On Urbach rule theory for impurity light absorption

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Abstract. The generating function of the optical line shape of impurity absorption is obtained, including both displacement of equilibrium positions of normal oscillators and the change of their frequencies. The line shape is investigated by the saddle-point method. It is shown that the frequency effect considerably changes the Gaussian line shape in the centre of the band and the Urbach constants in the long-wave edge. Urbach's rule also describes the long-wave wing for forbidden transitions reduced by lattice vibrations.

In many crystals, the long-wave tail of the optical line shape (for excitons and for local excitations) and also impurity light absorption is described by the Urbach rule (Urbach 1953)

\[ W(\Omega, T) = W_0 \exp \left( -\frac{\sigma (\Omega_0 - \Omega)}{kT} \right) \]

where \( \Omega \) is photon frequency; \( W_0, \sigma, \Omega_0 \) are the parameters which characterize the crystal. The formula (1) describes the change of the absorption coefficient over several orders of magnitude. To explain the temperature dependence of the absorption coefficient one sometimes has to introduce a weak temperature dependence for the parameter \( \sigma \), which differs slightly from unity (Mahr 1962).

A review paper by Kurik (1971) contains an extensive bibliography. Toyozawa (1959), Mahr (1963) and Keil (1966) investigated the edge of the optical band in the semiclassical approximation which can describe only a Gaussian region (in the absence of dynamic Jahn–Teller coupling). Keil (1966) also introduced some special assumptions (imaginary frequencies, that is, lattice instability). It is clear that the semiclassical method is a poor technique in the long-wave tail, as is also evident from the method of moments (Perlin 1963). Davidov (1968) showed that Urbach's rule can be obtained by a direct summation of the transition probabilities from all phonon levels of the ground electron state to the zero vibrational level of upper electron state. The formula of Pekar and Krivoglaz (1953) expresses these processes and a proper asymptotic form is obtained for the edge of the spectrum (Davidov and Lubchenko 1968). Vinogradov (1970) applied the saddle-point method for determining the line shape on the long-wave wing. He obtained Urbach's rule in the linear approximation including phonon dispersion.

It is clear from physical considerations that transitions from vibrational levels which correspond to large amplitudes of nuclear vibrations give the main contribution to the edge of the band. Including only linear terms in the electron–phonon interaction may turn out to be insufficient. In this paper the long-wave edge of the absorption band was studied.
by the saddle-point method in the form offered by Vinogradov including both displacement of equilibrium positions of normal oscillators and the change of their frequencies. The frequency effect considerably modifies the Urbach constants, the optical region and temperature conditions where Urbach's rule is applicable. The criterion for the validity of the saddle-point method is also changed in this case.

The band edge for forbidden transitions induced by lattice vibrations is also investigated in the present paper. We obtain a strong temperature dependence of Urbach's constants in this case which distinguishes forbidden transitions from allowed ones.

The generating function for impurity light absorption including the frequency effect has the following form to second order:

\[
W(\Omega) = \int_{-\infty}^{\infty} dt \left( \prod_x \frac{\sinh \frac{1}{2} \beta_x}{\sinh \frac{1}{2} \beta_x + i(\omega_{g_x} - \omega_{u_x}) t} \right) \\
\times \exp \left[ it(\Omega_{u_g} - \Omega) - \sum_x \frac{\Delta_x^2}{2} \left( \coth \frac{1}{2} \beta_x + i(\omega_{g_x} - \omega_{u_x}) t \right) \right] \\
\times \exp \left[ \frac{1}{2} \left( \beta_x + i(\omega_{g_x} + \omega_{u_x}) t \right) \right],
\]

where \( \Omega_{u_g} \) is the frequency of pure electronic transition, \( \Delta_x \) are displacements of equilibrium positions of normal oscillators, \( \omega_{g_x} \) and \( \omega_{u_x} \) are normal frequencies in the ground and the upper electron states, respectively, \( \beta_x = h\omega_{g_x}/kT \). The expression (2) is a special case (nondiagonal quadratic terms which mix normal coordinates are neglected) of the general result obtained by Kubo and Toyoza (1955).

