Theory of edge optical absorption in crystals

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Edge optical absorption through multiphonon processes is viewed as the tunneling of a lattice in an adiabatic potential. The case of an exactly solvable single-mode model is used in a quasiclassical approach to classify the various tunneling paths for absorption at an impurity center and in an ideal lattice with weak and strong exciton-phonon coupling. Mechanisms of absorption to free and bound states of an exciton are distinguished. The intervals of the temperature and the photon energy in which one mechanism or other is dominant are studied. The optimum tunneling path for each mechanism is also determined.

INTRODUCTION

Optical absorption below the edge of the exciton band has been studied quite thoroughly on the experimental side. The best-known property of this absorption, which is characteristic of many crystalline substances, is the so-called Urbach rule.[1,2] This is an exponential decrease in the absorption with distance from the edge of the exciton band, with an argument which is essentially linear in the photon frequency and in the reciprocal temperature. The surprisingly general applicability of this rule has attracted the interest of many theoreticians,[3–8] who have attempted to explain it at a correspondingly general level. These attempts have in fact been unsuccessful, but they have nevertheless accomplished much in improving our understanding of optical absorption processes in solids.

There are two basic directions in the theory of edge absorption. The first is concerned with the absorption which results from static variations in the potential. This direction dates back to the study by Dow and Redfield,[9] in which the Urbach rule arose from the broadening of a exciton line caused by a random electric field. Further developments of this direction, which we will not be discussing here, have centered on an analysis of fluctuations in the concentrations of lattice defects or impurities (see the reviews[10,11]). The second direction, which is the subject of the present paper, is concerned with the blurring of the edge of a band due to thermal vibrations of the lattice. The multiphonon absorption mechanism is always predominant at high temperatures; in pure crystals, it is also predominant at low temperatures.

Dexter's study[6] can be regarded as the first step in this direction. Dexter suggested that edge absorption stemmed from deformation-induced fluctuations of the band gap. Dexter did not consider the dynamic nature of the thermal fluctuations; i.e., the random strain energy was assumed to be static, and the temperature appeared only in its amplitude. That remained the basic approach in several subsequent studies.[7,8] Toyozawa[7] succeeded in reproducing the Urbach rule through the introduction of a purely quadratic coupling with the lattice, but the validity of the model which he used is problematical. Despite the fact that the dynamic nature of lattice fluctuations can be ignored only at high temperatures, Dexter's approach continues to be followed. Several studies[12–14] take it over the entire temperature range, down to absolute zero. In this approach the time dependence of the fluctuation potential is ignored, and—the major point—the inverse effect of the appearance of an exciton on the motion of the lattice is also ignored. In particular, energy conservation in the absorption event is not considered; as a result, the absorption below the band edge turns out to be finite even at absolute zero.

The dynamic nature of lattice fluctuations has been taken into account in several studies[15–19] based on a perturbation theory in the electron-phonon coupling. Although that approach does lead to a law which is approximately the same as the Urbach rule, the range of applicability of the approximation of a weak electron-phonon coupling is extremely narrow. In particular, the weak-coupling approximation fails completely to describe substances in which self-trapping is observed (see, for example, the review by Rashba[20]). Generally speaking, the effectiveness of a perturbation theory is degraded by the multiquantum nature of the absorption process.

The most systematic approach to multiphonon processes is quasiclassical, in which the interaction of excitons or charge carriers with the lattice is treated adiabatically. That approach, which dates back to Iordanskiĭ and Rashba's continuum self-trapping theory[21] and which is essentially a dynamic version of the optimum-fluctuation method,[22–24] was developed by Ioselevich.[25] Ioselevich used a two-particle Green's function to study the absorption of a photon and the creation of an electron and a hole, which interact with polar optical phonons. It was assumed that the energy deficiency of the photon, Δ, is much larger than the exciton rydberg E_i. The influence of exciton effects at $E_i \gg \Delta$ was studied by Kusmartsev.[26] It was found that the width of the exciton absorption band depends on the difference between the masses of the electron and the hole. Ioselevich[27] studied the shape of the Urbach edge in a model problem incorporating the coupling of a Frenkel' exciton with deformation-induced optical phonons. In a cubic crystal this coupling operates only in the case of a degenerate exciton band (one corresponding to a spin $S = 1$). Incorporating band degeneracy leads to a new effect, spontaneous breaking of the symmetry of an optimum lattice fluctuation.[28]

The fact that the absorption remains finite at $T = 0$ can be explained in a natural way in terms of self-trapping of the quasiparticles which form. Self-trapping was first identified as an absorption mechanism by Rashba.[29] Self-trapping was also assumed to be the reason for absorption at absolute zero in Refs. 12–14, which we mentioned earlier, but in their approach the absorption actually results from a blurring of the

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band edge caused by zero-point lattice vibrations. In fact, this blurring is fictitious since the zero-point vibrations of a lattice carry no energy.

An important advantage of the quasiclassical approach is its transparency, which makes it a comparatively easy matter to qualitatively analyze various situations which arise during absorption. The complex models used in Refs. 25–28, however, have yielded only particular solutions in certain limiting cases. It has turned out to be a difficult matter to draw a comprehensive picture of the dependence of the tunneling path on the parameters of the problem and to distinguish the qualitatively different absorption regimes in the problem. In the present paper we attempt to draw such a picture for the case of Frenkel' excitons with a broad band. We will use the adiabatic approximation and the quasiclassical approach directly and (we think) more systematically than in Refs. 25–28. We introduce the concept of independent absorption mechanisms associated with different final states of the exciton and the concept of absorption regimes associated with different types of tunneling lattice paths. We will not discuss specific realistic formulations of the problem; we will demonstrate the approach in the case of the single-mode model which can be solved analytically. The diagrams constructed below to show the arrangement of the various regions in the temperature-(photon frequency) plane qualitatively show the various typical pictures of absorption in various systems.

1. GENERAL FORMALISM

Since we are interested only in the exponential dependence of the absorption coefficient on the photon frequency and the temperature, we are not obliged to develop a complicated apparatus of the type which would be required for a complete description of the absorption process. For our purposes it is sufficient to use the Franck-Condon principle, supplemented with some simple mechanical ideas similar to those which have been developed in the quasiclassical analysis of radiationless multiphonon transitions.[30]

We describe the lattice by means of a set of coordinates X_j which are combined in a vector $\mathbf{X}$ (there is no difficulty in transforming to a continuum picture in specific applications). Everywhere below we replace the photon frequency by the difference between the energies required for the creation of a free exciton at rest in the undeformed lattice (i.e., we use the fundamental absorption edge E_g) and the energy of the absorbed photon, $\hbar\Omega$. We call this quantity,

$$\Delta \equiv E_g - \hbar\Omega > 0,$$

the "deficiency."

