Multiphoton processes in light absorption by homopolar crystals. Self-trapping and classical solutions

A. S. Ioselevich
L. D. Landau Institute of Theoretical Physics, USSR Academy of Sciences

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The absorption of light with a photon energy deficit $\Delta = E_g - \hbar\Omega \gg \hbar\omega_0$, with participation of a large number of optical strain phonons at frequency ω_0, is considered. It is shown that at low temperatures $T < \hbar\omega_0$ two alternate mechanisms exist. The first is connected with absorption of the required number of phonons from the thermostat, and the second with tunnel self-trapping. The Δ-dependent temperature limit $T^* < \hbar\omega_0$ above and below which the first and second process dominate, respectively, is found. The existence of several absorption mechanisms manifests itself in the fact that the classical solution that describes a multiphonon transition of an electron-phonon system is not unique. The absorption coefficient agrees well with the Urbach rule at $T^* < T < \hbar\omega_0$ and becomes practically independent of temperature at $T < T^*$. At $T > \hbar\omega_0$ the absorption is accompanied by formation of an optical classical fluctuation that has a level of energy $-\Delta$.

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1. INTRODUCTION

Optical absorption has in many crystals an exponential long-wave tail frequently described with the aid of the empirical Urbach rule[1]

$$K_a \propto \exp(-\sigma\Delta/T). \qquad (1)$$

Here K_a is the absorption coefficient, $\Delta = E_g - \hbar\Omega$ is the photon energy deficit, Ω is the light frequency, E_g is the fundamental absorption edge, T is the temperature, and σ is a number of the order of unity and depends frequently on temperature, especially at low temperatures.

The present paper deals with the mechanism of optical absorption in nonpolar crystals, wherein many optical strain phonons participate in the photon absorption and in the creation of an electron-hole pair (exciton). The distinguishing feature of strain phonons, for which the electron-phonon interaction is short-range, lead to substantial differences from the previously considered[2] case of polarized optical phonons in an ionic crystal. We consider only optical strain phonons, since a consistent continual theory can be constructed only for optical phonons. An investigation of the contribution of the acoustic phonons shows that an important role is played for the latter by momenta of the order of the reciprocal lattice constant, so that inclusion of the acoustic phonons in the theory calls for knowledge of the details of the electron and phonon spectra, as well as of the electron-phonon interaction at large momenta. Yet the interaction between an electron and optical strain phonons does not differ in principle from the interaction with Debye acoustic phonons (only the phase space can differ substantially). In particular, if the coupling is strong both phonon types lead to formation of autolocalized states. It is therefore to be hoped that the model considered reflects the main features of the real situation.

For simplicity, only the single-particle problem is investigated here. This simplification can be justified if at least one of the following two conditions is satisfied: 1. The elementary excitations in the crystal are Frenkel excitons or at least excitons having a radius much smaller than the characteristic spatial scale $\hbar/(m\Delta)^{1/2}$ of the problem. To be definite, we shall refer hereafter to excitons. Possible two-particle effects are discussed in Sec. 4. 2. The interaction of one of the produced particles with the phonons is much stronger than the interaction of the second.

A consistent quantitative theory that describes the exponential dependence of K_a and is valid at arbitrary temperature T and at a deficit $\Delta \gg \hbar\omega_0$ is expounded in Sec. 3. It is based on the use of the classical solutions for the functional integral that represents the exciton Green's function. The possibility of using the saddle-point method in the functional integral (i.e., of using classical solutions) is ensured by the fact that the number of phonons is large, $\Delta \gg \hbar\omega_0$. A similar approach was first applied by Iordanskiĭ and Pitaevskiĭ[3] to the problem of multiphonon decay of quasiparticles in He II.

The distinguishing features of a system consisting of an exciton and phonons that interact with the exciton but not with one another is the possibility of accurately excluding the phonon fields and reducing the role of the phonons to an effective self-action of the exciton. It is then possible to seek classical solutions for this self-acting field rather than for the initial system. In the case of a strong exciton–phonon coupling, another nontrivial feature is that the classical solution is not unique (in contrast to Ref. 2), owing to the presence of two "ground" states of the exciton, free and autolocalized.[1)] The first is metastable[4,5] and its decay is due to tunnel self-trapping, whose probability was calculated (at $T = 0$) by Iordanskiĭ and Rashba.[6]

Assume that an optical transition produced in the crystal and virtual exciton with a certain energy deficit. For this transition to end up in absorption of a photon and production of a real exciton, the latter must go over in one way or another into a real state (i.e., a state with non-negative kine-

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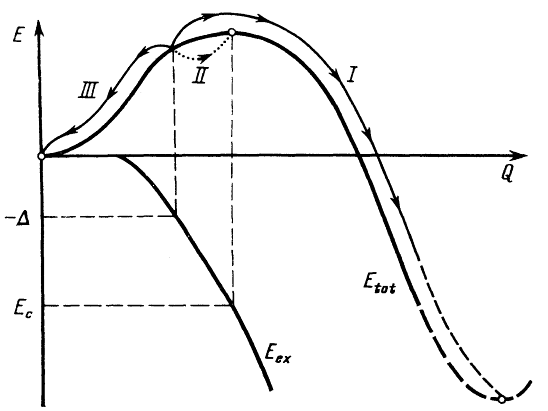

