Optical absorption in conducting polymers

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Optical absorption in a Peierls dielectric with various electron concentrations c has been studied. The concentration range correponding to a model of doped trans-polyethylene was investigated. The frequency dependence of the absorption between various singularities in the electron spectrum was found. It was shown that all direct transitions lying above the fundamental absorption edge Δ are, in the dipole approximation, forbidden for an ideal periodic structure. The restoration of the transitions due to destruction of long-range order (for $c \gg \Delta_1/v_F$) or due to melting (for $c \ll \Delta_1/v_F$) of the periodic structure was studied.

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I. INTRODUCTION

Intense experimental study of conducting polymers and analysis of the corresponding theoretical models (see reviews of the literature in Refs. 1–3) point to the essential role of disordered states such as domain walls, polarons, periodic superstructures. Optical absorption effects for various electron concentrations are important in the study of these systems.

In the present work optical absorption in a Peierls dielectric as a function of the number of electrons per atom, ρ, is studied. The concentration region examined was $c = |\rho - 1|/a \ll a^{-1}$, where a is the mean interatomic distance. The model considered is suitable for describing doped trans-polyethylene.

In the concentration region $|\rho - 1| \ll 1$ we can restrict ourselves to the continuum approximation[4,5] for the electron wave functions and the lattice deformation potential $\Phi(x)$:

$$\psi(x) = 2^{1/2}[U(x)\cos(\pi x/a) + iV(x)\sin(\pi x/a)],$$
$$\Phi(x) = \Delta(x)\cos(\pi x/a).$$

To the same approximation the components of $\bar{\psi}(x) = (U(x), V(x))$ and $\Delta(x)$ are related by the equations for the eigenvalues of the energy E_μ:

$$\left(Iv_F\frac{\partial}{\partial x} + \sigma_x\Delta + \sigma_y E_\mu\right)\bar{\psi}_\mu = 0, \tag{1}$$

where v_F is the Fermi velocity in the metallic phase; I and $\sigma_{x,y,z}$ are the unit matrix and Pauli matrices. The current density operator is of the form

$$J = v_F\sigma_x. \tag{2}$$

For calculating the optical absorption we use the usual expression for the imaginary part of the permittivity in the dipole approximation:

$$\varepsilon_2(\omega) = \frac{4\pi e^2}{\omega^2 s_\perp L}\sum_{\mu_1\mu_2}|J_{\mu_1\mu_2}|^2\delta(E_{\mu_2} - E_{\mu_1} - \omega), \tag{3}$$

where L is the length of the system and $s_\perp$ is the cross section for one chain,

$$J_{\mu_1\mu_2} = \int \bar{\psi}_{\mu_2}^*\sigma_x\bar{\psi}_{\mu_1}dx. \tag{3a}$$

In the absence of external fields and without taking thermal and quantum fluctuations into account, the equilibrium state of the system is determined from the self-consistency condition

$$\frac{\Delta}{g^2} + \frac{1}{2}\sum_\mu \bar{\psi}_\mu^*\sigma_x\bar{\psi}_\mu = 0, \tag{4}$$

where the sum is taken over doubly filled (taking account of spin) states μ; g is the electron-phonon interaction constant. The system of Eqs. (1) and(4) have a solution[6] with one forbidden band $E_+^2 > E^2 > E_-^2$ in the E_μ^2 spectrum under the condition that $\Delta(x)$ satisfies the equation

$$\Delta''' - 6\Delta^2\Delta' + A\Delta' = 0, \quad A = 2(E_+^2 + E_-^2). \tag{5}$$

Eq. (5) has various types of solutions, describing a periodic structure,[6] isolated domain walls[7] and polarons.[8]