From the quasiclassical standpoint, the absorption of light below the edge of the exciton band must be treated as an optical transition between lattice terms, i.e., between different branches of the potential energy of the lattice.

The initial term, which we will call the "empty term" and denote by E, is the purely elastic energy of the lattice, $U_E(\mathbf{X})$. The final terms are formed by adding to this energy the energy of the exciton which has been created. An exciton has a continuous spectrum of free states, which undergo essentially no coupling with the lattice; in a certain region of lattice configurations it also has bound states. For the energies of these states, $E_{ex}(\mathbf{X})$, we place the origin of the scale at the edge of the exciton band. Adding $E_{ex}(\mathbf{X}) \leqslant 0$ to the elastic energy of the lattice, we find a term which we call a "bound term" and denote by B:

$$U_B(\mathbf{X}) = U_E(\mathbf{X}) + E_{ex}(\mathbf{X}) + \Delta. \tag{1}$$

The origin on the energy scale has been chosen for convenience, in such a way that the potential energy has no discontinuity in an optical transition from the empty term E to the bound term B, which occurs (according to the Franck-Condon principle) in any lattice configuration with a binding energy equal to the deficiency,

$$E_{ex}(\mathbf{X}) = -\Delta, \tag{2}$$

A bound state of an exciton and thus the bound term B may not be unique, but for simplicity we will consider only the bound state which has the lowest energy. When there is a deficiency, absorption can occur only to a bound state of an exciton. This state may fall into the continuum as a result of a subsequent radiationless liberation from the lattice potential well.

According to the quasiclassical theory of trapping,[30] the optimum case is a continuous transition from an exciton bound in a potential well to a free exciton which is at rest. In contrast, the repulsion of a bound state deep into the continuum is disadvantageous. For this reason, we can ignore the entire continuum except for the bottom of the exciton band, adding its energy to the elastic energy of the empty lattice. We call the resulting term, with a potential energy

$$U_F(\mathbf{X}) = U_E(\mathbf{X}) + \Delta, \tag{3}$$

a "free term" (F). Since the origin of the energy scale has been chosen in the same way in (1) and (3), the bound term joins smoothly[30] with the free term at the boundary of the region in which the former exists,

$$E_{ex}(\mathbf{X}) = 0. \tag{4}$$

From the quasiclassical standpoint, the absorbing system can be characterized completely by the shapes of the free and bound terms $U_F(\mathbf{X})$ and $U_B(\mathbf{X})$. There can be several quite different types of exciton terms, with configurational schemes as shown in Fig. 1:

a) A lattice with a defect which has a level in the undeformed state. A deformation of the lattice may either increase the exciton binding energy or reduce it, to the point that the level is pushed into the continuum. This event corresponds to a merging of the bound branch and the free branch.

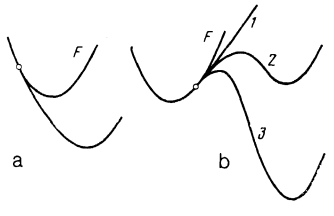

FIG. 1. Configuration schemes of exciton terms. a—Impurity center; b—ideal crystal. The behavior of a bound term is shown for the cases of (1) weak, (2) intermediate, and (3) strong exciton-phonon coupling.

b) An ideal lattice. A level arises only if there is a certain deformation of the lattice. The subsequent course of events depends on the strength of the exciton-phonon coupling. 1—If the coupling is weak, the elastic energy of the lattice increases more rapidly than the exciton binding energy with increasing deformation, so the adiabatic energy of the lattice has no minima in the region in which bound states exist. 2—If the coupling is strong, the bound branch of the exciton term has a minimum (a self-trapping state), which is an absolute minimum of the exciton-plus-lattice system. 3—There is an intermediate situation in which the self-trapping state exists but is metastable with respect to a transition to the free branch of the exciton term.

Each minimum on the F or B term is a possible final state of the absorption process. We thus see that in an ideal lattice with a weak exciton-phonon coupling (case 1b) there exists a unique absorption mechanism, absorption to a free state of an exciton. In other cases there are two absorption mechanisms: there is also an absorption to an impurity state (case a) or to a self-trapping state (2b,3b). In a real crystal, of course, both of these additional mechanisms may operate, but they differ in nature, and we will study cases a and b separately. We wish to stress that the presence (and number) of different mechanisms is determined exclusively by the type of exciton term. At any temperature and at any deficiency, these mechanisms coexist, although the absorption by one of these mechanisms may overwhelm that by the other because of the exponential behavior involved.

The motion of the lattice is described by the classical equations of motion

$$\frac{\partial^2 L}{\partial \dot{X}_i \partial \dot{X}_j}\ddot{X}_i + \frac{\partial L}{\partial X_j} = 0. \tag{5}$$

The Lagrangian $L(\mathbf{X},\dot{\mathbf{X}})$ contains $U_B(\mathbf{X})$ or $U_E(\mathbf{X})$ or $U_F(\mathbf{X})$ as potential energy, in accordance with the particular term occupied by the lattice. By virtue of our choice of origin for the energy scale for the B and F terms, the lattice potential energy has no discontinuities in an optical transition from an empty term to a bound term or in a radiationless transition from a bound term to a free term. For this reason we can speak in terms of a classical motion of the lattice, (5), in a complex (and generally multivalued) potential relief $U(\mathbf{X})$, formed by "splicing" the E and B terms at points determined by Eq. (2) and of B and F terms at the points determined by Eq. (4). In this picture the absorption process reduces to tunneling in a static potential and is completely analogous in this regard to the radiationless transitions studied in Ref. 30.

This analogy allows us to immediately formulate a general recipe for calculating (with an exponential accuracy) the optical absorption coefficient with a deficiency Δ at a finite temperature $T=\beta^{-1}$. We need to find the classical path $\mathbf{X}(t)$ in the potential constructed by the method described above, which has an imaginary period $i\hbar\beta$, and we need to calculate the action

$$S(\Delta,\beta) = \int_{-i\hbar\beta/2}^{i\hbar\beta/2} L(\mathbf{X},\dot{\mathbf{X}})\,dt$$

along this optimum path. The absorption coefficient $K(\Delta)$ is proportional to an exponential function of the action:

$$K(\Delta) \propto \exp[i\hbar^{-1}S(\Delta,\beta)]. \tag{6}$$

A qualitative analysis of edge absorption in any model reduces to enumeration of the various possible types of periodic paths in each absorption mechanism, determination of the nature of the transition from one type of path to another as the parameters Δ and β vary, and identification of regions in which one of the absorption mechanisms is predominant. Carrying out an analysis of this sort for realistic specific models is an extremely complicated matter. We will accordingly limit ourselves to analyzing a simplified model which can be solved analytically and which, from all appearances, draws a qualitatively correct picture of the absorption. The results can then be compared with the results of more-complicated calculations.