FIG. 1. Dependence of the total energy $E_{\rm tot}$ and of the exciton energy $E_{\rm ex}$ on the arbitrary configuration coordinate Q. The light circles show three "ground" states of the system: ($E_{\rm tot}=0$), self-trapping ($E_{\rm tot}<0$) and unstable saddle ($E_{\rm tot}>0$); E_c is the exciton energy at the saddle point. The possible paths of an exciton with a deficit Δ are shown: I-self-trapping, II-path into a saddle state (unphysical), III-transition to a free state. The picture described is meaningful at $T\ll\hbar\omega_0$.

tic energy). Corresponding to the presence of two ground states are two possible manners of action for an exciton having an energy deficit Δ relative to the ground state (Fig. 1). The first is to absorb phonons from the thermostat and go over to a free state. The second is tunnel self-trapping (which, generally speaking, does not call for external energy). It is clear that the probability of the first process decreases with decreasing temperature or with increasing Δ; the probability of the second, on the other hand, is small but finite, and is practically independent of T and Δ if they are small. At sufficiently low temperature self-trapping is therefore always more probable (as $T\to0$ there are no phonons and their absorption, needed for the transition to a free state, is impossible). At higher temperature, conversely, the process with phonon absorption is more probable.

At sufficiently low temperatures, when there are few phonons, the transition to the free state proceeds with absorption of the minimum number $n=\Delta/\hbar\omega_0$ of phonons. In this case the problem can be treated by high-order perturbation theory, as was done earlier[2] (see also Ref. 7).

With further rise in temperature, perturbation theory no longer holds, since processes with reradiation of phonons becomes probable. In this situation, however, we can use the optimal-fluctuation method. Just as for polarization phonons, static fluctuations are ensured by the short lifetime of the exciton in the fluctuation state compared with the reciprocal frequencies of the phonons that make up this state. A qualitative investigation of the described limited cases is carried out in Sec. 2, where all the main results of the study are also presented.

A semiquantitative theory of the Urbach rule with account taken of the self-trapping states was first proposed by Sumi and Toyozawa.[8] Their model and approximations, however, are in our opinion unfounded. They regard the potential of the exciton–lattice interaction to be static, but we shall show this to be valid only at very high temerpatures (see Sec. 2). The same holds for the introduction of an interaction mode, a procedure permissible, by its very meaning, only in the static case. But even in the static case the optimal-fluctuation method used in Sec. 2 of the present paper and the method of Sumi and Toyozawa lead to different dependences of $\ln K_a$ on Δ (Δ^2 in Ref. 8 and $\Delta^{1/2}$ in the present paper), although their ideas seem close. The point is that Sumi and Toyozawa regard the radius of the potential connected with the interaction mode to be independent of Δ and equal to the lattice constant. It will be shown below, however, that although the localized state itself has the same scale as the lattice constant, the scale of the optimal fluctuation is macroscopic ($a=\hbar/(m\Delta)^{1/2}\gg d$). In this sense there exists for each Δ a separate interaction mode that is no way equal to the mode that is essential in the self-trapping state. Thus, the single-node approximation of Sumi and Toyozawa, wherein the momentum dependence of the self-energy is neglected, is incorrect.

We discuss now the weak-coupling case. If the exciton–phonon interaction is not strong enough, there is no trapping state, and the only thing the exciton can do is absorb phonons and go over to a free state. In this case $K_a\to0$ as $T\to0$, in contrast to the strong-coupling case, when K_a is finite at $T=0$ and is equal to the self-trapping probability. Therefore, in terms of the Urbach rule, σ is constant as $T\to0$ for weak coupling, while σ/T is constant for strong coupling, in good agreement with the experimental data (see, e.g., Ref. 8). The last result is similar to that obtained in Ref. 2 for polarization phonons. The difference is that the polarization cloud in the ionic crystal is produced without a barrier,[9] and it is meaningless to speak of transitions to a free state, since it is absolutely unstable. In addition, owing to the absence of a barrier, the probability of fluctuation of a polarization with a level Δ becomes large as $\Delta\to0$, in contrast the probability of self-trapping on account of strain phonons, which remains exponentially small also at $\Delta=0$.

2. QUALITATIVE APPROACH AND PRINCIPAL RESULTS

The Hamiltonian of an exciton interacting with the phonon field is of the form

$$\hat{H}=-\frac{\nabla^2}{2m}+\sum_{\mathbf{q}}\left(\hbar\omega_{\mathbf{q}}a_{\mathbf{q}}^+a_{\mathbf{q}}+V_{\mathbf{q}}a_{\mathbf{q}}e^{i\mathbf{q}\mathbf{r}}+V_{\mathbf{q}}^*a_{\mathbf{q}}^+e^{-i\mathbf{q}\mathbf{r}}\right), \tag{2}$$

where $\mathbf{r}$ is the exciton coordinate, m is its translation mass (we disregard the internal degrees of freedom of the exciton, see the Introduction), a^+ and a are the creation and annihilation operators of a phonon with wave vector $\mathbf{q}$, $\omega_{\mathbf{q}}$ is the phonon frequency, and $V_{\mathbf{q}}$ is the matrix element for the exciton–phonon interaction and takes for strain phonons the form

$$V_{\mathbf{q}}=(E_{\rm FC}\hbar\omega_{\mathbf{q}})^{1/2}. \tag{3}$$

Following Ref. 6, we have introduced the Franck-Condon energy $E_{\rm FC}$. For optical deformation phonons we have[2)]

$$E_{\rm FC}=\gamma^2\hbar\omega_0, \tag{4}$$

where γ is a dimensionless coupling constant and ω_0 is the frequency of the phonons, which we assume to have no dispersion.