II. OPTICAL TRANSITIONS IN A PERIODIC STRUCTURE

The solution of Eqs. (1) and (4) for an ideal periodic structure has the form[6]

$$\Delta(x) = \Delta_k\,\mathrm{sn}\left(\frac{\Delta_k(x - x_0)}{kv_F}, k\right), \quad \Delta_k = k^{1/2}\Delta_1,$$

$$U_E = \left|\frac{p+b}{2L(\bar{p}+b)}\right|^{1/2}\exp\left\{\pm iE\gamma\int_0^x\frac{dy}{|p+b|}\right\},$$

$$V_E = \pm\left|\frac{q+b}{2L(\bar{q}+b)}\right|^{1/2}\exp\left\{\pm iE\gamma\int_0^x\frac{dy}{|q+b|}\right\}, \tag{6}$$

$$\gamma = (b^2 - \Delta_1^4)^{1/2}, \quad b = 2E^2 - \Delta_k^2(1 + k^{-2})/2,$$
$$\bar{p} = \bar{q} = \bar{\Delta}^2 = \Delta_k^2k^{-2}(1 - E(k)/K(k)),$$

where $2\Delta_1$ is the gap in the electron spectrum for a Peierls dielectric with $\rho = 1$, when $\Delta(x) = \Delta_1 = \text{const}$. The parameter k ($0 \leq k \leq 1$) is determined by the concentration of additional electrons $c = \Delta_k/2K(k)k$; $K(k)$ and $E(k)$ are the complete elliptical integrals of the first and second order, and $\mathrm{sn}(x, k)$ is the Jacobi elliptical sine.

The wave function is characterized by the quasimomentum $\varkappa$. The $\varkappa(E)$ dependence is shown in Fig. 1 where $\varkappa_0 = \pi/l = \pi/2c$, where l is the period of the function $\Delta(x)$. The spectrum of the system consists of three allowed $|E| > E_+$, $|E| < E_-$ and two forbidden bands $E_- < |E| < E_+$, where $E_\pm = \Delta_k(k^{-1} \pm 1)/2$. A splitting occurs at the edges of the band for

$$E(\varkappa) - E_\pm = (\varkappa - \varkappa_0)^2/2M_\pm, \quad M_\pm = (1 \pm k\bar{p})^2/2(1 \pm k)v_F^2. \tag{7}$$

The choice of the sign in Eq. (6) is determined by the branch of the spectrum; the sign is + for branch 1 and – for branch 2. The central allowed band $|E| < E_-$ must

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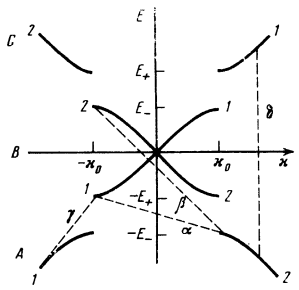

FIG. 1.

be empty for $\rho<1$ or completely full for $\rho>1$. The observed optical properties should be the same for these two cases.

We shall consider the case when the central band is empty, $\rho<1$. This case corresponds to acceptor-doped polyethylene. It is evident that optical transitions take place with conservation of quasi-momentum and the total momentum $\varkappa$ is conserved, in general, to within a reciprocal lattice vector: $\varkappa_2-\varkappa_1=2\varkappa_0 n$. Equation (5) takes the form

$$\varepsilon_2(\omega)=\frac{4\pi e^2}{\omega^2 s_\perp}\sum_{n=0,\pm1,\ldots}\int\frac{d\varkappa}{2\pi}\times\delta(E_2(\varkappa+2\varkappa_0 n)-E_1(\varkappa)-\omega)\times\left|\int(U_2^*(\varkappa+2\varkappa_0 n)V_1(\varkappa)+V_2^*(\varkappa+2\varkappa_0 n)U_1(\varkappa))\,dx\right|^2. \tag{8}$$

To evaluate the matrix element in Eq. (8) it is convenient to express the function V in terms of U. Using Eqs. (4) and (6) we obtain

$$U(x+l/2)=\pm V(x)\exp(i\varkappa l/2),\qquad V(x+l/2)=\pm U(x)\exp(i\varkappa l/2),$$

for the upper and lower bands

$$V=\frac{U}{p+b}[2E\Delta(x)i\pm\gamma], \tag{9a}$$

for the middle band

$$V=\frac{U}{|p+b|}(-2E\Delta(x)i\pm\gamma). \tag{9b}$$

We shall consider the main optical transitions.

1. Absorption from band A to band C (transition δ in Fig. 1). Using Eq. (9) we obtain for the direct transition with $n=0$

$$J_\delta^{(0)}=\int U_2^*U_1\left[2i\Delta(x)\left(\frac{E_1}{p+b_1}-\frac{E_2}{p+b_2}\right)-\frac{\gamma_1}{p+b_1}+\frac{\gamma_2}{p+b_2}\right]dx. \tag{10a}$$

Since $E_2=-E_1$, $\gamma_2=\gamma_1$ and $b_2=b_1$, we obtain from Eq. (9)

$$J_\delta^{(0)}=\frac{E}{(\bar p+b)L}\int\Delta(x)\,dx=0. \tag{10b}$$

The transition considered is thus forbidden in the dipole approximation for an ideal periodic system, i.e., the absorption c is absent.