2. CLASSIFICATION PRINCIPLES

In this section of the paper we introduce some concepts which we will be using to classify the paths traced out by the lattice in the absorption process. For simplicity we consider a "lattice" which has a single degree of freedom, with a coordinate X. The path traced out by the lattice is determined completely by the total energy ε. For this reason, it is convenient to analyze the various types of paths and the dependence $S(\Delta,\beta)$ by parametrizing the path specifically by means of the energy ε and then relating this energy to the temperature $T=\beta^{-1}$ with the help of a periodicity condition.

Those regions of the potential energy $U(X)$ which lie below ε correspond to motion in real time and do not contribute to the imaginary action $S(\Delta,\beta)$. The only regions which are of importance to the transition probability are the classically forbidden regions, $U(X)>\varepsilon$. Depending on the energy ε and the deficiency Δ, the tunneling may occur along different numbers of terms. We will accordingly speak in terms of different absorption regimes, designating them by means of the order in which the terms (E,B,F) are crossed in the forbidden region.

The beginning and end of a tunneling are stopping points, i.e., solutions of the equation $U(X)=\varepsilon$. The initial stopping point X_i corresponds to the time $t_i=0$, and the final stopping point X_f corresponds to the time t_f, which is imaginary, in accordance with the tunneling nature of the motion ($it_f>0$). In our problem, in which the potential energy is made up of arcs of different terms, the tunneling path $X(t)$ must also be made up of segments which join together smoothly (i.e., X and $\dot{X}$ are continuous) and which correspond to a sequential motion through each of the terms in the forbidden region of $U(X)$. Proceeding in this fashion, we can find a path $X(t)$ for each value of ε; in particular, we can find the final stopping point $t_f(\varepsilon)$. By construction, the path is of even parity with respect to the initial stopping point, $X(t)=X(-t)$, so it has a period

$$2t_f(\varepsilon) = -i\tau(\varepsilon),$$

where $\tau(\varepsilon)$ is a real oscillation period in the inverted potential, $-U(X)$, with an energy $-\varepsilon$. The optimum path for a given temperature is defined by the condition

$$\tau(\varepsilon) = \hbar\beta. \tag{7}$$

There is not necessarily a single optimum path which corresponds to a given value of the temperature. It can be

seen from Eq. (7) that a path is unique only if the functional dependence $\tau(\varepsilon)$ is monotonic. On the whole, the period $\tau(\varepsilon)$ tends to increase with decreasing energy ε. In particular, it diverges as ε approaches the bottom of any of the terms involved in the transition. For this reason, a deviation of $\tau(\varepsilon)$ from monotonic behavior would have to be N-shaped and would have to give rise to three extrema of the action in a certain temperature region. The $S(\Delta,\beta)$ dependence in this case acquires the "swallowtail" shape shown in Fig. 2. One of the extrema turns out to be unstable and is definitely not favored, so only two paths are left in contention. At each value of the temperature it is necessary to choose the path which has the smallest value of $\mathrm{Im}[S(\Delta,\beta)]$, so that a transition from one extremum to another occurs discontinuously at the point where the rays intersect the swallowtail. The curves of the action and thus the absorption coefficient versus the deficiency and the temperature change slope at this point. Analyzing the single-mode model, we can easily understand the following general behavior. If the potential has a slope change at some slope, then as the energy approaches the level of this slope, ε^*, from below the period $\tau(\varepsilon)$ has a square-root singularity:

$$\tau(\varepsilon)=\text{const}+(\varepsilon^*-\varepsilon)^{1/2}.$$

In principle, this singularity could have either sign, but in our problem the change in the slope of the potential occurs at the point at which the E and B terms cross, and the sign of the square-root increment is always negative. An N-shaped deviation from a monotonic $\tau(\varepsilon)$ dependence forms, so the transition between the regime which contains tunneling along the E terms and a regime in which this term is traversed in real time is necessarily accompanied by a change in the slope of $S(\Delta,\beta)$. We will call such a change in regime, which is analogous to a first-order phase transition, a "hard" transition. We will call a change of regime which does not disrupt the monotonic $\tau(\varepsilon)$ dependence, and which is analogous to a second-order phase transition, a "soft" transition. In this case the action $S(\Delta,\beta)$ is a smooth function of the parameters.

The nature of the path $X(t)$ can be quite varied; it is determined by the shape of the barrier. The potential energy in this problem is constructed in such a way that in addition to barriers of the ordinary type (Fig. 3a) there can be barriers with an "underhanging" initial or final slope (Fig. 3, b and c). We will call the ordinary tunneling "horizontal" tunneling, and we will call tunneling with an underhanging initial or final slope "ascending" or "descending" tunneling, respectively. The tunneling paths $X(t)$ corresponding to these barriers are shown in Fig. 3 under the diagrams of the

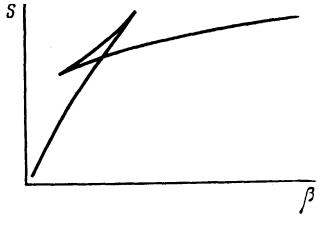

FIG. 2. "Swallowtail" on the plot of the action S versus the reciprocal temperature β, which leads to a discontinuous change in optimum path (a hard transition).

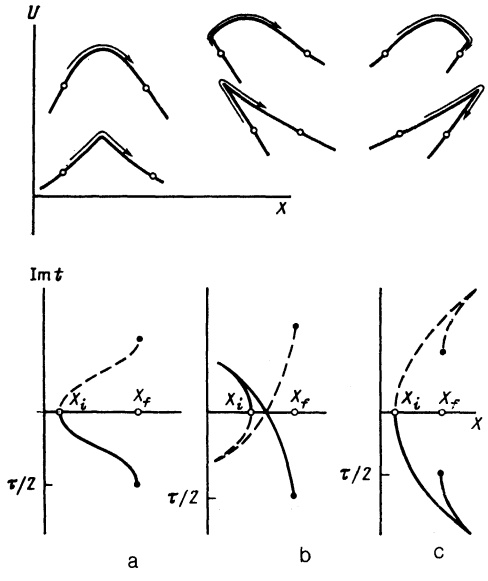

FIG. 3. Top: Types of barriers. Bottom: Corresponding paths. a—For horizontal tunneling; b—for ascending tunneling; c—for descending tunneling.

barriers. In the case of horizontal tunneling the path takes the form of an oscillatory motion in imaginary time; in the case of ascending or descending tunneling a region with a retrograde motion in time arises at respectively the beginning or end of the path, since the potential is double-valued (cf. Ref. 30).