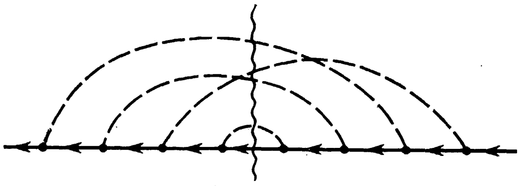

FIG. 2. Typical diagram corresponding to the absorption of $n = 4$ phonons. The solid and dashed lines show the exciton and phonon Green's functions, respectively.

The light-absorption coefficient is proportional to the imaginary part of the exact Green's function of the exciton[2]:

$$K_a \propto \int d^3\mathbf{r}\, \operatorname{Im} G_{-\Delta}(0,\mathbf{r}). \tag{5}$$

Since we are interested only in the exponential dependence, we do not write out the proportionality coefficient.

When perturbation theory is applicable, we can carry out, in analogy with Ref. 2, a diagram analysis of expression (5). Consider the diagram shown in Fig. 2 and containing $n = \Delta/\hbar\omega_0$ phonon lines. Assuming that all the phonon momenta and that the exciton momenta in the intermediate state are of the same scale q, we see that the order of magnitude of the diagram does not change when the sequence of phonon absorption is changed, so that the contribution of all these diagrams is proportional to the number $n!$ of permutation of the phonon lines (see Ref. 2). Counting the number of vertices and free exciton Green's functions and expanding the factorial in accord with Stirling's law, we obtain

$$K_a \propto w_q^{\,n}, \tag{6}$$

$$w_q = \frac{nNV_q^2 q^3 v}{(\Delta+\hbar^2q^2/2m)^2} = \frac{E_{FC}\Delta N v q^3}{(\Delta+\hbar^2q^2/2m)^2}, \tag{7}$$

where $N = [\exp(\hbar\omega_0/T) - 1]^{-1}$ is the phonon occupation number. In the derivation of (7) we took into account that

$$\sum_{\mathbf{q}} (\ldots) = v \int \frac{d^3\mathbf{q}}{(2\pi)^3}(\ldots),$$

where v is the volume of the unit cell. Of course, perturbation theory remains valid only if $w_q \ll 1$. Otherwise the diagrams with more than n phonon lines make a comparable contribution to K_a. The scale of the momentum q in (7) and (8) should be determined from the condition that K_a be a maximum. It is easily seen that w_q reaches a maximum at $q \sim (m\Delta)^{1/2}/\hbar$. Therefore

$$K_a^{\mathrm{III}} \propto \exp\left\{-\frac{\Delta}{\hbar\omega_0}\ln\left(\frac{B}{\lambda N}\left(\frac{\hbar\omega_0}{\Delta}\right)^{1/2}\right)\right\}, \tag{8}$$

$$\lambda = E_{FC} m^{3/2} v \omega_0^{1/2}/\hbar^{5/2} \sim (E_{FC}/E_B)(\hbar\omega_0/E_B)^{1/2}, \tag{9}$$

where $E_B = \hbar^2/2v^{2/3}m$ is the width of the exciton band and B is a number of the order of unity and takes into account the difference between the permuted diagrams. The condition for the applicability of the continual approximation can be written in the form $\Delta \ll E_B$. The condition for the applicability of perturbation theory is a large argument of the logarithm in (8).

At low temperature ($T \ll \hbar\omega_0$) the main factor under the logarithm sign is N^{-1} and expression (8) can be *rewritten in* the form (1), where

$$\sigma = 1 + \frac{T}{\hbar\omega_0}\ln\left(\frac{B}{\lambda}\left(\frac{\hbar\omega_0}{\Delta}\right)^{1/2}\right). \tag{10}$$

We see that according to (10) we have $\sigma \approx 1$, and the correction should have, besides the temperature dependence, also a weak (logarithmic) dependence on Δ.

As $T \to 0$ the absorption described by Eqs. (1) and (10) vanishes. However, as already noted in the Introduction, at sufficiently low temperature self-trapping becomes more probable. The absorption coefficient in this region is proportional to the probability of the tunnel self-trapping:

$$K_a^{\mathrm{I}} \propto \exp\{-\lambda^{-2} f(\lambda^2\Delta/\hbar\omega_0)\}. \tag{11}$$

Here $f(x)$ is a certain universal dimensionless function with the following asymptotics, which are calculated in Sec. 3:

$$f(x) = S_0 + \tau_0^{\mathrm{I}} x - S_1 x^{3/2} \quad (x \ll 1),$$
$$f(x) = 13.3 x^{1/2} \quad (x \gg 1).$$

Here S_0, τ_0^{I}, and S_1 are positive constants. At $\Delta = 0$ Eq. (11) should coincide with the free-exciton self-trapping probability calculated in Ref. 6, where it is estimated that $S_0 < 73$. Equation (11) is valid when the argument of the exponential is large. It follows from (9) that $\lambda \ll 1$ in the case of strong or intermediate coupling, and this condition is satisfied.