We shall write the matrix element for transitions with $n\neq0$ in a form which is more convenient for the present case, using Eq. (9):

$$J_\delta^{(n)}=\frac{L}{l}\int_0^{l/2}(U_2^*V_1+V_2^*U_1)\,dx+\frac{L}{l}\int_0^{l/2}[(\pm U_2^*)(\pm V_1)+(\pm V_2^*)(\pm U_1)]\times\exp\frac{i\varkappa nl}{2}dx. \tag{11}$$

From Eq. (11) we obtain for transitions with $\varkappa_1\varkappa_2>0$ $(A_2\to C_1,\ A_1\to C_2)$

$$J_\delta^{(n)}=\frac{L}{l}\int_0^{l/2}(U_2^*V_1+V_2^*U_1)[1-(-1)^n]dx.$$

Transitions with $n=2m$ are consequently forbidden. In an analogous way we find that for $\varkappa_1\varkappa_2<0$ $(A_1\to C_1,\ A_2\to C_2)$, transitions with $n=2m+1$ are forbidden.

Suppose now that $\varkappa_1-\varkappa_2=(2n+1)2\varkappa_0$, $\varkappa_1\varkappa_2>0$. We obtain from Eqs. (6) and (11), after simple transformations,

$$J_\delta^{(2n+1)}=\frac{4L}{l}\frac{1}{2L(\bar p+b_2)(\bar q+b_1)]^{1/2}}\left\{-\int_0^{l/4}[(p+b_2)(q+b_1)]^{1/2}\times\cos\left(\varepsilon_2\gamma_2\int_0^x\frac{dy}{p+b_2}-\varepsilon_1\gamma_1\int_0^x\frac{dy}{q+b_1}\right)dx+\int_0^{l/4}[(q+b_2)(p+b_1)]^{1/2}\times\cos\left(\varepsilon_2\gamma_2\int_0^x\frac{dy}{q+b_2}-\varepsilon_1\gamma_1\int_0^x\frac{dy}{p+b_1}\right)dx\right\}. \tag{12}$$

Transitions with $n\neq0$ are most important in the limit $c\xi_0\ll1$, $\varkappa_0\ll\Delta_1$ $(\xi_0=v_F/\Delta_1)$, when the transition frequencies become close together. In this limit we obtain for $0<x<\frac14$

$$\Delta\approx\Delta_1\,\mathrm{th}\,(x/\xi_0),\quad p\approx\Delta_1^2,\quad q\approx\Delta_1^2[1-2\,\mathrm{ch}^{-2}(x/\xi_0)],\quad \varepsilon\approx\Delta_1+(\delta\varkappa)^2/2\Delta_1,\quad \delta\varkappa=\varkappa-\varkappa_0,\quad b=\Delta_1^2+2(\delta\varkappa)^2,\quad \gamma\approx2\Delta_1\delta\varkappa,$$
$$\varepsilon\gamma\int_0^x\frac{dy}{q+b}\approx\delta\varkappa x+\frac{\pi}{2},\qquad \varepsilon\gamma\int_0^x\frac{dy}{p+b}\approx\delta\varkappa x. \tag{13}$$

Substituting Eq. (13) into Eq. (12) we obtain

$$J_\delta^{2n+1}=\frac{4}{l\Delta_1^2}\int_0^{l/4}\Delta_1^2\,\mathrm{th}\frac{x}{\xi_0}\sin[(\varkappa_2-\varkappa_1)x]dx\approx\frac{2}{\pi(2n+1)}. \tag{14}$$