In addition to the absorption regimes with tunneling which we have been discussing there is yet another possible regime, which we will call an "activation" regime and designate as regime A. It occurs at high temperatures in cases in which the barrier has a smooth saddle point. In such cases, in contrast with cases in which the barriers have a "sharp" crest, the period of the oscillations in the inverted potential $\tau(\varepsilon)$ is bounded from below. A solution of the equations of motion which has the necessary period $i\hbar\beta$ is trivial at small values of β; it describes a lattice which is lying at rest at the crest of the barrier, $X(t)=\text{const}$. We know (Ref. 30, for example) that this case corresponds classically to passage over the potential barrier. In this temperature region, quantum-mechanical effects influence only the coefficient of the exponential function in the tunneling probability (in our case, in the absorption coefficient). In the case of a barrier with a sharp crest the period $\tau(\varepsilon)$ approaches zero as the energy ε approaches the crest (or, in the multidimensional case, as it approaches the saddle point), so at an arbitrarily high temperature the path has a tunneling region, although this region is small. In the edge-absorption problem a barrier with a a smooth saddle point occurs on the B term if there is a strong exciton-phonon coupling in the ideal lattice (Sec. 6).

We wish to stress that the nature of the tunneling is determined by the form of the potential only in the classically forbidden part—i.e., the part which rises above the ε level—of the barrier, $R(X)>\varepsilon$. The nature of the tunneling may thus change with the energy ε. Let us examine the upper barrier in Fig. 3b as an example. The overhanging initial slope of this barrier goes into the classically allowed region as the energy is raised, and the tunneling converts from as-

cending to horizontal with a smooth saddle point of the type shown by the upper barrier in Fig. 3a.

These new concepts remain meaningful in the multimode case. The only fundamental distinction is that it is necessary to search for a periodic path among the paths with a given energy ε. This procedure is extremely complicated to carry out in practice, but the presence of a solution is guaranteed by the very nature of the problem. That this solution is ngle-valued for each mechanism is a fairly natural assumpalthough unproved.

3. THE MODEL

We turn now to a quantitative analysis of the model, in which the sole oscillatory mode is harmonic, and the "exciton-phonon coupling" is described by a zero-range potential which is related to the lattice coordinate in a linear way. A similar model has been used in the theory of the radiationless capture of charge carriers at a natural impurity center and in self-trapping theory,[30,31] where only transitions between free and bound terms were considered (charge carriers and self-trapped particles neither appeared nor disappeared). To apply this mode to edge absorption we need to add a third (empty) term, but there is no difficulty in doing so.

In our model the lattice coordinate X is the sole coordinate, and the Lagrangian of the lattice without an exciton is quadratic:

$$L_0(X, \dot{X}) = {}^1/_2 M\dot{X}^2 - {}^1/_2 M\omega_0^2 X^2, \tag{8}$$

where M is the mass of a lattice atom, and ω_0 is the frequency of its free vibrations. The exciton is treated in the effective-mass approximation, while the potential well which binds the exciton is described by a zero-range potential with a reciprocal scattering length $\varkappa(X)$ which depends linearly on the lattice coordinate:

$$\varkappa(X) = \varkappa_0 + \varkappa_1 X. \tag{9}$$

A bound state exists in the region $\varkappa(X) > 0$ and has an energy

$$E_{ex}(X) = -\hbar^2\varkappa^2(X)/2m,$$

where m is the effective mass of an exciton. The potential energies corresponding to the empty and free exciton terms differ by an amount Δ according to (3) and are described by

$$U_B(X) = M\omega_0^2 X^2/2, \quad U_F(X) = \Delta + M\omega_0^2 X^2/2.$$

Because of the linear relationship (9), the adiabatic potential energy of the lattice is also quadratic in X on a bound term and is described by

$$U_B(X) = U_F(X) + E_{ex}(X) = -U^* + \Delta + M\nu\omega_0^2 (X - X^*)^2/2,$$

where

$$\nu = 1 - \varkappa_1^2\hbar^2/mM\omega_0^2, \quad U^* = \hbar^2\varkappa_0^2/2m\nu, \quad X^* = \hbar^2\varkappa_0\varkappa_1/\nu\omega_0^2 Mm.$$

The free and bound terms merge at the point $X_0 = -\varkappa_0/\varkappa_1$. Switching to dimensionless quantities, we can set, M, m, ω_0, and $\hbar$ equal to unity. The picture of the terms will then depend only on the parameters of the linear relationship (9): $\varkappa_0$ and $\varkappa_1$. We will use ω_0^{-1} as the unit of time, $\hbar\omega_0$ as the unit of energy and temperature, $(\hbar/M)^{1/2}$ as the unit of the coordinate X, and $(m\omega_0/\hbar)^{1/2}$ and $(mM)^{1/2}/\hbar$ as the units of the coefficient $\varkappa_0$ and $\varkappa_1$, respectively. In this system of units the lattice Lagrangian becomes

$$L(X, \dot{X}) = {}^1/_2\dot{X}^2 - U(X) \tag{10}$$

with a potential energy

$$U_B(X) = X^2/2 \tag{11}$$

on the empty term,

$$U_F = \Delta + X^2/2 \tag{12}$$

on the free term, and

$$U_B(X) = \Delta + \frac{1}{2}X^2 - \frac{1}{2}\varkappa^2(X)$$

$$= \Delta - \frac{\varkappa_0^2}{2\nu} + \frac{\nu}{2}\left(X - \frac{\varkappa_0\varkappa_1}{\nu}\right)^2, \quad \nu = 1 - \varkappa_1^2, \tag{13}$$

on the bound term [in the region $\varkappa(X) > 0$].

How successful would our model, with purely parabolic terms, be in qualitatively describing the various type of exciton terms which were listed in Sec. 2? With no loss of generality we can assume that the parameter $\varkappa_1$ is positive. A lattice with a defect corresponds to $\varkappa_0 > 0$ (there is a level at $X = 0$). In accordance with our choice $\varkappa_1 > 0$, the point $X_{bf} = -\varkappa_0/\varkappa_1$ at which an exciton is repelled into the band is negative. The absence of an exciton bound state in the undeformed ideal lattice corresponds to $\varkappa_0 < 0$, and the point X_{bf} is positive. The bound term branches away from the free term at this point. The presence or absence of a self-trapping absorption mechanism corresponds to a negative or positive value of the parameter ν, which we call the "curvature" of the bound term.

