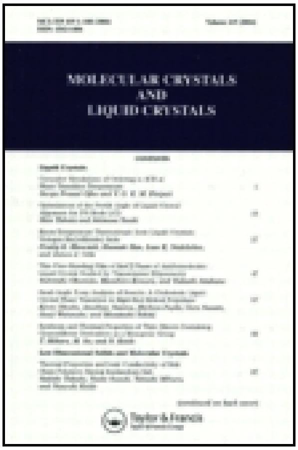

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Frequency-dependent conductivity of polyacetylene

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FREQUENCY-DEPENDENT CONDUCTIVITY OF POLYACETYLENE*

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The finite-temperature frequency-dependent conductivity of a polymer chain such as trans-polyacetylene has been calculated using a two-band tight-binding model. A collective mode in the dielectric response gives rise to energy absorption below the interband threshold even when no account is taken of possible soliton modes. The effect of impurities on this mode has been included phenomenologically by introducing a collision time. The effect of impurities on the density of states has been studied with diagram techniques and the CPA approach. The contributions of these effects to the optical and electron energy loss spectra of trans-polyacetylene are discussed.

INTRODUCTION

Considerable interest has been generated recently by the suggestion[1] that soliton-like excitations may exist in doped trans-polyacetylene and that these excitations have a strong effect on magnetic and optical properties of the

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*Computer time for this project was supplied by the Computer Science Center of the University of Maryland system. One of the features of the optical absorption spectrum[2] which has been considered as evidence for the connection between doping and soliton formation is the peak which lies in the midst of the region below the threshold for interband excitations and whose height depends on impurity density. Because this midgap absorption is such important evidence for the midgap states that result from the soliton formation, it is essential that other possible contributions to this midgap absorption be considered. We recently pointed out[3] that an alternative explanation of the peak is possible based on the dielectric response of the system without solitons. In this paper we briefly describe a calculation of the finite-temperature frequency-dependent conductivity of a two-band tight-binding model. The contribution of impurities is included phenomenologically by introducing a collision time. A detailed presentation will be made elsewhere.[4] We discuss the collective mode in the di-electric response and its effect on the optical absorption of doped trans-polyacetylene and we present preliminary results of a more fundamental study of impurity effects on the dielectric response.

THEORY

The two-band tight-binding model[1] is used to describe the ground state properties of $(CH)_x$. The electronic Hamiltonian for one spin subsystem of π electrons is

$$H = \Sigma_n V_n (C^+_{n+1} C_n + C^+_n C_{n+1}). \qquad (1)$$

The sum is over the π orbitals of each of the CH groups. In the Peierls distorted ground state, the bond length between adjacent sites alternates between long and short bonds and an alternating pattern of single and double π bonds results. The hopping integral is

$$V_n = t_o + (-1)^n t_1 \qquad (2)$$

with t_1 proportional to the amplitude of bond alternation. With this V_n there are two π-electron bands with a gap between conduction and valence bands of $2\Delta = 4|t_1|$, a maximum band energy $E_m = 2|t_o|$, and a density of states which has square-root singularities at the band edges. Additional soliton-like distortions of the lattice can occur when trans-$(CH)_x$ is doped, resulting in new forms for V_n. To investigate alternative explanations of the optical spectrum, we have assumed that <u>no</u> distortion of the lattice occurs upon doping and that the V_n remain unchanged from Eq. (2).

The optical and electron energy loss spectra are both related to the dielectric response function ε. To estimate ε we[4] first calculate the finite-temperature frequency-dependent conductivity $\sigma(\omega)$ using the Kubo formula for the linear response and then relate σ to ε. To make the problem tractable we assume that $(CH)_x$ is a matrix of parallel linear chains with no inter-chain conduction so that $\sigma = \rho_c\sigma_c$ where ρ_c is the density of chains and σ_c, the conductivity of a single chain. The calculation is further simplified by only evaluating the conductivity when the component of the field wavevector parallel to the chain vanishes. In this limit the electric field can be described with a time-dependent scalar potential and the Kubo formula requires the evaluation of a density-current correlation function. The current flowing between sites n-1 and n and between sites n and n+1 need not be the same in a two band model so the results are averaged to eliminate the local corrections.