Similarly we obtain for transitions $\delta(A_1\to C_1)$ with $\varkappa_2-\varkappa_1=2\varkappa_0\cdot2n$

$$J_\delta^{(2n)}\approx2/\pi(2n-1). \tag{15}$$

Substituting Eqs. (14) and (15) into Eq. (8) we obtain

$$\varepsilon_2(\omega)=\frac{4\pi e^2}{\omega^2 s_\perp}\sum_n\int\frac{d\varkappa}{2\pi}\frac{4}{\pi^2(2n+1)^2}\delta\left[2\Delta_1-\omega+\frac{(\delta\varkappa_1)^2}{2\Delta_1}v_F^2+\frac{(\delta\varkappa_2)^2v_F^2}{2\Delta_1}\right] \tag{16}$$
$$=\frac{4\pi e^2}{\omega^2 s_\perp}\sum_n\frac{\Delta_1}{\pi^3(2n+1)^2}\frac{\theta[\omega-2\Delta_1-\varkappa_0^2v_F^2/2\Delta_1-(\varkappa_0+2n\varkappa_0)^2v_F^2/2\Delta_1]}{[\Delta_1(\omega-2\Delta_1)-\varkappa_0^2(2n)^2]^{1/2}}\Bigg],$$

where $\theta(x)$ is the Heaviside function.

It follows from Eq. (16) that the fundamental absorption edge splits into a sequence of thresholds $\omega-2\Delta_1\approx n^2\varkappa_0^2/\Delta_1$, $n\gg1$, with intensity falling off as $1/n^2$. For $\omega-2\Delta_1\gg c^2$, evaluation of the summation in Eq. (16) leads to the expression

$$\varepsilon_2(\omega)\approx e^2v_F/2s_\perp\Delta_1^2[\Delta_1(\omega-2\Delta_1)]^{1/2},$$

agreeing with the result for absorption in a uniform Peierls dielectric. Umklapp processes thus produce continuity in the average optical absorption for $c\to0$ in spite of the direct optical transition being forbidden.

2. Absorption from band A to band B. It is easy to deduce from Eqs. (7) and (8) that for a transition from the lower edge of band B with $\varkappa_1 = \pm\varkappa_0$, $\varkappa_2 = \mp\varkappa_0$, $n = 1$ (transition α in Fig. 1)

$$J_\alpha^{(1)} = \frac{1}{2L(\bar p^2-\Delta_1^2)^{1/2}} \int (p-\Delta_1^2)^{1/2}(q+\Delta_1^2)^{1/2}dx, \qquad (17)$$

$$\varepsilon_2(\omega) = \frac{4e^2}{\omega^2 s_\perp} J^2 \left(\frac{M^*}{\omega-(E_+-E_-)}\right)^{1/2}, \quad \frac{1}{M^*} = \frac{1}{M_+} + \frac{1}{M_-}.$$

For $c \to 0$ we have $k \to 1$, $M^* \to \Delta_1/v_F^2$, $J \to \pi(c\xi_0)^{1/2}/2$ and we find that in the limit of small concentrations Eq. (17) goes over into the expression for absorption by widely spaced solitons.[9,10] For $c \gg \xi_0^{-1}$ we have $k \ll 1$ and Eq. (17) becomes the expression corresponding to absorption across the gap $E_g = \Delta_k$ in the Fröhlich model. Using Eq. (11) we find for a transition to the upper edge of band B (transition β in Fig. 1) that $J_\beta^{(1)} = 0$. It follows that in the dipole approximation transition β ($A_1 \to B_1$, $A_2 \to B_2$) is forbidden for any frequencies.

We shall consider other transitions from band A to band B with a change in momentum $\varkappa_2 - \varkappa_1 = 2\varkappa_0 n$, $n > 1$. We obtain for transitions $A_1 \to B_1$, $A_2 \to B_2$ (transition γ in Fig. 1)

$$J_\gamma^{(n)} = \frac{L}{l}\int_0^{l/2} (U_2^* V_1 + V_2^* U_1)[1+(-1)^n]dx,$$

i.e. $J_\gamma^{(2n+1)} = 0$. On the other hand $J_\alpha^{(2n)} = 0$ for transitions $A_2 \to B_1$, $A_1 \to B_2$.

