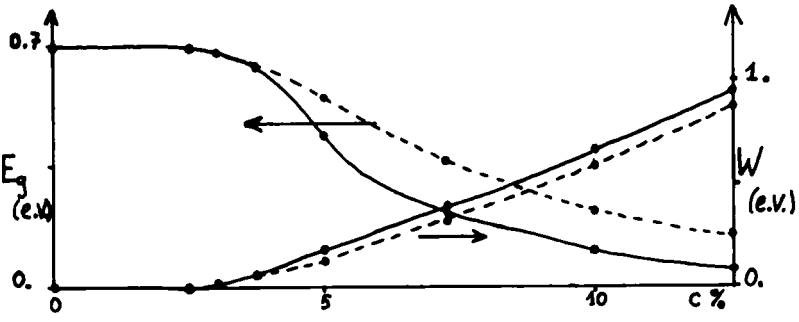

FIGURE 4 Half-width W of the soliton band and energy gap Eg as functions of the dopant concentration.
---- curve obtained with a fixed value of the soliton width l = 7.
____ curve obtained with the value of l which minimizes the total energy.

the soliton band W evolves regularily from 0 at 2.5 % to 0.9 eV at 12.5 %. The gap Eg evolves also regularily from 0.7 eV at 2.5 % to 0.05 eV at 12.5 %. The same qualitative behaviour was found by Mele and Rice[6] in their study of a lattice of solitons in a finite chain.

We thus find, in accordance with them, that within this concentration range, the Peierls instability is strong enough to prevent the closing of a gap and thus the appearance of a finite number of states at the Fermi level. On can also note from these curves that Eg is more sensitive than W to the relaxation of the soliton.

In figure 5 we have plotted the energy per soliton $E_s(n_s)$ with respect to the concentration of solitons. Here we also find that up to a 2.5 % concentration, this energy E_s is practically the energy of an isolated soliton in an infinite chain (0.44 eV). Due to the repulsive interactions between the solitons this energy then increases with increasing concentrations. The curve which is drawn is the energy law $E_s(n_s)$ found by Horovitz[5] in his study of the soliton lattice in the continuum limit.Note that we were unable to detect the absolute mininum he found at a 3 % concentration because it is too shallow and lies within our calculation

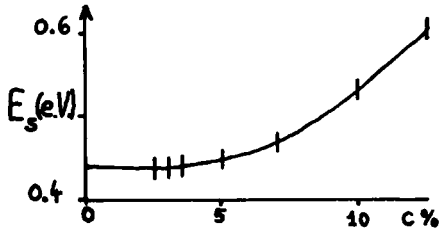

FIGURE 5 Energy per soliton $E_s(n_s)$ as a function of their density. The curve is that obtained theoretically by Horowitz.

uncertainties. However the general agreement is quite good, even up to a concentration as high as 12.5 % where our trial function is rather approximate.

CONCLUDING REMARKS

In this work we have determined the characteristics of the electronic structure of a periodic array of charged solitons in infinite chains of $(CH)_x$. The soliton lattice produces a narrow band in the middle of the dimerization gap. However the Peïerls instability is strong enough to prevent the closing of the gap up to a 12.5 % concentration. This soliton band is normally electrically inactive because it is either completely full or empty. However, as it was noted by Lin-Liu and Maki[4] the occurence of a neutral soliton in the lattice will provide an electron or a hole in this band which leads now to an active band both electrically and magnetically. The required energy δE to introduce such a neutral soliton is given by :

$$\delta E = E_s(n_s) - W$$

When δE is negative, it is thus energetically favorable to introduce neutral solitons and the polyacetylene becomes metallic. We find this semi-conductor-metal transition at $\sim$ 7 %. Although this critical soliton density appears to be too large compared with the experimental data ($\sim$ 1 %) we feel that inclusion of disorder, interchain coupling, interactions with impurities can reduce this value significantly.

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