Comparing (11) with (1) we obtain a self-trapping temperature

$$T^* = \lambda^2\Delta/S_0 \tag{12}$$

such that Eq. (11) is valid at $T < T^*$, and Eq. (1) at $T^* < T < \hbar\omega_0$. We note also that expression (11) was obtained in the strong-coupling approximation $E_{FC} \gg E_B$ (see Ref. 6). On the whole, self-trapping states exist only at $E_{FC} > E_{\min} \sim E_B$ (see Ref. 4),[3)] and when this condition is violated there is no self-trapping region ($T^* = 0$).

To determine the absorption coefficient in the high-temperature region we use the optimal-fluctuation method.[2] We assume that a thermal fluctuation was produced in the crystal, with a characterstic sublattice displacement u and with a spatial dimension a. The energy consumed in its production is then

$$E_{def} \sim \hbar\omega_0 (u/d)^2 a^3,$$

where d is the lattice constant. On the other hand, for an excitonic level with energy $-\Delta$ to be present in the fluctuation well the following conditions must be satisfied:

$$\gamma\hbar\omega_0 u/d \gtrsim \Delta, \qquad (m\Delta)^{1/2} \gtrsim \hbar/a.$$

From this we get the minimum allowable deformation energy

$$E_{def}^{min} \sim \hbar\omega_0 \frac{\hbar^3}{(m\Delta)^{3/2}}\left(\frac{\Delta}{\gamma\hbar\omega_0}\right)^2 \sim \frac{E_B^{3/2}\Delta^{1/2}}{E_{FC}}.$$

The absorption coefficient is proportional to the probability of the onset of a fluctuation with a minimum energy

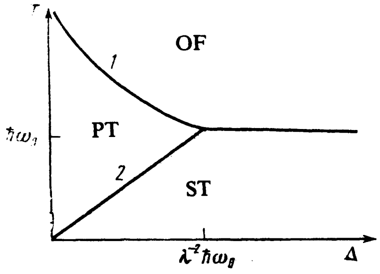

FIG. 3. Regions of realization of different limiting regime on the $T\Delta$ plane. OF-optimal classical fluctuation, PT-perturbation theory, ST-self-trapping; 1-$T=\lambda^{-1}\hbar\omega_0(\hbar\omega_0/\Delta)^{1/2}$, 2-$T=T^*=\lambda^2\Delta/S_0$.

$$K_a\propto\exp(-E_{def}^{min}/T)=\exp\left(-\frac{6.7\Delta^{1/2}(2E_B)^{3/2}}{TE_{FC}}\right). \qquad (13)$$

The numerical coefficient in the argument of the exponential is obtained in Sec. 3.

The condition for the applicability of (13) is that the fluctuation be static over times on the order of the free path time of an exciton having an energy Δ for scattering by optical strain phonons. This time is easy to calculate by using the Hamiltonian (2):

$$\tau_s\sim E_B^{3/2}\hbar/TE_{FC}\Delta^{1/2}. \qquad (14)$$

The condition that the fluctuation be static is of the form

$$\omega_0\tau_s\sim E_B^{3/2}\hbar\omega_0/TE_{FC}\Delta^{1/2}\ll 1. \qquad (15)$$

It is easy to verify that the condition (15) coincides with $w_q \gg 1$, i.e., perturbation theory and the optimal-fluctuation method are alternate methods that complement each other.

Figure 3 shows, in the $T\Delta$ plane, the regions of realization of the various limiting cases considered in this paper. Expressions (8), (11), and (13) cover practically the entire temperature region and the deficit region $\hbar\omega_0\ll\Delta\ll E_B$.

3. RIGOROUS APPROACH. CLASSICAL SOLUTIONS

In Ref. 2 were derived, for the case of polarization optical phonons, self-consistent-field equations that make it possible to obtain the imaginary part of the Green's function at $\Delta\gg\hbar\omega_0$. To this end we excluded from the functional integral the phonon fields, and a saddle point lying in the imaginary time domain was obtained from the exciton fields. The Euler equations that determine the classical saddle-point solution are in fact the self-consistent-field equations.

We can obtain in perfect analogy equations for phonons of any other kind. The general equation is of the form (we put $\hbar=1$ in this section):

$$K_a\propto\exp\{-\Delta\tau-\tilde S(\tau)\}, \qquad (16)$$

$$\tilde S(\tau)=\int_0^\tau dt\int d^3\mathbf{r}\frac{|\nabla\psi(\mathbf{r},t)|^2}{2m}$$
$$+{}^1/_2\int_0^\tau\int_0^\tau dt_1\,dt_2\iint d^3\mathbf{r}_1\,d^3\mathbf{r}_2 U(\mathbf{r}_1-\mathbf{r}_2,t_1-t_2)|\psi(\mathbf{r}_1,t_1)\psi(\mathbf{r}_2,t_2)|^2, \qquad (17)$$

$$U(\mathbf{r},t)=-v\int\frac{d^3\mathbf{q}}{(2\pi)^3}e^{i\mathbf{qr}}V_\mathbf{q}^2(D(\mathbf{q},t)+D(\mathbf{q},-t)), \qquad (18)$$

$$D(q,t)=\exp(\omega_q t)\cdot\begin{cases}N_q & (t>0),\\ N_q+1 & (t<0).\end{cases} \qquad (19)$$