The details of this calculation are presented elsewhere.[4] Here we present the final result for $\sigma(\omega)$. Choosing units such that

$$\varepsilon(\omega) = \varepsilon_o + \frac{i\alpha\sigma(\omega)}{\omega}, \tag{3}$$

we have

$$\sigma(\omega) = \frac{2i}{\hbar\omega}\int \frac{dz}{[(E_m^2-z^2)(z^2-\Delta^2)]^{1/2}}\left(\frac{1}{\exp(-\beta(E_f+z))+1} - \frac{1}{\exp(-\beta(E_f-z))+1}\right) \times \left(z^2 - \frac{E_m^2\Delta^2}{z^2-(\frac{\hbar\omega}{2})^2}\right). \tag{4}$$

β is the inverse temperature and α is a constant of order one whose exact value depends on ρ_c. We have set α to one to obtain our results. The branch cuts of the square root function in Eq. (4) are chosen to occur for z inside the bands. The integral is evaluated by contour integration around the branch cuts. When $\hbar\omega/2$ is inside one of the bands, the contour integration must be performed carefully to obtain the contribution from the pole in the last factor of Eq. (4).

Eq. (4) is exact for a system of independent electrons that are governed by Eqs. (1) and (2). It is also exact for any arbitrary filling of the bands. The effect of impurities as donors or acceptors can be included by varying E_f. The simplest method of including the scattering by impurities is to replace ω with $\omega+i\lambda$ in σ.
Here λ represents a phenomenological inverse collision time. This replacement does not, however, account for changes in the density of states induced by the dopants. Once this replacement has been made, the integrals can be done numerically to determine σ.

The R_e for energy absorption from inelastic electron scattering is given in the long wavelength limit[5] by

$$R_e(\omega) \sim \operatorname{Im} \varepsilon^{-1}(\omega) \; . \tag{5}$$

The rate R_o of optical absorption of a transverse field incident perpendicular to the chains is[4]

$$R_o(\omega) \sim \operatorname{Im} (k^2-\omega^2\varepsilon(\omega)/c^2)^{-1} \tag{6}$$

$$= \frac{\omega^2\varepsilon_2(\omega)/c^2}{(k^2-\omega^2\varepsilon_1(\omega)/c^2)^2 + (\omega^2\varepsilon_2(\omega)/c^2)^2} \tag{7}$$

Here k is the wavevector of the field and ε_1 and ε_2 are the real and imaginary parts of ε. According to Eq. (7), R_o peaks when ε_2 peaks provided ε_2 is small compared to $(kc/\omega)^2-\varepsilon_1$. This condition is satisfied for ω where transitions are allowed. However, R_o is also enhanced whenever the denominator in Eq. (7) passes through a minimum. This latter situation occurs when a collective mode in the dielectric response enhances the field in the system and thus increases the energy absorption. The midgap states due to soliton formation enhance R_o by enhancing ε_2. Our aim in this study is to examine the importance of collective modes for midgap absorption.

RESULTS

Typical results for the real and imaginary parts of the conductivity, σ_1 and σ_2 , are shown in Fig. 1. All of the results were obtained using $E_m = 5.0$ eV and $\Delta = 1.0$ eV to approximate the band structure of $(CH)_x$. The inverse temperature β is 100 eV^{-1} . These results are almost identical to those at zero temperature with the important