For transitions γ with even n, $\varkappa_2 - \varkappa_1 = 2\varkappa_0 \cdot 2n$, we obtain analogously to Eq. (12)

$$J_\gamma^{(2n)} = \frac{4L}{l}\int_0^{l/4} \frac{dx}{2L|(\bar p+b_2)(\bar q+b_1)|^{1/2}} \Big\{ |(p+b_2)(q+b_1)|^{1/2} \times \cos\left(\varepsilon_2\gamma_2 \int_0^x \frac{dy}{|p+b_2|} - \varepsilon_1\gamma_1 \int_0^x \frac{dy}{|q+b_1|}\right) + |(q+b_2)(p+b_1)|^{1/2} \times \cos\left(\varepsilon_2\gamma_2 \int_0^x \frac{dy}{|q+b_2|} - \varepsilon_1\gamma_1 \int_0^x \frac{dy}{|p+b_1|}\right)\Big\}. \qquad (18)$$

In the limit $c\xi_0 \ll 1$ the parameter $k \to 1$ and Eq. (18) can be evaluated by using relations (13) and formulae for band B analogous to them:

$$\varepsilon_2\gamma_2 \int_0^x \frac{dy}{|p+b_2|} \approx \delta\varkappa x + \frac{\pi}{2}, \quad \varepsilon_2\gamma_2 \int_0^x \frac{dy}{|q+b_2|} \approx \delta\varkappa_2 x, \qquad (19)$$

$$b_2 \approx -\Delta_1^2, \quad M_+ = \Delta_1/v_F^2, \quad M^* \approx M_+.$$

From Eqs. (18) and (19) we obtain $J_\gamma^{(2n)} \approx \pi(c\xi_0)^{1/2}$, i.e., for $c \to 0$ the matrix element is weakly dependent on n. Evaluation of the matrix elements $J_\alpha^{(n)}$ and $J_\beta^{(n)}$ leads to the same results.

We obtain from Eq. (8) for the optical absorption

$$\varepsilon_2(\omega) \approx \pi^2 e^2 c v_F/s_\perp \Delta_1 \omega [2\Delta_1(\omega-\Delta_1)]^{-1/2}. \qquad (20)$$

Eq. (20) is similar to the expressions found for absorption by widely spaced solitons.[9,10]

III. THE CHANGE IN THE OPTICAL PROPERTIES ON DESTROYING THE PERIODIC SUPERSTRUCTURE

The most important study is of the previously forbidden optical transitions. Small non-uniformity in the system can be produced by quantum and thermodynamic fluctuations in the phase of the deformation $\Delta(x)$, by interaction with external fields and by impurities. We can consider that in expression (6) for $\Delta(x)$ the coordinate x_0 is a slowly varying function of x and t. The order in the system is then destroyed and the correlation length becomes finite. For small concentrations $c\xi_0 \ll 1$ such that

$$\exp(-1/c\xi_0)/(c\xi_0) < (\omega_0/\Delta_1)^2 \sim 10^{-2} \qquad (21)$$

[ω_0 is the phonon frequency for the deformation $\Delta(x)$] short range order is destroyed; the crystal melts.

We shall consider the direct transition from A to C with $n = 0$ for $c\xi_0 > 1$. Long range order in the system is then destroyed, but short range order is preserved. We can then use Eq. (10) for the matrix element of the transition. We obtain from Eq. (10)

$$\langle (J_\delta^{(0)})^2\rangle = \frac{E^2}{(\bar p+b)^2 L^2}\left\langle \int \Delta(x)\Delta(y)dx\,dy \right\rangle = \frac{E^2}{(\bar p+b)^2 L}\int K(z)dz, \qquad (22)$$

$$K(z) = \langle \Delta(z,t)\Delta(0,t)\rangle.$$

From Eqs. (22) and (7) and (8) we obtain for $\omega - 2E_+ \ll \Delta_1$

$$\varepsilon_2(\omega) = \frac{4\pi e^2}{\omega^2 s_\perp}\langle (J_\delta^{(0)})^2\rangle \left(\frac{M_+}{\omega-2E}\right)^{1/2}. \qquad (23)$$

In the limit $c\xi_0 \gg 1$, $k \ll 1$, corresponding to the Fröhlich model,

$$\Delta(x) = \Delta_k \sin(qx + \varphi(x)), \quad q = 2\varkappa_0 = \pi c.$$

Consequently,

$$\langle (J_\delta^{(0)})^2\rangle = \frac{2E^2\Delta_k^2}{L(\bar p+b)^2} S(q),$$

$$S(q) = \int \langle \exp[i\varphi(x) - i\varphi(y)]\rangle \exp[iq(x-y)]dy, \qquad (24)$$

where $S(q)$ is the structure factor of the system.