Here D is the phonon D-function continued into the imaginary time domain at finite temperature. The wave function ψ is assumed normalized to unity and should be obtained from the condition that the action $\tilde S$ be an extremum. The time τ is determined from the condition

$$d\tilde S(\tau)/d\tau=-\Delta. \qquad (20)$$

For the case of optical strain phonons, the integral (18) can be easily calculated:

$$U(\mathbf{r},t)=\{Ne^{\omega_0|t|}+(N+1)e^{-\omega_0|t|}\}vE_{FC}\omega_0\delta(\mathbf{r}). \qquad (21)$$

Making the change of variables

$$\mathbf{r}\to(N+1)vE_{FC}\omega_0 m\mathbf{r},\quad \psi\to((N+1)vE_{FC}\omega_0 m)^{-3/2}\psi,$$
$$\tilde S\to((N+1)vE_{FC}\omega_0 m)^{-2}m^{-1}S,\quad t\to\omega_0^{-1}t \qquad (22)$$

and introducing the symbol $\beta=\hbar\omega_0/T$, we obtain

$$S(\tau)=\int_0^\tau dt\int d^3\mathbf{r}\frac{|\nabla\psi(\mathbf{r},t)|^2}{2}-{}^1/_2\int_0^\tau\int_0^\tau dt_1\,dt_2(e^{-|t_1-t_2|}$$
$$+e^{|t_1-t_2|-\beta})\int d^3\mathbf{r}|\psi(\mathbf{r},t_1)\psi(\mathbf{r},t_2)|^2. \qquad (23)$$

The corresponding nonlinear Schrödinger equation is of the form

$$\left\{-\frac{\nabla^2}{2}+V(\mathbf{r},t)-E_\tau(t)\right\}\psi(\mathbf{r},t)=0, \qquad (24)$$

$$V(\mathbf{r},t)=-\int_0^\tau dt'(e^{-|t-t'|}+e^{|t-t'|-\beta})|\psi(\mathbf{r},t')|^2. \qquad (25)$$

The wave functions and the energy have the obvious symmetry property:

$$\psi(\mathbf{r},t)=\psi(\mathbf{r},\tau-t),\quad V(\mathbf{r},t)=V(\mathbf{r},\tau-t),\quad E_\tau(t)=E_\tau(\tau-t).$$

Differentiating (23) directly and taking into account the condition $\delta S/\delta\psi=0$, we obtain

$$dS(\tau)/d\tau=E_\tau(0)=E_\tau(\tau). \qquad (26)$$

It is easy to prove for S the virial theorem (see Ref. 6), which leads to the relation

$$S(\tau)=-\int_0^\tau E_\tau(t)\,dt. \qquad (27)$$

Relations (26) and (27) will play an important role in the analysis that follows.

Unfortunately, the ability to investigate Eqs. (23)–(25) analytically is quite limited. Nonetheless, supported by analytic results, we can discern the qualitative features of the solutions. We therefore present first three asymptotically correct solutions, which we use next to construct a practically complete picture of the behavior of $S(\tau)$.

1) At $\tau\ll 1$ we may assume that

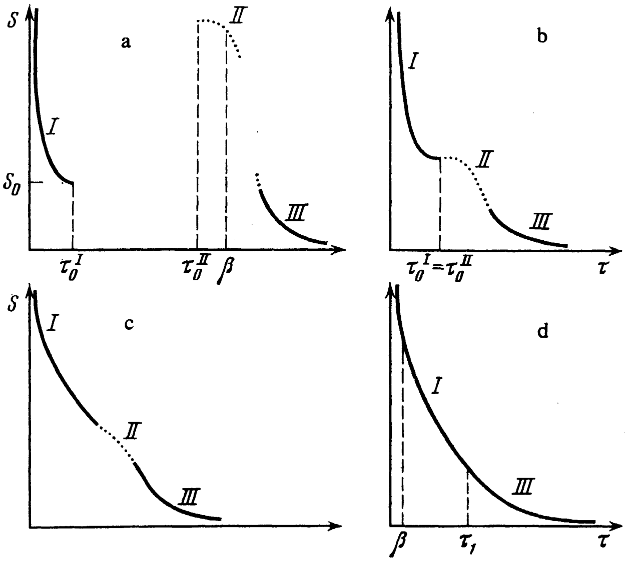

FIG. 4. Approximate plots of $S(\tau)$ at different temperatures: a-$\beta = \hbar\omega_0/T \gg 1$, b-$\beta = \beta_0 \sim 1$, c-$\beta_1 < \beta < \beta_0$, d-$\beta < \beta_1$.

$$\psi(\mathbf{r}, t) \equiv \psi(\mathbf{r}), \quad V(\mathbf{r}, t) \equiv V(\mathbf{r}), \quad E_\tau(t) \equiv E_\tau. \tag{28}$$

Actually, the characteristic time in which the potential energy (25) changes is $t \sim 1$, it is clear therefore that at $\tau \ll 1$ the time dependence does not come into play. The substitutions

$$\mathbf{r} \to \tau(1+e^{-\beta})\mathbf{r}, \quad \psi \to (\tau(1+e^{-\beta}))^{-3/2}\psi,$$

yield then

$$S_\mathrm{I}(\tau) = \frac{A}{(1+e^{-\beta})^2\tau}, \quad E_\tau = -\frac{A}{(1+e^{-\beta})^2\tau^2} \quad (\tau \ll 1),$$
$$A = \int d^3\mathbf{r}\left\{\frac{|\nabla\psi|^2}{2} - \frac{|\psi|^4}{2}\right\} = 44. \tag{29}$$

To find the constant A we have used the results of the numerical calculations of Zakharov, Sobolev, and Synakh.[10] Equation (29) describes the initial sections of the curves in Figs. 4a–4d.