With $\varkappa_0 < 0$ and a positive curvature, the bound term formally has a minimum $U^* = -\varkappa^2/2\nu$, but this minimum occurs outside the region in which the bound term itself exists. If the curvature is negative, the minimum converts into a maximum of the bound term; this maximum actually exists and describes a self-trapping barrier. Obviously, our model has no bound-term minimum corresponding to a self-trapped exciton. Accordingly, we cannot use our model to quantitatively illustrate the effects which stem from the presence of this minimum in a real situation, e.g., the difference between the cases of strong and intermediate coupling (2b and 3b). We will discuss these effects at a qualitative level in the Conclusion. We will not consider at all the case in which the bound term has negative curvature in connection with absorption at a defect ($\varkappa_0 > 0$, $\nu < 0$), since the only distinction between this and the case $\varkappa_0 > 0$, $\nu > 0$ is that there is no minimum on the bound term. This situation does not correspond to the physical situation. An extremum of a barrier type, on the other hand, occurs in this case in the region forbidden by the condition $\varkappa(X) \geqslant 0$.

In the following sections of this paper we will systematically analyze various configurations of this new model. In each configuration, the order of operations is the same. We list the possible absorption mechanisms and the regimes which occur in them, writing the corresponding expressions for the action $S(\Delta, \beta)$ along an extremal path. For each mechanism, and for each value of the parameters Δ and β,

we find an optimum regime and construct a "phase" diagram in the (Δ,T) plane. On this diagram we specify the regions in which each of the regimes prevails and the nature of the transition between neighboring regimes. By comparing the various mechanisms we identify the regions in which one mechanism or another is predominant. We will go through this series of operations more or less in detail for the case of absorption at an impurity center, while for the other cases we will simply describe the qualitative distinctions, present the diagrams, and discuss them briefly. The diagrams presented here are illustrative and do not correspond to any specific values of the parameters of the model. They generalize the qualitative aspects of the specific diagrams which are generated in a numerical solution of the problem.

4. ABSORPTION OF LIGHT AT AN IMPURITY CENTER

As we mentioned above, there are two mechanisms for the absorption of light at impurity centers. Figure 4 shows the configurations of the terms of an impurity center in our model with the parameter values $\varkappa_0 > 0$ and $\varkappa_1 > 0$ for various values of Δ.

We first consider the absorption mechanism corresponding to a bound state. In this mechanism, regardless of the value of the energy ε, tunneling occurs along two terms: the empty term E and the bound term B. In other words, there is only a single regime, EB, in our terminology. The lattice begins the tunneling on the empty term at the time $t = 0$, moving in accordance with the law

$$X(t) = A_e \cos(t) \tag{14}$$

with a coefficient A_e which is related to the energy by

$$\varepsilon = A_e^2/2. \tag{15}$$

The time at which the transition from term E to B occurs is determined by the equation

$$\varkappa_0 + \varkappa_1 A_e \operatorname{ch}(\tau_{eb}) = (2\Delta)^{1/2}. \tag{16}$$

On the bound term the law of motion is

$$X(t) = \varkappa_0\varkappa_1 + A_b \cos(\nu^{1/2}(t + i\tau_b)), \tag{17}$$

where the coefficient A_b and the stopping time $t_b = -i\tau_b$ are determined by the conditions that $X(t)$ and $\dot{X}(t)$ are continuous at the time of the transition:

$$\begin{aligned} A_c \operatorname{ch}(\tau_{eb}) &= \varkappa_0\varkappa_1 + A_b \operatorname{ch}(\nu^{1/2}(\tau_{eb} - \tau_b)), \\ A_e \operatorname{sh}(\tau_{eb}) &= A_b \nu^{1/2} \operatorname{sh}(\nu^{1/2}(\tau_{eb} - \tau_b)). \end{aligned} \tag{18}$$

System (16), (18) with real values of the path parameters A_e, A_b, τ_b, and τ_{eb} is closed by the periodicity condition

$$\tau_b = \beta/2. \tag{19}$$

Evaluation of the action

$$\begin{aligned} S(\Delta,\beta) = &\int_{-i\tau_{eb}}^{-i\beta/2} (\dot{X}^2/2 - X^2/2)\,dt + \int_{i\beta/2}^{i\tau_{eb}} (\dot{X}^2/2 - X^2/2)\,dt \\ &+ \int_{i\tau_{eb}}^{-i\tau_{eb}} (\dot{X}^2/2 - U_b(X))\,dt \end{aligned} \tag{20}$$

along the optimum path gives rise to the expression

$$\begin{aligned} iS(\Delta,\beta) = &(\varkappa_0^2/2\nu - \Delta)(\beta - 2\tau_{eb}) \\ &+ \varkappa_0^2\nu^{-1}[1 - (2\Delta/\varkappa_0^2)^{1/2}]\operatorname{th}(\tau_{eb}), \end{aligned} \tag{21}$$

which involves the time of the absorption, τ_{eb}, which is determined by the equation

$$\begin{aligned} &[1 - (2\Delta/\varkappa_0^2)^{1/2}]\operatorname{th}(\tau_{eb}) \\ &= [1 - \nu(2\Delta/\varkappa_0^2)^{1/2}]\nu^{-1/2}\operatorname{th}(\nu^{1/2}(\tau_{eb} - \beta/2)). \end{aligned} \tag{22}$$

Depending on the deficiency Δ, the point $X_{eb} = [(2\Delta/\varkappa_0^2)^{1/2} - 1]\varkappa_0/\varkappa_1$ at which the bound term crosses the empty term may be in different positions with respect to the minima involved in the tunneling of the terms, $X_e = 0$ and $X_b = \varkappa_0\varkappa_1$; the differences are reflected in the shape of the optimum path. In the case of absorption to a bound state the change in the nature of the tunneling occurs at the deficiency values $\Delta = \varkappa_0^2/2$ and $\Delta = \varkappa_0^2/2\nu^2$.