Later on, for simplicity, we will confine ourselves only to one mode, although the saddle-point method does not require this assumption.

The saddle point \( t_0 \) is defined from the equation

\[
\Omega - \Omega_{u_g} = \Delta^2 \{ (1 - \lambda) \cosh \left[ \beta + \frac{1}{2} (1 + \lambda) i t_0 \right] \\
- (1 + \lambda) \cosh \frac{1}{2} (1 - \lambda) i t_0 + 2\lambda \}/8 \sinh^2 \frac{1}{2} (\beta + i\lambda t_0),
\]

where \( \lambda = (\omega_{g} - \omega_{u})/(\omega_{g} + \omega_{u}) \) is the frequency effect parameter; obviously \( |\lambda| < 1 \).

The maximum of the absorption band corresponds to the solution of equation (3) lying at the zero point of the coordinate complex plane \( t \). In the absence of the frequency effect, while the light frequency changes from its value in the maximum of the band to the long-wave wing, the saddle point moves up from zero along the imaginary axis. In the general case this is true under the condition that \( \lambda t' < \beta \), \( (t = it', t' > 0) \) which the saddle-point equation (3) gives for \( \Omega < \Omega_{u_g} \). We have to note that large values of \( t \) lying in the lower part of the imaginary axis also satisfy the equation (3) in the long-wave region for negative \( \lambda \) under the condition \( -\lambda t'' > \beta \), \( (t = -it'', t'' > 1) \). We consider the solution of the equation (3) at \( |t_0/2| \ll 1 \) when the spectral distribution assumes a Gaussian shape

\[
W(\Omega) = (2\pi^{1/2}/B) \exp \left[ - (\Omega - \Omega_{u_g} - A)^2/B^2 \right]
\]

in the region of the band maximum, that is, where

\[
|\Omega - \Omega_{u_g} - A| < B^2/(\omega_{g} + \omega_{u}),
\]

where

\[
A = \frac{\Delta^2}{2} \frac{1 - \lambda}{1 + \lambda} \omega_{g}; \quad B = \Delta^2 \left( \frac{1 - \lambda}{1 + \lambda} \right)^2 \omega_{g}^2 \coth \frac{1}{2} \beta.
\]
It is clear that the negative frequency effect \((\lambda < 0)\) makes the Gaussian region wider and moves the curve up in energy. For positive frequency change \((\lambda > 0)\) the Gaussian range is narrower and the curve is lower.

The formula (4) is valid when the criterion of the saddle-point method for the central region

\[
f = \frac{1 - \lambda(3 \coth^2 \frac{1}{2} \beta - 2)}{(1 - \lambda) \coth^{3/2} \frac{1}{2} \beta} \left( \frac{2}{\Delta^2} \right)^{1/2} \ll 1
\]

is satisfied. In the case of large heat release and in the absence of the frequency effect, the inequality (6) is valid. At low temperatures \(kT \ll \hbar \omega_0\), the inequality (6) reduces to the simple form \((2/\Delta^2)^{1/2} \ll 1\), the validity of which depends only on the interacting force between the impurity electron and the vibration mode.

Table 1 presents values of \(f\) calculated for different temperatures and force constants.

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with $\lambda = \pm \frac{1}{3}, \pm 0.1$. The frequency effect essentially changes the criterion for the validity of the saddle-point method. For finite and quite large $\lambda$ one cannot use the saddle-point method at high temperatures.