2) It is easy to verify that at $\tau = \beta$ the condition (28) is satisfied exactly (for arbitrary β). Indeed, substituting $\psi(\mathbf{r}, t) \equiv \psi(\mathbf{r})$ and $\tau = \beta$ in (25) we obtain

$$V(\mathbf{r}, t) = -2(1-e^{-\beta})\psi^2(\mathbf{r}) \equiv V(\mathbf{r}),$$

which confirms the assumption made. Next, in analogy with (29), we obtain

$$S(\beta) = A\beta/4(1-e^{-\beta})^2, \quad E_\beta = -A/4(1-e^{-\beta})^2. \tag{30}$$

3) At $\tau - \beta \gg 1$ we can neglect the first term of (25). Then, making the substitution

$$t_2 \to \tau - t_2, \quad \mathbf{r} \to e^{\tau-\beta}\mathbf{r}, \quad \psi \to e^{-3/2(\tau-\beta)}\psi,$$

we obtain

$$S(\tau) = (B^2/2e)\, e^{2(\beta-\tau)}, \tag{31}$$

$$\frac{B^2}{4e} = \int_0^{\tau^*} dt \int d^3\mathbf{r}\, \frac{|\nabla\psi(\mathbf{r}, t)|^2}{2} - \frac{1}{2}\int_0^{\tau^*}$$
$$\times \int_0^{\tau^*} e^{-t_1-t_2}\, dt_1\, dt_2 \int d^3\mathbf{r}\, |\psi(\mathbf{r}, t_1)\psi(\mathbf{r}, t_2)|^2, \tag{32}$$

where $\tau^* \sim 1$ is determined from the condition $E_\tau(\tau^*) = 0$. The existence of a finite τ^* is confirmed by the following considerations. It can be seen from (32) that $V(\mathbf{r}, t) = e^{-t}V(\mathbf{r})$. Since the potential $V(\mathbf{r})$ is short-range, the level will inevitably be pushed out at a certain $t = \tau^*$. Equation (31) describes the tails of the $S(\tau)$ curves in Figs. 4a–4d as $\tau \to \infty$. Unfortunately, it is impossible to obtain a simple analytic estimate for the universal constant B.

We proceed now to a qualitative investigation of Eqs. (23)–(25). We being with the case $T = 0$ ($\beta = \infty$). An analysis of the next higher corrections in $\tau \ll 1$ to the solution (29) shows that the absolute value of the potential $V(t)$, and hence of the energy $E_\tau(t)$, decreases somewhat near the ends of the interval $(0, \tau)$ (Fig. 5a). At a certain $\tau = \tau_0^\mathrm{I} \sim 1$ the energy vanishes at the end points of the interval (Fig. 5b). The potential remains constant in this case. The level pushed out because of the short-range character of the potential. We note that in the case of polarization phonons we had a Coulomb potential and the level was not pushed out.[2] It is clear from dimensionality considerations that the relation $Va^2 \sim 1$ holds for the characteristic value of the potential V and for its radius a. It is known, however, that the level is pushed out at the same relation, and this is therefore possible already at $\tau \sim 1$, when the parameters of the potential change by an amount equal to their own value in the $(0, \tau)$ interval. According to (20) and (26) the solution with $E_\tau(0) = dS/d\tau = 0$ corresponds to $\Delta = 0$, i.e., describes tunnel self-trapping of a