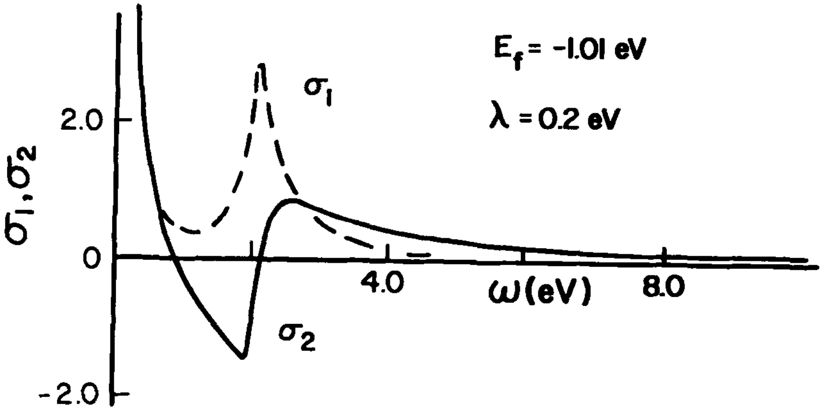

FIGURE 1. Real and imaginary parts of the frequency dependent conductivity

difference being the broadening of the various peaks. The inverse collision time used in Fig. 1 is 0.2 eV.

For λ=0 and zero temperature, σ_1 has a δ-function singularity at ω=0 if one of the bands is partially filled. Otherwise it is finite only for max $(2\Delta, 2|E_f|) < h\omega < 2E_m$. Furthermore, σ_1, has a singularity at the upper edge of this region and is cut off at a finite value at the lower edge when $|E_f|>\Delta$. At finite temperature and λ this structure is broadened with the singularity at $2E_m$ no longer apparent. Moreover, the δ-singularity is weaker and σ_1 is small, but finite, in the gap. Similarly, σ_2 has singularities at 2Δ and $2E_m$ when λ=0 and has a Drude part proportional to $1/\omega$ near the origin when T > 0 or when a band is partially filled. When λ is finite, the singularity at $2E_m$ is not apparent, and the singularity at 2Δ and the Drude part are broadened.

When the wavevector k in Eq. (7) for R_o is zero, R_e and R_o are proportional to $\mathrm{Im}(1/\varepsilon)$. We calculate R_e and R_o in this limit to simplify the presentation. The $\mathrm{Im}(1/\varepsilon)$ is shown in Figs. 2 and 3 as a function of E_f and λ. The results were found by ignoring core polarization and using ε_o = 1 (see Eq. (3)).

A peak in absorption occurs above the gap due to interband transitions. Moreover, absorption also occurs in the gap because ε_2 is finite in the gap when impurity scattering occurs. A peak appears near midgap because a collective mode occurs when $|\varepsilon|$ has a minimum in the

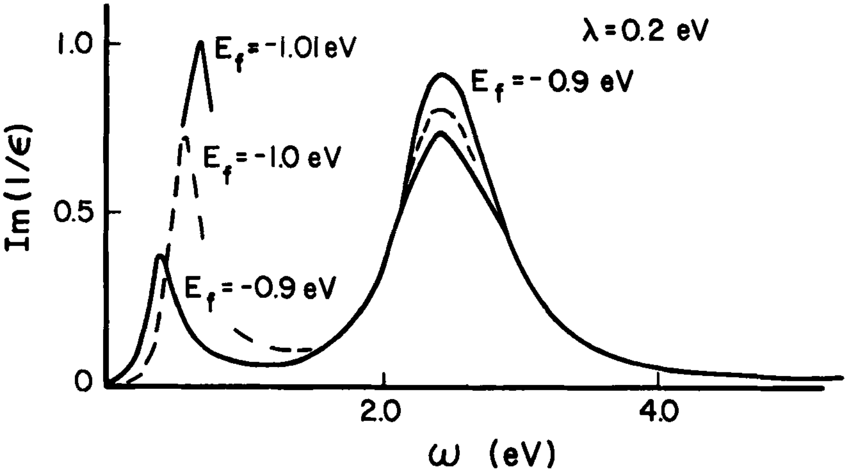

FIGURE 2. Absorption spectra as a function of band filling.