In the classical case, $T/\omega_0 \gg q\xi_0 \gg 1$ (Ref. 11),

$$S(q) = \frac{4(\xi_i^{-1}+\xi_T^{-1})[(\xi_i^{-1}+\xi_T^{-1})^2+q^2]}{(\xi_i^{-1}-\xi_T^{-1})^2+2q^2(\xi_T^{-2}+\xi_i^{-2}+q^2/2)} \approx \frac{2}{q^2\xi}, \qquad (25a)$$

$$\xi_T = v_F/2\pi T, \quad \xi^{-1} = \xi_i^{-1} + \xi_T^{-1}, \quad \xi_0 = v_F/\Delta_k,$$

ξ_i is the correlation length of the impurities.

In the quantum case, $q\xi_0 \gg T/\omega_0$, the structure factor without taking account of random impurities is known[4]

$$S(q) = \omega_0\xi_0/\Delta_k(\xi_0 q)^\alpha, \quad \alpha = 1 - 2\omega_0/\Delta_k \approx 1. \qquad (25b)$$

Substituting Eqs. (24), (25a) and (25b) in Eq. (23), we obtain

$$\varepsilon_2(\omega) = \frac{2e^2 v_F \Delta}{s_\perp L\omega^2}[2\omega(\omega-2E_+)]^{-1/2} \begin{cases} v_F^2/\xi\omega^2, & T/\omega_0 \gg q\xi_0 \gg 1 \\ \omega_0 v_F/\Delta_1^2, & T/\omega_0 \ll q\xi_0 \end{cases}. \qquad (26)$$

Other causes which lead to a finite value of the matrix element for the direct transition from A to C can be the allowance for the finite momentum of light and higher multipole contributions.

For small concentrations satisfying Eq. (21) the system appears as a number of randomly distributed domain walls. The solution for a single domain wall has been found earlier[7]:

$$\Delta(x) = \Delta_1 \operatorname{th}(x/\xi_0), \quad \xi_0 = v_F/\Delta_1.$$

For a system of widely spaced domain walls the function $\Delta(x)$ can be expressed approximately in the form

$$\Delta(x)=\Delta_1\prod_{j=1}^{N}\operatorname{th}\frac{x-x_j}{\xi_0},\quad 0\leqslant x\leqslant L. \tag{27}$$

In writing Eq. (27) we are neglecting corrections $\sim\exp(-1/c\xi_0)$, arising from the interaction of solitons. We obtain the electron wave functions U and V to the same accuracy from Eq. (1).

For a continuous spectrum with $(x_{2j}+x_{2j-1})/2<x<(x_{2j}+x_{2j+1})/2$

$$U_{2j}=\frac{kv_F+i\Delta_1\operatorname{th}[(x-x_{2j})/\xi_0]}{(2L)^{1/2}E_k}\exp[ikx+i\varphi(2j-1)],$$
$$V_{2j}=(2L)^{-1/2}\exp[ikx+i\varphi(2j-1)], \tag{28a}$$

and for $(x_{2j-2}+x_{2j-1})/2<x<(x_{2j-1}+x_{2j})/2$

$$U_{2j-1}=(2L)^{-1/2}\exp[ikx+i\varphi(2j-2)],$$
$$V_{2j-1}=\frac{kv_F+i\Delta_1\operatorname{th}[(x-x_{2j-1})/\xi_0]}{(2L)^{1/2}E_k}\exp[ikx+i\varphi(2j-2)], \tag{28b}$$

where $e^{i\varphi}=(kv_F+i\Delta_1)/E_k$, $E_k=\pm(v_F^2k^2+\Delta_1^2)^{1/2}\pm\varepsilon_k$, U_j and V_j are the functions $U(x)$ and $V(x)$ in the vicinity of the j-th soliton. The wave functions for localized states with $E=0$ are, in the tight binding approximation:

$$V_\alpha=\sum_{j=1}(2\xi_0)^{-1/2}A_{2j-1}^{\alpha}\Big/\operatorname{ch}\left(\frac{x-x_{2j-1}}{\xi_0}\right),$$
$$U_\alpha=\sum_{j=1}(2\xi_0)^{-1/2}A_{2j}^{\alpha}\Big/\operatorname{ch}\left\{\frac{x-x_{2j}}{\xi_0}\right\},\quad \sum_{j=1}^{N}A_j^{\alpha}(A_j^{\alpha'})^*=\delta_{\alpha\alpha'}, \tag{29}$$

$\alpha=1,\ldots\ldots,N$, N is the number of solitons.