The long-wave edge is considered in the range $\Omega < \Omega_{ug}$. Changing variable $t_0 = 2i\beta/(1 + \lambda) + t'$ for the saddle point in the equation (3) and considering $|\frac{1}{2}t'| \ll 1$, the spectral distribution assumes the form

$$W(\Omega) = \frac{2\pi^{1/2} \sinh \frac{1}{2} \beta}{B \sinh \left[ \frac{1}{2} \beta(1 - \lambda)/(1 + \lambda) \right]} \exp \left( \frac{\hbar(\Omega - \Omega_{ug})}{kT} - \frac{(\Omega - \Omega_{ug} + A_1)^2}{B^2} \right)$$

in the photon range determined by the inequality

$$|\Omega - \Omega_{ug} + A_1| \ll B^2/(\omega_g + \omega_e),$$

where $A_1 = \frac{1}{2} \Delta^2 \omega_g$, $B^2 = \Delta^2 \omega_g^2 \coth \left[ \frac{1}{2} \beta(1 - \lambda)/(1 + \lambda) \right]$. The criterion for the validity of the saddle-point method in this case does not essentially differ from the criterion (6) in the central optical region.

Then, taking into account the conditions at high temperatures (sufficiently small frequency effect) we can obtain from (7) a curve which has the shape of a Gaussian tail with the centre in the vicinity of the maximum of the absorption band.

At moderately low temperatures ($kT \lesssim \hbar \omega_g$) the validity criterion for the method is better satisfied and the spectral distribution (7) reduces within the region defined by (8) to a form which corresponds to Urbach’s rule with

$$\sigma = 1 + 2kT \tan \left( \frac{1 - \lambda}{1 + \lambda} \frac{\hbar \omega_g}{2kT} \right)$$

where $|\sigma| \ll 1$ slightly depends on photon frequency.

Finally we consider the extremely low energy region. Now let the saddle point move up from $2i\beta/(1 + \lambda)$ along the imaginary axis. A position of $\frac{1}{2}t' \gg 1$ corresponds to the long-wave region. The criterion for the saddle-point method

$$[\omega_g/(\Omega_{ug} - \Omega)]^{1/2} \ll 1$$

does not depend on temperature and is well satisfied here. The saddle-point equation cannot be solved analytically in the general form. Its solution gives the Urbach rule with

$$\sigma = 1 + \frac{kT}{\hbar \omega_g} \ln \left( \frac{\Omega_{ug} - \Omega}{\frac{1}{2} \Delta^2 \omega_g} \right)$$

for low temperatures $\beta(1 - \lambda)/(1 + \lambda) > \lambda t'$ and $\lambda = -\frac{1}{3}$.

The equation for the saddle point (3) includes also a solution $t = -it''$, $(t'' \gg 1)$, which corresponds to the long-wave tail for the negative parameter $\lambda \neq 0$. The spectral distribution is observed here for temperatures $\beta < -\lambda t''$ and it results in the same Urbach rule for $\lambda = -\frac{1}{3}$. If we set $\lambda = 0$ we can easily obtain the Urbach rule for linear approximation (Vinogradov 1970).

We now turn to Urbach’s rule for forbidden transitions induced by lattice vibrations. We shall consider linear electron-phonon interaction and neglect the dispersion of normal oscillators of the crystal. Then, using the theory of many-phonon processes (Perlin 1963) one can calculate the line shape for forbidden transitions induced by the lattice vibrations:
On Urbach rule theory for impurity light absorption

\[ W(\Omega) = \exp \left[ -\frac{a}{2} \coth \frac{\beta}{2} - p \frac{\beta}{2} \right] \left( \frac{b^2}{16 \sinh^2 \frac{1}{2} \beta} \left[ I_{p-2}(x) + I_{p+2}(x) \right] + \frac{1}{2 \sinh \frac{1}{2} \beta} \left[ \left( c - \frac{b^2}{2} \right) I_{p+1}(x) + \left( c + \frac{b^2}{2} \right) I_{p-1}(x) \right] + b^2 \frac{2 \sinh^2 \frac{1}{2} \beta - 1}{8 \sinh^2 \frac{1}{2} \beta} I_p(x) \right) \],

(11)

where

\[ b = \sum_x N_x \Delta x, \quad c = \sum_x N_x^2, \quad a = \sum_x \Delta x^2, \quad x = x/2 \sinh \frac{1}{2} \beta; \]

\( N_x \) are expansion coefficients of normal modes in the interaction Hamiltonian and \( I_p \) is the Bessel function of power \( p = (\Omega_{ug} - \Omega)/\omega \).