The case $\Delta < \varkappa_0^2/2$ is formally equivalent to the capture of a particle with a negative energy by an impurity center. Its path corresponds to a descending tunneling (Fig. 3c). At the boundaries of the next region, with $\Delta = \varkappa_0^2/2$ and $\Delta = \varkappa_0^2/2\nu^2$, the tunneling path characterizing the absorption degenerates into a static path. Throughout the duration of the tunneling from $-i\beta/2$ to $i\beta/2$ the system lies at the bottom of an empty term (in the case $\Delta = \varkappa_0^2/2$) or a bound term ($\Delta = \varkappa_0^2/2\nu^2$). In the region $\varkappa_0^2/2 < \Delta < \varkappa_0^2/2\nu^2$ itself the tunneling is horizontal (Fig. 3a). At $\Delta > \varkappa_0^2/2\nu^2$ a retrograde region reappears on the path $X(t)$, but now the empty term is the underhanging term, and the tunneling becomes ascending (Fig. 3b).

We turn now to the light absorption mechanism in which the exciton in the final state is free. This second mechanism has a greater diversity of paths. The critical values of the deficiency in this mechanism are

$$\begin{aligned} &\Delta_1 = [\varkappa_0(1 - (1-\nu)^{1/2})/\nu]^2/2, \quad \Delta_2 = [\varkappa_0(1 + (1-\nu)^{1/2})/\nu]^2/2, \\ &\Delta_3 = 2(\varkappa_0/\nu)^2 \quad (\Delta_1 < \Delta_2 < \Delta_3); \end{aligned}$$

Fig. 4 shows the positions of the terms corresponding to these values.

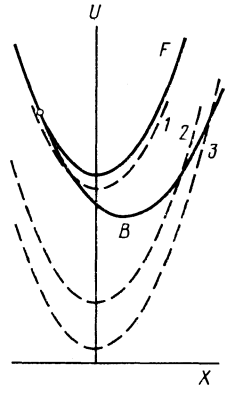

FIG. 4. Relative positions of the terms of an impurity center for various values of the deficiency, $\Delta_1 < \Delta_2 < \Delta_3$. To simplify the figure, the positions of terms B and F and fixed, and the height of term E is varied. The bottom of the latter term is actually the origin for the energy scale (as in Figs. 6 and 8).

At deficiencies $\Delta < \Delta_1$ the point where the empty term E crosses the bound term B is, on the energy scale, above the bottom of the free term. Accordingly, again in this region of deficiencies two light absorption regimes are possible, depending on the temperature. In the first of these regimes, which is characteristic of high temperatures, the motion under the barrier occurs along terms B and F. The absorption of a photon occurs in the classically allowed region, not in the tunneling region. The motion along the bound term is described by expression (16) with $\tau_B = 0$ (the beginning of tunneling), while the motion along the free term is described by

$$X(t) = A_f \cos(t + i\tau_f). \tag{23}$$

We analyze this case by analogy with the mechanism for absorption to an exciton bound state, but the joining equations differ from (18) (in particular, they do not contain the deficiency). For this reason the optimum path depends only on the temperature, and the action along the optimum path,

$$iS(\Delta, \beta) = -\Delta\beta + \varkappa_0^2 \nu^{-1} [\tau_{bf} - \mathrm{th}(\tau_{bf} - \beta/2)], \tag{24}$$

depends linearly on the deficiency. Here τ_{bf} is the time of the transition from a bound term to a free term, which is determined by the equation

$$\mathrm{th}(\tau_{bf} - \beta/2) = \nu^{-1/2} \mathrm{th}(\nu^{1/2}\tau_{bf}). \tag{25}$$

In the second regime, *EBF*, which is characteristic of low temperatures, we need to use all three laws of motion: (14), (17), and (23). We join them at the transition times τ_{eb} and τ_{bl}. Elementary but tedious calculations yield an expression for the action:

$$iS(\Delta, \beta) = \Delta(2\tau_{eb} - \beta) + \varkappa_0^2 \nu^{-1} [\tau_{bf} - \mathrm{th}(\tau_{bf} - \beta/2) - \tau_{eb} + (1-D)\,\mathrm{th}(\tau_{eb})]. \tag{26}$$

The time τ_{eb} is determined by the equation

$$\tau_{eb} = \frac{\beta}{2} + \frac{1}{2\nu^{1/2}} \ln\left\{\left[\frac{1 - \nu D + \nu^{1/2}(1-D)\,\mathrm{th}(\tau_{eb})}{1 - \nu D - \nu^{1/2}(1-D)\,\mathrm{th}(\tau_{eb})}\right]\left(\frac{1-\nu^{1/2}G}{1+\nu^{1/2}G}\right)\right\} + \frac{1}{2}\ln\left(\frac{1+G}{1-G}\right), \tag{27}$$

where we have introduced

$$G = [(1-D)^2 \mathrm{th}^2(\tau_{eb}) + D(2-\nu D)]^{1/2}, \quad D = (2\Delta)^{1/2}/\varkappa_0,$$

to streamline the equations. The time τ_{bl} is expressed in terms of the solution of Eq. (27) by

$$\tau_{bf} = \frac{1}{2}\left[\beta + \ln\left(\frac{1+G}{1-G}\right)\right]. \tag{28}$$

The three-term paths of regime *EBF* correspond to an ascending tunneling, regardless of the value of the deficiency Δ (Fig. 3b).

The transition between regimes *BF* and *EBF* occurs in a hard fashion, with a discontinuous change of the dominant path. The line of the transition in the (Δ, T) plane, on which the values of the action given by (24) and (26) are equal, is shown in Fig. 5. At deficiencies $\Delta_1 < \Delta < \Delta_2$ the point at which the empty and bound terms cross lies below the bottom of the free term on the energy scale, so there is only a single regime, *BF*, with action (20).

At deficiencies $\Delta > \Delta_2$ the point at which the empty and bound terms cross again lies above the bottom of the free term, but now on the other slope of the bound term. With this arrangement of terms, two barriers must be crossed for absorption to a free state; i.e., two successive tunnelings are required (at low temperatures). In this regime the lattice initially tunnels from the empty term to the bound term; it then goes in real time from the right side of the bound term to the left side, and with the same energy it tunnels from the bound term to the free term. We denote this absorption regime as *EB–BF*. The first tunneling is described by the same equations as describe regime *EB* in the bound channel, but β must be replaced by the time of the first tunneling, β_1. Correspondingly, the second tunneling is described by the equation for regime *BF*, with β replaced by β_2. The periods of the tunneling paths, β_1 and β_2, are determined by the condition that the overall tunneling time be equal to the reciprocal temperature,

$$\beta = \beta_1 + \beta_2$$

and the condition that the values of the energy in the two tunneling regions be equal. The resulting action is given by the sum

$$S(\beta, \Delta) = S_1(\beta, \Delta) + S_2(\beta, \Delta), \tag{29}$$

where S_1 is found from (21), and S_2 from (24).