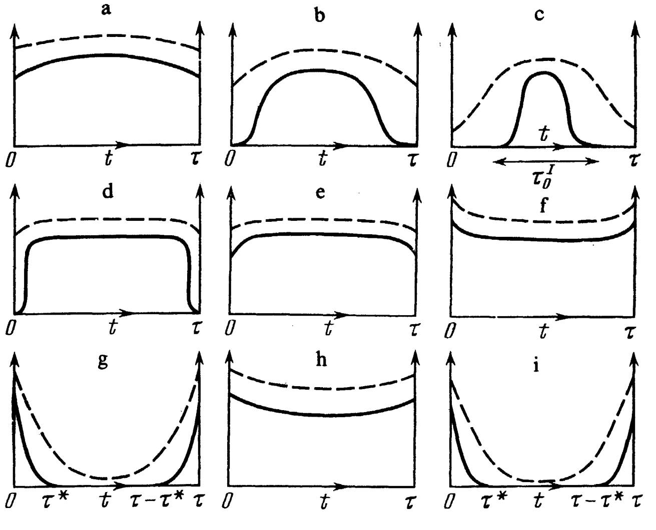

FIG. 5. Evolution of the $E(t)$ dependence with increasing τ. The abscissas and ordinates are the times in the $(0, \tau)$ interval and the energy, respectively. The solid and dashed lines are plots of $|E(t)|$ and $|V(t)|$, respectively. Figures a–g, arranged in increasing order of τ, pertain to the case $\beta \gg 1$: a-$\tau \ll 1$, b-$\tau = \tau_0^\mathrm{I} \sim 1$, c-$\tau > \tau_0^\mathrm{I}$, d-$\tau = \tau_0^\mathrm{II} = \beta - c(c \sim 1)$, e-$\tau_0^\mathrm{II} < \tau < \beta$, f-$\tau > \beta$, g-$\tau - \beta \gg 1$. Figures 5h and 5i pertain to the case $\beta \ll 1$: h-$\beta < \tau \ll 1$, i-$\tau \gg 1$.

free exciton (a transition between the free and self-trapping vacuum). We shall therefore call this an instanton solution, in analogy with the known field-theory problems.

We consider now the behavior of $S(\tau)$ near $\tau = \tau_0^{\mathrm{I}}$. The potential $V(0, r)$ is a smooth function of the parameter τ. However, as is well known (see, e.g., Ref. 11), if a level vanishes at $\lambda < 0$ in a potential $V(\lambda, r)$ that depends smoothly on the parameter λ, then $E(\lambda) \sim \lambda^2$ as $\lambda \to +0$. Consequently $dS/d\tau \sim (-\tau_0^{\mathrm{I}} - \tau)^2$ and

$$S(\tau) - S(\tau_0^{\mathrm{I}}) \sim (\tau_0^{\mathrm{I}} - \tau)^3. \tag{33}$$

Substituting (29) and (33) in (22), (20), and (16) we arrive at Eq. (11) for the absorption coefficient as $T \to 0$. We note that further increase of $\tau(\tau > \tau_0^{\mathrm{I}})$ is meaningless, since $E_\tau(t) \equiv 0$ outside an interval of length τ_0^{I} (Fig. 5c).

The described classical solution corresponds to transitions from the vicinity of the free vacuum to the self-trapping one. At $T = 0$ this solution is unique, for only a transition into a self-trapping state can proceed without an energy influx from the outside. At a finite temperature there appear two other solutions corresponding to transition into a free and a saddle vacuum. The latter, however, does not satisfy the saddle-point condition (incorrect sign of $d^2S/d\tau^2$) and, at least in this problem, has no physical meaning.

Let the temperature be low but finite ($\beta \gg 1$). In the already described solution S_{I}, this leads only to corrections small in the parameter $\exp(-\beta)$. At a certain finite β, however, the solution (30) becomes meaningful. Obviously, at $\beta \gg 1$ it describes a transition into a saddle vacuum. Indeed, the solution (30) corresponds to $\Delta = -E_c$ (Fig. 1). In this case the exciton lands immediately in a fluctuation that corresponds to a stationary saddle state, so that the solution (30) is found to be stationary.

An analysis of the corrections in $\tau - \beta \ll 1$ to the solution (30) shows that at $\tau < \beta$ the absolute values of the potential and of the energy decrease near the ends of the interval $(0, \tau)$ (Fig. 5e), and at $\tau = \tau_0^{\mathrm{II}} = \beta - c$ (where $c \sim 1$) the energy becomes equal to zero, and a second instanton solution is obtained, corresponding to the transition from the free to the saddle vacuum (Fig. 5d). It is seen from Fig. 4a that the described solution S_{II} has an incorrect convexity and does not correspond to a saddle point in Im G, although formally it is a stationary point of the action; we shall therefore not describe its properties in greater detail.

In the region of large τ there exists a third solution S_{III} that describes a transition to a free vacuum (Fig. 5g). It is this solution which should contain the perturbation-theory result (8). Unfortunately, it is impossible to investigate fully the picture of the vanishing of the solution S_{II} and the onset of S_{III}. This phenomenon apparently takes place at $0 < \tau - \beta \sim 1$, and the action S should undergo in this case a jump (Fig. 4a). There exists possibly a small interval where the solutions S_{II} and S_{III} coexist. We note incidentally that the transition region $\tau - \beta \sim 1$ is of no practical importance. Indeed, when Δ decreases along the S_{III} curve (Fig. 4a) the quantity $|dS/d\tau| \sim \Delta$ increases. However, as shown in Sec. 2, when Δ increases the solution change $S_{\mathrm{III}} \to S_{\mathrm{I}}$ takes place (Fig. 3). At low temperature($\beta \gg 1$) this change corresponds to a small Δ, i.e., to a large $\tau - \beta$, so that only the region $\tau - \beta \gg 1$ is of practical interest in the solution S_{III}. In this region, however, S_{III} is described by the asymptotic solution (31). Substituting (31) in (22), (20), and (16) we obtain ultimately expression (8) for K_a^{III}.

Thus, the behavior of the solutions S_{I}, S_{II}, and S_{III} at low temperature can be regarded as determined. How do these solutions evolve when the temperature is raised?