Under the conditions \( p \gg 1, a/2 \sinh \frac{1}{2} \beta > 1 \), using the asymptote of the Bessel function of high power (Bateman 1953):

\[ I_p(x) = \frac{1}{\pi \sqrt{2} (p^2 + x^2)^{1/2}} \exp \left[ (p^2 + x^2)^{1/2} - p \sinh^{-1} \left( \frac{p}{x} \right) \right] \left[ \sqrt{\pi} + O \left( \frac{1}{x} \right) \right], \]

(12)

expression (11) can be written in the form of Urbach's rule:

\[ W(\Omega) = R \exp \left[ -\frac{a}{2} \coth \frac{\beta}{2} \right] \exp \left( \frac{\hbar (\Omega - \Omega_{ug})}{kT} (1 + \xi_0) \right) \]

(13)

where

\[ \xi_{\pm s} = \beta^{-1} \ln \frac{p + s}{2ea (\tilde{n} + 1)}, \quad s = 0, 1, 2. \]

The factor \( R \) includes expressions of the form

\[ \exp \left\{ -p \beta \left[ \xi_{\pm s} - \xi_0 \right] \right\} = (1 + s/p)^{-p} \]

(where \( s = 1, 2 \)) which at sufficiently large values of \( p \) (long-wave region) does not depend on the frequency of light within the limits \( \exp(\pm s) \). The function \( \xi_{\pm s} \) depend weakly on photon energy at

\[ \Omega_{ug} - \Omega > \frac{1}{2} a (\tilde{n} + 1) \omega \]

and in the wide interval of their values they can be considered in theory as parameters proportional to temperature.

As a result the typical factor \( R \) for forbidden transitions becomes

\[ R = \frac{b^2}{16 \sinh^2 \frac{1}{2} \beta} \left[ \left( \frac{\pi}{2(p + 1)} \right)^{1/2} \exp \left[ \beta(1 + 2 \xi_{-2}) + 2 \right] + \left( \frac{\pi}{2(p - 1)} \right)^{1/2} \right] \times \exp \left[ -\beta(1 + 2 \xi_2) - 2 \right] + \frac{1}{2 \sinh \frac{1}{2} \beta} \left[ \left( c - \frac{b^2}{2} \right) \left( \frac{\pi}{2(p + 1)} \right)^{1/2} \right] \times \exp \left[ -\beta \frac{x}{2} + \xi_1 \right] + \left( c + \frac{b^2}{2} \right) \left( \frac{\pi}{2(p - 1)} \right)^{1/2} \exp \left[ \beta \frac{x}{2} + \xi_{-1} \right] + \left( \frac{\pi}{2p} \right)^{1/2} b^2 \frac{2 \sinh^2 \frac{1}{2} \beta - 1}{8 \sinh^2 \frac{1}{2} \beta}. \]

(14)
At high temperatures ($\beta \ll 1$) the value of the typical factor $R$ becomes large. At sufficiently low temperatures

$$a/2 \sinh \frac{1}{2} \beta \ll 1$$

the Bessel function transforms to the following asymptote expression:

$$I_p(x) = \frac{1}{p!} \left( \frac{x}{2} \right)^p \left( 1 + \frac{x^2}{4(p + 1)} \right),$$

(15)

and the long-wave edge is described by Urbach's rule (13). In this approximation the typical factor $R$, does not depend on temperature.

Thus, Urbach's rule for forbidden optical transitions includes an additional factor which depends weakly on the frequency of light and exhibits a strong temperature dependence. This typical factor (14) characterizes the temperature intensity of Urbach absorption for forbidden optical transitions induced by lattice vibrations.

Acknowledgments

I wish to thank Dr B Tsukerblat for suggesting this problem and to Professor J Jortner for fruitful discussions of the results.