We use Eqs. (3) and (3a) with $\mu_1\to p_1$, $\mu_2\to p_2$ to find $\varepsilon_2(\omega)$. We note that because of the non-uniformity the optical transitions will occur with a change in momentum, $p_1\neq p_2$.

In the region of the fundamental edge $\omega\approx 2\Delta_1$ we obtain from Eqs. (28)

$$J(p_1,p_2)=\frac{v_F}{2L}\sum_{j=1}^{N}\exp[i(\varphi_1-\varphi_2)(j-1)]\left\{\left[\exp\frac{i(p_1-p_2)(x_{j+1}+x_j)}{2}\right.\right.$$
$$\left.-\exp\frac{i(p_1-p_2)(x_j+x_{j-1})}{2}\right]\frac{1}{i(p_1-p_2)}\left(\frac{p_2v_F}{\varepsilon_{p_2}}-\frac{p_1v_F}{\varepsilon_{p_1}}\right)$$
$$-\left[\exp\frac{i(p_1-p_2)(x_j+x_{j+1})}{2}+\exp\frac{i(p_1-p_2)(x_j+x_{j-1})}{2}\right.$$
$$\left.\left.-\frac{(p_1-p_2)\pi\exp[i(p_1-p_2)x_j]}{\Delta_1\operatorname{sh}[(p_1-p_2)\pi/2\Delta_1]}\right]\frac{1}{(p_1-p_2)}\left(\frac{\Delta_1}{\varepsilon_{p_2}}+\frac{\Delta_1}{\varepsilon_{p_1}}\right)\right\}, \tag{30}$$
$$\varphi_1=\varphi(p_1),\quad \varphi_2=\varphi(p_2),\quad x_0=-x_1,$$
$$x_{N+1}=2L-x_N,\quad \varepsilon_{p_j}=|E_{p_j}|.$$

Since, essentially, $p_1-p_2\sim c\ll\Delta_1/v_F$ we obtain from Eq. (30)

$$J(p_1,p_2)=J(q,p)=\frac{v_F}{2L}\sum_{j=1}^{N}(-1)^{j-1}\left\{\left[\exp\frac{iq(x_{j+1}+x_j)}{2}-\exp\frac{iq(x_j+x_{j-1})}{2}\right]\right.$$
$$\left.\times\frac{iv_F}{\varepsilon_p}-\left[\exp\frac{iq(x_{j-1}+x_j)}{2}+\exp\frac{iq(x_j+x_{j+1})}{2}-2\exp iqx_j\right]\frac{2\Delta_1}{\varepsilon_pq}\right\}; \tag{31}$$
$$q=p_1-p_2,\quad p=(p_1+p_2)/2.$$

The first term in Eq. (31) becomes zero for $q=0$ so that it does not make a singular contribution to $\varepsilon_2(\omega)$.

The main second term remaining in Eq. (31) gives

$$J^2(q,p)=\frac{4\Delta_1^2v_F^2}{\varepsilon_p^2q^2L^2}\sum_{j,l}(-1)^{j+l}\exp[iq(x_j-x_l)]. \tag{32}$$

We shall assume that under the influence of random impurity fields, thermal and quantum motion of solitons, the coordinates x_j are distributed randomly and that they have negligible correlation. Using a Poisson distribution, we then obtain for large N

$$J^2(q,p)\approx 4\Delta_1^2/L^2(4c^2+q^2). \tag{33}$$

We have from Eq. (3) for $q\ll\Delta_1/v_F$

$$\varepsilon_2(\omega)=\frac{4\pi e^2L}{\omega^2s_\perp}\int\frac{dq}{(2\pi)^2}\frac{2\Delta_1|J(q,p)|^2}{[4\Delta_1(\omega-2\Delta_1)-q^2]^{1/2}}. \tag{34}$$

Substituting Eq. (33) into (34), we obtain

$$\varepsilon_2(\omega)=\frac{8e^2\Delta_1^3v_F\theta(\omega-2\Delta_1)}{\omega^4s_\perp[v_F^2c^2+\Delta_1(\omega-2\Delta_1)]^{1/2}}. \tag{35}$$