At a certain $\beta = \beta_0 \sim 1$ the solutions S_{I} and S_{II} should merge (Fig. 4b). At the point $\beta = \beta_0$ the two instanton solutions coincide ($\tau_0^{\mathrm{I}} = \tau_0^{\mathrm{II}}$), and with further decrease of β ($\beta < \beta_0$) they vanish completely, and the region of the solutions S_{I} begins to absorb the region S_{II} (Fig. 4c). Similar merging and absorption takes place for solutions S_{III} and S_{II}. Finally, at a certain $\beta = \beta_1 < \beta_0$ the solution S_{II} vanishes completely, while the solutions S_{I} and S_{III} are preserved also at $\beta \ll 1$ (Fig. 4d).

The exact results 1), 2), and 3) are valid at any temperature. At $\beta \ll 1$, however, the solution (30) belongs already to class S_{I} and not to S_{II} as at $\beta \gg 1$ (Fig. 4d). The evolution of the solution (29) with increasing τ also differs from the case $\beta \gg 1$. Indeed, at $\beta < \tau \ll 1$ the absolute value of the energy increases towards the end points of the interval $(0, \tau)$ (Fig. 5h), leading at $\tau = \tau_1 \sim 1$ to a direct transition from S_{I} to S_{III} (Fig. 5i). The use of the asymptotic expression (29) at $\tau \ll 1$ and $\beta \ll 1$ leads to the result (13) of the optimal-fluctuation method, and the use of (31) at $\tau \gg 1$ leads to the perturbation-theory result (8).

It should be noted that in contrast of the low-temperature case, at high temperature there is only one classical solution. The reason is that at $T \gg \hbar\omega_0$ the coherence of the state is violated (i.e., the absorption process terminates) before the system manages to find itself in any one of the stationary states shown in Fig. 1, so that one cannot say which of them is the final state of the absorption process. The probability of the onset of a classical fluctuation with any exciton level turns out to be quite high, and the lifetime of the exciton at this level small enough, so that it is precisely such an optimal fluctuation which determines the absorption process, and the exciton state in it is the final state.

4. POSSIBLE TWO-PARTICLE EFFECTS

If the electron and hole are not too strongly attracted, so that the electron binding energy $R < \Delta$, an important role is assumed by the internal degrees of freedom of the exciton. The wave function ψ depends in this case already not on one but on two coordinates, $\mathbf{r}_e$ of the electron and and $\mathbf{r}_h$ of the hole. The electron–hole interaction that leads to exciton formation should be included explicitly in the Hamiltonian (see Refs. 2 and 12). Besides the effective self-action of the electron and of the hole, described by expressions of the type (18), where V_q^2 should be replaced by V_{qe}^2 and V_{qh}^2, respectively, there appears also their effective interaction, which is proportional to the product $V_{qe}V_{qh}$. In contrast to the case of polarization phonons, where the sign of the interaction constant is determined entirely by the sign of the particle charge, V_{qe} and V_{qh} can have arbitrary signs, that the effective interaction can correspond to repulsion (if $V_{qe}V_{qh} < 0$) as well as attraction (if $V_{qe} V_{qh} > 0$). When the direct exciton interaction turns out to be stronger than the effective interaction via the phonons, we return to the case considered above in detail, when the exciton can be regarded as a single structureless particle. In the opposite case, however, the sign of the effective interaction is extremely important.

In the case of effective attraction, the electron and hole are located in the same jointly dug well and are close to each other. The situation should then be qualitatively different from that of an exciton.

In the case of effective repulsion, the electron and hole can no longer be in one well: what is a well for the hole is a potential hump for the electron, and vice versa. For polarization phonons this effect led to overscreening of the Coulomb attraction, as a result of which the electron and hole became separated by a large distance limited only by the decrease of the overlap integral.[1,12] Strain phonons, however, lead to a different situation. The effective electron–hole interaction due to exchange of optical strain phonons is short-range and while dominant at short distances, at large distances the is always predominant. At a reasonable value of the Coulomb attraction the particles therefore cannot move too far apart and the distance between the wells will be comparable with their width. At $V_{qe} V_{qh} < 0$, however, the absorption coefficient K_a should be considerably smaller than at $V_{qe} V_{qh} > 0$, owing to the smallness of the overlap integral for an electron and hole trapped in different wells.

5. CONCLUSION

In conclusion, we wish to emphasize once more that the described mechanism explains well the Urbach rule (1) and that at low temperature regardless of the value of Δ, the absorption ceases to depend on T. This fact could not be explained completely in the case of polarization phonons. Indeed, although at strong coupling there existed in that case a region of deficits Δ where the absorption remained finite at $T = 0$, the temperature dependence began to manifest itself in that region at a very high temperature, where the frequency dependence no longer correspond to the Urbach rule.[2] In the model described here, the temperature dependence manifests itself first already at the low temperature T^*(12), and the Urbach rule holds immediately at $T > T^*$, while deviations from this rule can occur only at very high temperature.

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[1)] Generally speaking, there exists also a third, saddle state, but it is absolutely unstable, and while corresponding classical solutions do occur, it will be shown in Sec. 3 that they have no physical meaning.

[2)] It should be noted that long-wave optical strain phonons interact with electrons only in the case of a degenerate band, but here we consider a simple band. Therefore the interaction (5) is model-based. One can hope, however, that it reflects correctly the main feature of the real situation.

[3)] Near $E = E_{\min}$ there is also a region where self-trapping state exists, but is metastable.

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