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Urbach's Rule in an Electron-Phonon Model

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(Received 1 April 1968)

We have investigated the optical absorption in the region below the direct edge in a model electron-phonon semiconductor. The absorption coefficient has been shown to have the form \( A(\omega) = A_0 \exp[-\sigma(E_\omega - \omega)/KT] \), and the temperature dependence of the coefficient has been found to agree, at least qualitatively, with the observed dependence. (This behavior of the absorption coefficient is associated with the name of F. Urbach.) To obtain these results we have used the method of electron Green's functions, and the electron self-energy has been determined in an approximation which involves the electron-phonon interaction to all orders.

1. INTRODUCTION

At low temperatures the optical absorption spectrum of a pure semiconductor exhibits a definite edge, that is, there exists a value of the photon energy \( E_\omega \) below which there is no absorption. This arises directly from the gap in the electron energy bands.

In some materials, as the temperature is raised, there appears a tail below the edge. Urbachfirst reported that in this region the absorption has an exponential dependence upon the photon energy:

\[
A(\omega) = A_0 \exp[-\sigma(E_\omega - \omega)/KT].
\]

(1)

is exponential (at least for \( KT < \omega_0 \)), but no precise conclusions are obtained.

We investigate the absorption using a model that is simple enough to enable us to obtain a nonperturbative solution, and yet is one that we feel contains all the essentials of the physics.

The model Hamiltonian is

\[
H = \sum_k (\epsilon_k^2/2m_e + \mu_e) a_{ke}^\dagger a_{ke} - \sum_k (\epsilon_k^2/2m_\sigma + \mu_\sigma) a_{k\sigma}^\dagger a_{k\sigma} + \omega_0 \sum_k b_k^\dagger b_k + g \sum_k a_{k+} a_{k-} (b_k^\dagger b_k).
\]

(3)

The operators \( a_{ke}^\dagger \) and \( a_{k\sigma}^\dagger \) create an electron of momentum \( k \) in, respectively, the conduction band and the valence band, and \( b_k^\dagger \) is the phonon creation operator. The energy gap between the valence and conduction bands is

\[
E_\omega = \mu_e + \mu_\sigma.
\]

The model assumes free conduction electrons but the valence electrons interact with monoenergetic phonons. The interaction matrix elements are also taken to be constant.

This, of course, is a gross oversimplification of the Hamiltonian for a real semiconductor where, in particular, the interaction matrix elements would be very complicated functions. For this reason we do not attempt a quantitative fit of any particular experimental results.

We find using this model that the absorption coefficient does indeed decay exponentially below the edge. However, the coefficient \( \sigma \) does not agree quantitatively with Eq. (2) for any value of \( E_\omega \) although qualitatively it shows the same sort of behavior.

We use a Green's-function formalism in the determination of the absorption coefficient and the only major approximations that are used in the solution of the Green's function, are the Migdal approximation and the use of a noninteracting phonon Green's function.

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2. ELECTRON GREEN'S FUNCTION

Many physical properties may be determined in terms of the electron Green's function\(^8\)

\[
G(\alpha,t) = i \langle T \bar{a}_\alpha(t)a_\alpha^*(0) \rangle, \tag{4}
\]
or more directly, in terms of its Fourier transform

\[
G(\alpha,E) = \int_{-\infty}^{+\infty} dt \, e^{iE t} G(\alpha,t). \tag{5}
\]

In the present problem \( \alpha \) represents either \((k,\pi)\) or \((k,c)\). Since, in our model, the conduction-band electrons do not interact, the corresponding Green's function is just that for free particles\(^9\):

\[
G(kc,E) = - \frac{f(k^2/2m_\pi + \mu_c)}{E - k^2/2m_\pi - \mu_c - i0} + \frac{1 - f(k^2/2m_\pi + \mu_c)}{E - k^2/2m_\pi - \mu_c + i0}, \tag{6}
\]

where \( f(x) \) is the Fermi-function

\[
f(x) = [\exp(x/KT) + 1]^{-1}.
\]

