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ELEMENTARY EXCITATIONS AND ENERGY DISPERSION IN TTF-TCNQ

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Abstract In a one-dimensional conductor such as TTF-TCNQ, boson-like excitations represent plasmons due to strand-strand interactions. The plasmon dispersion relation may be dipped due to polarons. This polaron effect may be important since both one- and two-band models of Williams and Bloch show some deviations from the data of Ritsko et al.

INTRODUCTION

At a conference on quasi-one-dimensional systems, Krivnov and Obchinnikov reported a Feynman-type relation for the excitation energy of a nearly ideal one-dimensional Fermi system.[1]

It is the purpose of the present article to show first that a similar structure factor-energy relation can be derived for a one-dimensional electron system without using a variational method. We shall then discuss the plasmon dispersion relation in TTF-TCNQ obtained experimentally by high-energy inelastic electron scattering by Ritsko et al.[2] They observed a negative plasmon dispersion in the chain direction.

POLARON EFFECT

In the long wavelength limit, the chain-diagram contribution to the structure factor S(q) is given by

$$S(q) = \frac{1}{\beta n} \sum_j \frac{\lambda_j}{1+\lambda_j u(q)} \qquad (1)$$

where $u(q)$ is the Coulomb potential, $\beta = 1/kT$, n is the electron density, and the λ_j are the eigenvalues of the effective propagator representing the unit of the chains which can be given exactly.

For small q, the eigenvalues can be expanded in a Taylor series. Introducing the result into Eq. (1), we obtain

$$S(q) = \frac{q^2}{\varepsilon(q)} [1+2f(\varepsilon)] , \qquad (\hbar = 1,\ 2m = 1) \tag{2}$$

where $f(\varepsilon) = 1/[e^{\beta\varepsilon}-1]$ and

$$\varepsilon(q) = \frac{q}{\sqrt{\pi}} \{4p_F u(q) + \pi(q^2+4p_F^2)\}^{\frac{1}{2}} \tag{3}$$

The appearance of the Bose distribution in Eq. (2) is natural. Note that it represents quasi bosons without mass. For absolute zero, Eq. (2) reduces itself to what Krivnov and Obchinnikov reported.

The excitation energy given by Eq. (3) can be plasmon-like if the interaction potential $u(q)$ is inversely proportional to q^2. This possibility can be expected for TTF-TCNQ through strand-strand interactions.

The negative dispersion relation observed experimentally may not be explained if the electrons are completely free. One possibility for causing such a negative dispersion is the electron-phonon interaction.

For slow electrons, one can use the polaron effective mass given by

$$m^* = m(1 + \alpha/6) \tag{4}$$

where α, the coupling constant, is less than 6. One can then show that in the long wave length limit, the dispersion relation is

$$\omega^2 = \omega_p^2 + [\frac{p_F q}{2m}]^2 (1 - \frac{\alpha}{3}) \tag{5}$$

where ω_p is the plasmon frequency (energy) which is determined by the electron density and the strength constant of the effective

electron interaction. Therefore, if the polaron coupling constant α is slightly larger than 3, the dispersion relation can be negative. Although the above approximation becomes poor for such a value of the coupling constant, the polarons seem to promote a negative dispersion relation.

DISCUSSIONS

The negative energy dispersion was predicted by Williams and Bloch[3] based on a single band tight binding model with energies given by $W(1-\cos qa)/2$ where W is the band width, a is the unit cell dimension of order 1.5A. Later, they generalized the treatment to two doubly degenerate band model suitable to TTF-TCNQ.

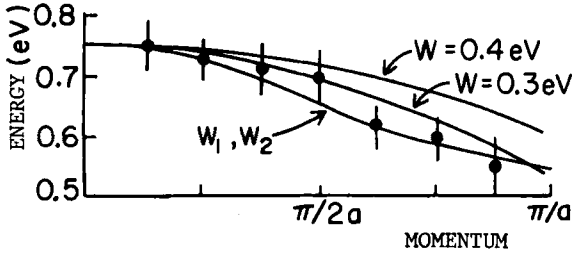

FIGURE 1 Energy Dispersion of TTF-TCNQ.

We have recalculated the energy dispersion curve of TTF-TCNQ to confirm their numerical results. We have found that either a single band model with W = 0.3 eV or a two double-band model with W_1 = 0.4 and W_2 = 0.2 eV fits the data of Ritsko et al fairly well, in agreement with Williams and Bloch (Figure 1). However, the single band model reproduces the small momentum region well, while the two band model fits the larger momentum region better. Therefore, it appears as though a cross-over between these two models takes place at momentum $\pi/2a$. Together with the possibility of a polaron effect and the observation of the acoustic mode, further investigations of the dispersion relation seem to be necessary.

Concerning the possible role played by polarons, we remark

that the ground state of all trans-polyathetylene is degenerate and topological defects called solitons have been used to explain the transport properties. On the other hand, polyparaphenylene has a nondegenerate ground state so that it seems difficult to apply the same soliton model for its transport properties even though the properties are similar. For this reason, Bredas, Chance and Silbey proposed a polaron model for these polymers.[4] The binding energy of a polaron is estimated to be .05 eV for polyathetylene and .03 eV for polyphenylene.

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