The existence of a classically allowed region between two tunnelings gives rise to resonance effects, which are superimposed on the exponential dependence $\exp[iS(\beta,\Delta)]$. We will not discuss these effects here; we assume that the resonances are completely smoothed over (by inhomogeneous broadening, for example). We might add that the picture of double tunneling becomes slightly more complicated in the multimode case. After the final stopping time of the first tunneling, the lattice moves along a complicated path and reaches the initial point of the second tunneling after a long (strictly speaking, infinite) real time. This circumstance is of importance, however, only for the coefficient of the exponential function in the absorption coefficient.

The transition between regime *BF* and double-tunneling regime *EB–BF* is soft. It corresponds to the vanishing of the part of the tunneling motion along the empty term; this event occurs under the condition

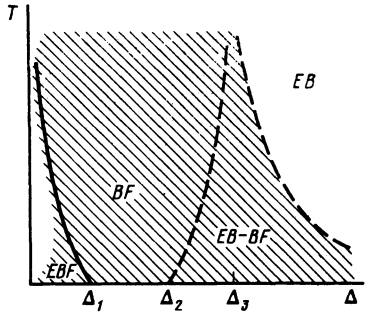

FIG. 5. Diagram showing the various regimes of absorption at an impurity center (the free mechanism). Solid lines—Hard transitions; dashed lines—soft transitions; hatching—region in which absorption to a bound state dominates.

$$\beta=\beta_1(\Delta)=-\nu^{-1/2}\ln\left[\frac{1+(2\nu D+\nu^2D^2)^{1/2}}{(1-\nu D)}\right]$$

$$+\ln\left[\frac{1+(2D-\nu D^2)^{1/2}}{(1-2D+\nu D^2)^{1/2}}\right] \qquad (30)$$

[see the notation which was introduced along with Eq. (27)].

At deficiences $\Delta > \Delta_3$ the point at which the E and B terms cross rises above the point at which the terms B and F cross. Accordingly, we find a region of high temperatures in which only the barrier EB is crossed by tunneling, while the barrier BF is crossed classically. In this regime, EB, the tunneling path obviously coincides with the path of absorption to an exciton bound state. This means that the optical absorption coefficients corresponding to the two mechanisms are the same, to within exponential terms. The relative numbers of the excitons which go to free and bound states are determined in this case by the coefficients of the exponential functions in the absorption coefficient, which depend on the relaxation mechanisms, among other factors.

A soft transition between regime EB and the double-tunneling regime EB–BF is determined by the condition that the time of motion along the bound term vanish:

$$\beta=\beta_2(\Delta)=-\nu^{-1/2}\ln[\nu D-1+(\nu^2D^2-2\nu D)^{1/2}]$$

$$+\ln\left[\frac{D-1+(\nu D^2-2D)^{1/2}}{(1+D^2-\nu D^2)^{1/2}}\right]. \qquad (31)$$

The double tunneling occurs in the region $\beta_1(\Delta) < \beta < \beta_2(\Delta)$.

Which of the absorption mechanisms dominates is decided by comparing the values of the action. A curve separating regions in which different optical absorption mechanisms are predominant is shown in Fig. 5. At small deficiencies, a transition of the system to a free state is preferable. As the deficiency increases, a transition of the system to an exciton bound state becomes preferable. Also shown here is the region of large deficiencies, in which the two mechanisms are equally probable, to exponential accuracy.

An exciton may also be in a free state if it is initially absorbed to a bound state, since the latter may be thermally ionized. Although this process does include two tunnelings, it is not described by a single path, since the first tunneling, from the empty term to the bound term, is followed immediately by thermalization, and the subsequent tunneling from the bound term to the free term requires activation. The probability for such a process is equal to the product of the probabilities of each of these transitions. Clearly, absorption directly to a free state is preferred.

5. ABSORPTION IN A HOMOGENEOUS CRYSTAL WITH WEAK EXCITON-PHONON COUPLING

In this relatively simple case there is a single absorption mechanism, for which the final state is an undeformed lattice with a free exciton. In the model which we are using here, this case corresponds to parameter values $\varkappa_0 < 0$ and $\varkappa_1 > 0$. A bound state exists in the region $X > -\varkappa_0/\varkappa_1$. The configuration of terms is shown in Fig. 6.

There are two absorption regimes, EB and EBF, which are completely analogous to the corresponding regimes in the case of an impurity center, which we discussed above. In regime EB, which is characteristic of high temperatures, the action is described by expressions (21) and (22); in regime EBF, which corresponds to low temperatures, it is described by (26)–(28).

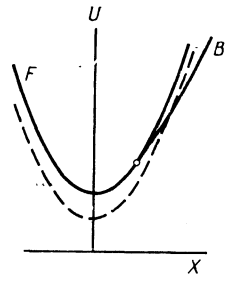

FIG. 6. Relative positions of the terms during absorption in an ideal crystal with weak coupling.

Figure 7 shows a diagram of the regimes. A transition between regimes occurs in different ways, depending on the value of the deficiency Δ. There exists a critical deficiency $\Delta_1 = \varkappa_0^2[(1+4\nu)^{1/2}-1]^2/8\nu^2$, below and above which the transition is respectively hard and soft. The temperature corresponding to the soft transition in the region $\Delta > \Delta_1$ can be found from the vanishing of the time of motion along the free term F:

$$\beta_{c3}=\nu^{-1/2}\ln\left[\frac{1-\nu D+[-\nu(2D+\nu D^2)]^{1/2}}{1-\nu D-[-\nu(2D+\nu D^2)]^{1/2}}\right]$$

$$-\ln\left[\frac{1-D+(\nu D^2+2D)^{1/2}}{1-D-(\nu D^2-2D)^{1/2}}\right]. \qquad (32)$$

At deficiencies $\Delta < \Delta_1$, where the transition is hard, the only way to find the point of the transition is to compare the values of the action calculated from (21) and (26).