The valence band, however, presents a greater problem. In this case the Green's function has to be determined from the following integral equations (see Ref. 6):

\[
G^{-1}(k\nu,E) = - \left[ E + k^2/2m_\pi + \mu_\pi + \Sigma(k,E) \right], \tag{7}
\]

\[
\Sigma(k,E) = -ig^2 \sum_{k'} \int_{-\infty}^{+\infty} (dE'/2\pi) G(k',E')D(E - E').
\]

\( D(E - E') \) is the phonon Green's function and we take this to be that of free phonons,

\[
D(E - E') = 2a_0 \left( \frac{1 + N(\omega_0)}{(E - E')^2 - \omega_0^2 + i0} - \frac{N(\omega_0)}{(E - E')^2 - \omega_0^2 - i0} \right), \tag{8}
\]

where \( N(\omega) \) is the function

\[
[\exp(\omega/KT) - 1]^{-1}.
\]

Equation (7) is just the Migdal approximation for the self-energy \( \Sigma \), and it involves the neglect of the so-called phonon vertex corrections.\(^10\) It follows from Eq. (7) that \( \Sigma \) is independent of the momentum, that is,

\[
\Sigma(k,E) \equiv \Sigma(E).
\]

The usual method of obtaining a solution of Eq. (7)


\(^9\) This function differs from that in Ref. 8 by a factor \(-2\pi\).

\(^10\) See Ref. 7 and also S. Engelsberg and J. R. Schrieffer, Phys. Rev. 131, 993 (1963).
or
\[
G(k, E) = \frac{1}{\pi} \int_{-\infty}^{+\infty} dE' \text{Im} G(k, E') \left( \frac{N(E')}{E' - E + i0} + \frac{1 + N(E')}{E' - E - i0} \right).
\]

In the former integration the principal value is taken.

If in Eq. (7) we insert the spectral form for \( G \) then, after performing the necessary integrations we obtain exactly
\[
\Sigma(E) = -g^2 \sum_k [G(k, E - \omega_0) N(\omega_0) + G(k, E + \omega_0) (1 + N(\omega_0))] + \Delta(E). 
\]  
(10)

The term \( \Delta(E) \) is given by
\[
\Delta(E) = -\frac{g^2}{\pi} \sum_k \int_{-\infty}^{+\infty} dE' \text{Im} G(k, E') (1 + N(E')) \times \left( \frac{1}{E' - E + \omega_0 - i0} - \frac{1}{E' - E - \omega_0 - i0} \right). 
\]  
(11)

The important regions in this latter integration are
\[ E' = E \pm \omega_0 \]
so that we expect the result to be proportional to the factor
\[ 1 + N(E \pm \omega_0). \]

As we shall see later, in order to determine the absorption coefficient in the tail region, we need to know \( \Sigma(E) \) for values of \( E \) that make the above factor negligible.

We therefore make the approximation that \( \Delta(E) \) is identically zero. This, and the simple \( k \) dependence of \( G(k, E) \), enables us to obtain the following equation for \( \Sigma(E) \):
\[
\Sigma(E) = (g^2 m_e k_0 / \pi^2) \coth(E/2kT) - \left[ \frac{g^2 (2m_e)}{2\pi} \right] \frac{N(\omega_0)(E - \omega_0 + \mu^* + \Sigma(E - \omega_0))}{(1 + N(\omega_0))(E + \omega_0 + \mu^* + \Sigma(E + \omega_0))}. 
\]  
(12)

\( k_0 \) is the maximum momentum and is of the order of the inverse atomic spacing.

In the above equations \( -\mu^* \) is the maximum valence band energy in the absence of the interactions. The corresponding quantity \( -\mu_{\ast}' \), in the presence of the interaction, is the solution of the equation
\[ \mu_{\ast}' = \mu_{\ast} + \text{Re} \Sigma(-\mu_{\ast}'). \]

It is this latter energy that contributes to the experimental energy gap and we shall assume that this is known.