It can be seen from Eq. (35) that the absorption peak is smoothed out for $\omega-2\Delta_1\sim v_F^2c^2/\Delta_1$. We obtain for transitions into the middle band, using Eqs. (3), (3a), (28), and (29)

$$\varepsilon_2(\omega)\approx\frac{\pi^2e^2v_Fc\,\theta(\omega-\Delta_1)}{s_\perp\omega(\omega^2-\Delta_1^2)^{1/2}}\operatorname{sech}\left(\frac{\pi(\omega^2-\Delta_1^2)^{1/2}}{2\Delta_1}\right). \tag{36}$$

Equation (36) shows that absorption into the middle band is proportional to the number of solitons, i.e., it occurs at each soliton independently. The absorption by widely spaced solitons was studied in Refs. 9 and 10, and Eq. (36) is analogous to the expressions obtained.

IV. CONCLUSIONS

The band structure of a Peierls dielectric with a number of electrons $\rho\neq 1$ has eight van Hove singularities, lying at points with wave vectors $\pm\varkappa_0$ with energies $\pm E_-$ and $\pm E_+$. The optical absorption coefficient for an ideal periodic structure should have a singularity $\varepsilon_2(\omega)\sim(\omega-\omega_i)^{-1/2}$ for the transition [Eq. (17)].

α: $(\pm\varkappa_0,-E_+)\to(\mp\varkappa_0,-E_-)$, $\omega_i=E_+-E_-=\Delta_k$.

Other transitions between singular points are dipole forbidden. Transitions with a change in momentum, occurring between singular and non-singular points are allowed:

β: $(\pm(\varkappa_0+(2n-1)2\varkappa_0),E<-E_+)\to(\mp\varkappa_0,E_-)$, $\omega_i>E_++E_-$,
γ: $(\pm(\varkappa_0+4n\varkappa_0),E<-E_+)\to(\pm\varkappa_0,-E_-)$, $\omega_i>E_+-E_-=E_g$,
δ: $(\pm(-\varkappa_0+2m\varkappa_0),E<-E_+)\to(\pm(2m+4n-3)\varkappa_0,E>E_+)$, $\omega_i>2E_+=E_g$,

where $m,n=1,2,\ldots\ldots$. Near transitions β,γ,δ the absorption coefficient must have a non-singular threshold.

For $\rho\to 1$, $E_-\to 0$, $\varkappa_0\to 0$ the frequencies of transitions δ with different m,n converge. As a result, the sum of the transitions of type δ reduce to the normal singularity $\varepsilon_2(\omega)\sim(E-\tilde{E}_g)^{-1/2}$, $\tilde{E}_g\approx 2\Delta_1$, characteristic of the fundamental absorption for the Peierls state with $\rho=1$.

The frequencies of transitions α, β and γ also converge and lead to a singularity $\varepsilon_2(\omega)\sim(1-\rho)(\omega-\Delta_1)^{-1/2}$, characteristic of transitions from the valence band

$E < -\Delta_1$ to the localized levels $E = 0$ of solitons with concentration $c = (1-\rho)/a$. In the limit $c \gg \Delta_1/v_F$ transition α assumes its normal form, characteristic of the fundamental absorption for an incommensurate Peierls-Fröhlich system.

The forbiddenness of direct ($\varkappa - \varkappa$) dipole transitions is lifted when the periodicity of the structure is destroyed. In a real system for $c \ll \Delta_1/v_F$ the periodic structure must go over into a system of randomly distributed solitons. In this case transition δ becomes allowed, but the absorption peak is smeared out in the region $\omega - 2\Delta_1 \sim c^2/\Delta_1$. For $c \gg \Delta_1/v_F$ the structure only becomes destroyed over large distances $\xi \gg v_F/\bar{E}_g$ by thermal and quantum fluctuations and through the action of random potentials. As a result, transition δ similarly becomes allowed [Eq. (26)] but with a very small oscillator strength.

The theory of optical absorption for systems of widely spaced solitons has recently been discussed (Refs. 9 and 10). The effect of broadening of the fundamental edge [Eq. (35)] was omitted and the specific features of optical transitions for periodic structures were not considered in these papers.

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