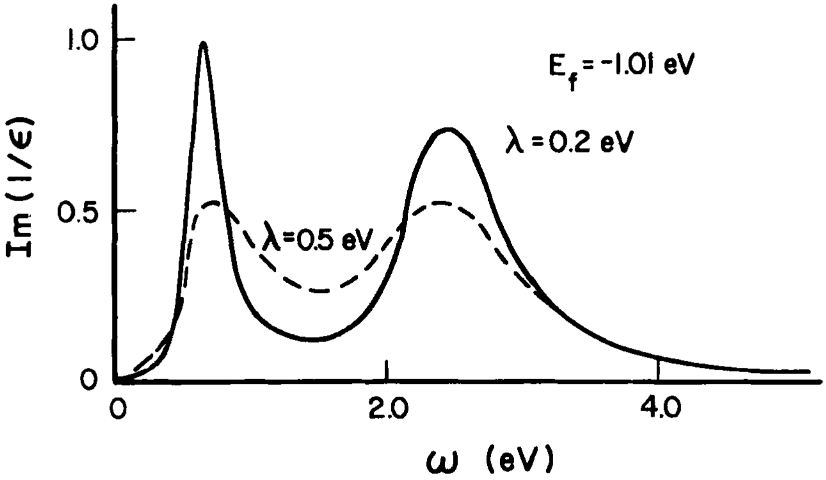

FIGURE 3. Absorption spectra as a function of collision time.

gap. This happens because σ_1 is small near midgap and σ_2 is rapidly varying through zero. These results strongly suggest that the collective mode makes an important contribution to the midgap absorption. The position of the peak in absorption does, however, depend on the choice of parameters. It shifts to slightly lower frequencies and is weaker if the small core polarization is included in Eq. (3) to insure that $\varepsilon(0)$ is in the range from 10 to 12 recently suggested[6] for $(CH)_x$. In contrast, the peak shifts to higher frequencies for the absorption of radiation with $k \neq 0$.

The observed midgap absorption[2] increases and the interband absorption decreases when the doping level increases. The dopant used, AsF_5, is an acceptor. Increasing such doping corresponds to decreasing E_f from -1.0 eV. It is apparent from Fig. 2 that the collective mode induced enhancement is consistent with this result. This happens because the Drude part of σ_2 increases when more holes in the lower band(more acceptors) are present. When the doping is compensated, the observed midgap absorption disappears while the interband absorption remains suppressed. Such compensation is modeled by allowing E_f to increase. Fig. 2 shows that the midgap peak is suppressed and the interband peak enhanced when E_f increases. During compensation λ should also increase. This suppresses both peaks. Thus increasing E_f and λ gives a result consistent with the effect of compensation. Nonetheless, it should be emphasized that phenomenological arguments using E_m and λ are only suggestive of the true effects of the doping. Fundamental calculations of σ as a function of doping are required. We mention briefly our initial results in this direction in the next section.

Finally, it should be noted that our results are also consistent with the low q electron energy loss spectra[7] of $(CH)_x$ in which a midgap peak is also seen after doping. However our present calculations were restricted to $q=0$ and so do not yet warrant a detailed comparison with the experimental results.

FUNDAMENTAL THEORY OF THE DOPING

A study of impurity doping has been begun[8] using diagram techniques[9] and the CPA formalism[10] within the context of a two-band tight-binding model with fixed hopping integrals. Attention has been focused so far on the simpler problem of obtaining analytical expressions for the density of states. This is an essential first step in the calculation of $\sigma(\omega)$. The impurity interaction has been modeled with an on-site energy shift. In this model the main bands are only slightly modified away from the edges and the square root singularities at the edges are reduced to fourth root singularities. A narrow impurity band does appear in the gap. This band appears near midgap only for impurity energy shifts comparable to the bandwidth and at high impurity densities. Optical absorption at midgap due to midgap states is unlikely in this model. Only enhanced absorption due to the collective mode will occur. We are presently investigating models using more realistic impurity potentials to determine if midgap states can be created in the absence of solitons. Preliminary results using the effective mass equation suggest that not all impurity states will lie near the band edges. Studies underway that go beyond the effective mass approximation should reveal how important impurity states in the gap, in conjunction with the collective mode, are for the midgap absorption.

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