The self-energy appears in the Green's function only in the combination
\[ \mu_{\ast} + \Sigma(E), \]
so that if we wish to use the experimental \( \mu_{\ast}' \) we must also use a renormalized self-energy, defined by
\[ \Sigma'(E) = \Sigma(E) - \text{Re} \Sigma(-\mu_{\ast}'). \]

The equation for this renormalized quantity is (we drop the primes from now on)
\[
\Sigma(E) = (g^2 m_e k_0 / \pi^2) \left( \coth(E/2kT) - \coth(-\mu_{\ast}/2kT) \right) - \left[ \frac{g^2 (2m_e)}{2\pi} \right] \left[ (1 + N(\omega_0)) \times \frac{N(\omega_0)(E - \omega_0 + \mu_{\ast} + \Sigma(E + \omega_0))}{(1 + N(\omega_0))(E + \omega_0 + \mu_{\ast} + \Sigma(E + \omega_0))} 
\]  
(13)
In principle, we see that the self-energy depends upon what value we assign to \( k_0 \). However, for the range of \( E \) in which we are interested,
\[
E = -\mu^* \\
\]
and for a large energy gap
\[
\mu^* \gg KT,
\]
the first term in Eq. (13) is negligible.
Equation (13) has been solved numerically using an IBM 360 computer and the results are shown in Figs. 1 and 2 for three temperature values. The dimensionless constant
\[
G = (e^2/2\pi)(2m^*/\omega_0)^4
\]
was taken to be 0.5.
It is immediately apparent from Fig. 1 that the imaginary part of the self-energy has an exponential dependence on energy (with a small periodic oscillation superposed). The results look very similar to those obtained by Mahan starting from the Frohlich Hamiltonian (compare Figs. 1 and 2 of Ref. 5). We shall see in the next section that this exponential behavior of the self-energy implies directly that the absorption coefficient also has the same exponential dependence.

3. ABSORPTION COEFFICIENT

The absorption coefficient for this model is given by (see Ref. 6)
\[
A(\omega) = A_0 \tanh(\omega/2KT) \Re \sum_k \int_{-\infty}^{+\infty} \frac{dE}{2\pi} (dE' / 2\pi) \times G(kc'E) G(kn', E = -\omega),
\]
(14)
and by using the appropriate forms for \( G(c) \) and \( G(v) \) we obtain
\[
A(\omega) = A_0 \tanh(\omega/2KT) \int_{0}^{\infty} dy \gamma \times \Im \left( \frac{1 + N(\omega - \mu^* - y) - \tilde{f}(y + \mu^*)}{y(1 + m^*/m^*) + E_{\omega} - \omega + \Sigma(y + \mu^* - \omega)} \right),
\]
(15)
The imaginary part in the integral is approximately proportional to \( \Im E \) and hence this leads to \( A(\omega) \) having an exponential behavior. This was confirmed by direct evaluation of the integral and the results are shown in Fig. 3.

These graphs demonstrate one part of the Urbach rule, the characteristic exponential decay of the absorption. The only remaining problem is the temperature dependence of the coefficient \( \sigma \) [see Eqs. (1) and (2)]. This is exhibited in Fig. 4. The curve shows the general shape of the experimental curves but it cannot be fitted very accurately by the form of Eq. (2) for any value of \( E_0 \). However, in view of the simplicity of the model, even a qualitative agreement with the observed behavior seems remarkable.

4. DISCUSSION

We have found that in our model Urbach's rule is obeyed as a consequence of the interaction between valence electrons and phonons.

We have not, of course, proved this for a real semiconductor, but it is difficult to believe that the use of a more realistic interaction and more realistic phonon energies would change the qualitative form of the absorption coefficient. This is confirmed to a certain extent by the similarity of the results obtained in this paper and in the paper by Mahan (using different interactions). It has, however, been pointed out to us by Haering that in certain cases there may be some cancellation between the two processes, one involving the conduction electron-phonon interaction and one involving the valence electron-phonon interaction. An appreciable cancellation is to be expected though, only if the interaction and the electron mass are roughly the same in both bands. This is usually not the case.