6. OPTICAL ABSORPTION IN A CRYSTAL WITH SELF-TRAPPING EXCITONS

For crystals with a strong exciton-phonon coupling there are typically two minima, which correspond to free and self-trapping exciton states; correspondingly, there are two absorption mechanisms. In this regard this situation is similar to absorption at an impurity center (Sec. 4), but here the adiabatic potential of a lattice with an exciton which is formed by B and F terms is single-valued. The two minima of

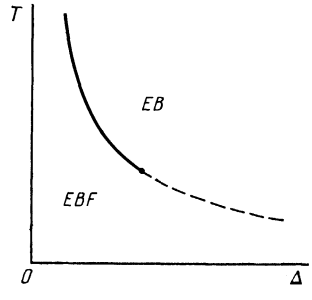

FIG. 7. Diagram of the various absorption regimes in an ideal crystal with weak coupling.

the adiabatic potential are separated by a rounded saddle point (a self-trapping barrier); at small and large values of the deficiency the saddle point lies respectively below and above the energy of the empty term at the same point, X. In the former case the saddle point of the self-trapping barrier lies on the path to the self-trapping state, and absorption to a free state occurs through the sharp crest formed by the intersection (splicing) of terms E and B; in the latter case, we have the opposite situation. As we pointed out in Sec. 2, if a barrier has a rounded saddle point at high temperatures only a static path, corresponding to crossing the barrier in an activated fashion, is possible. This result means that a new regime, A, appears in the picture of the absorption. This new regime has no analog in the absorption at an impurity center or in the case of weak coupling with the lattice. This regime appears in that mechanism to which the saddle point of the barrier corresponds.

In the model which we are using here (see the configuration diagram in Fig. 8) this strong-coupling case corresponds to a negative value of the curvature ν. Nearly all of the equations required for analyzing this case were derived in the analysis of absorption at an impurity center. All we need to do, because of the imaginary nature of the frequency of the bound term, is to replace the hyperbolic tangents by simple tangents in the corresponding places in the equations for the parameters of the tunneling path (more on this below). Figure 9 shows diagrams of regimes in the (Δ,T) plane.

We first consider the optical absorption mechanism which has a free exciton in an undeformed lattice as final state. In this mechanism there are three characteristic values of the deficiency: $\Delta_1 = -\varkappa_0^2/2\nu$, at which the point at which the empty and bound terms cross is at the crest of the barrier; $\Delta_2 = -2\varkappa_0^2/\nu$, at which this point moves to the right to the height of the splice of terms B and F; and $\Delta_3 = -\varkappa_0^2(1+\varkappa_1-\varkappa_1^{-1})/2\nu$, at which this point is at the level of the bottom of the free term. In the region $0<\Delta<\Delta_1$, these regimes are identical to the corresponding regimes in the case of a weak coupling (Sec. 5). Regime EB, which corresponds to high temperatures, is described by the following expressions for the action, which we find from (21) and (22):

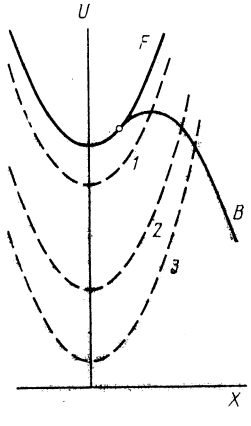

FIG. 8. Relative positions of the terms during absorption in an ideal crystal with weak coupling. The dashed lines show the positions of term E for deficiency values Δ_1, Δ_2, and Δ_3.

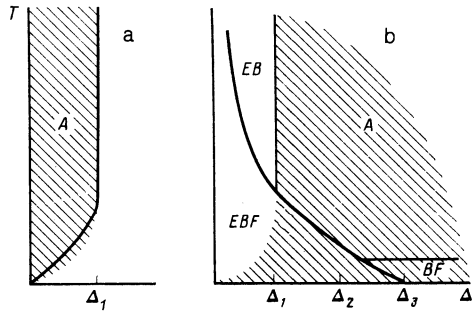

FIG. 9. Diagrams of the various absorption regimes in an ideal crystal with strong coupling. a—Free mechanism; b—self-trapping mechanism. For each mechanism, the hatching shows the regions in which the mechanism is not dominant.

$$iS(\Delta,\ \beta)=(\varkappa_0^2/2\nu-\Delta)\,(\beta+2\tau_{eb})$$
$$+(\varkappa_0^2/\nu)\,[1-(2\Delta)^{1/2}/\varkappa_0]\,\mathrm{th}\,(\tau_{eb}), \qquad (33)$$

The time τ_{eb} at which the transition from the empty term to the bound term takes place is found from

$$[\varkappa_0-(2\Delta)^{1/2}]\ \mathrm{th}\ (\tau_{eb})$$
$$=(-\nu)^{-1/2}[\varkappa_0-\nu(2\Delta)^{1/2}]\ \mathrm{tg}\ ((-\nu)^{1/2}(\tau_{eb}+\beta/2)).$$

In regime EBF, which corresponds to low temperatures and which is separated from regime EB by a hard transition, the action is given by

$$iS(\Delta,\ \beta)=\Delta(2\tau_{eb}+\beta)+\varkappa_0^2\nu^{-1}[\tau_{bf}-\mathrm{th}\ (\tau_{bf}+\beta/2)$$
$$-\tau_{eb}+(1-D)\ \mathrm{th}\ (\tau_{eb})], \qquad (34)$$

and the transition times τ_{eb} and τ_{bf} are found from the equations

$$\tau_{bf}=-\beta/2+\mathrm{arcth}\,H,\quad H=[(1-D)^2\,\mathrm{th}^2\,(\tau_{eb})+\nu D^2+2D]^{1/2},$$
$$\tau_{eb}=-\beta/2+\mathrm{arcth}\,(H)-(-\nu)^{-1/2}\,\mathrm{arctg}\,((-\nu)^{1/2}H)$$
$$+(-\nu)^{-1/2}\,\mathrm{arctg}\,[(-\nu)^{1/2}(1-D)\ \mathrm{th}\ \tau_{eb}/(1+\nu D)],$$

which are found from the expressions in Sec. 4 when the negative sign of ν is taken into account. As before, we use the notation $D=(2\Delta)^{1/2}\varkappa_0<0$. In the region $\Delta_1<\Delta<\Delta_2$, these two regimes are supplemented by an activation regime, which is designated A in the diagram. In this regime the lattice does not tunnel. Over the entire time $-i\hbar\beta$ it is at rest at the crest of the barrier, so the action is linear in Δ and β:

$$iS=(-\varkappa_0^2/2\nu+\Delta)\beta. \qquad (35)$$

An activation is involved in the dependence of the absorption coefficient on the deficiency and the temperature. In the region $\Delta_1<\Delta<\Delta_2$ tunneling along terms E and B is allowed by the positions of the terms, but at this temperature such tunneling is not optimum, so there is no regime EB in the diagram at $\Delta>\Delta_1$.

For $\Delta>\Delta_2$ tunneling from term B to F becomes possible with crossing of term E in real time. This is a horizontal tunneling and is described by the action

$$iS(\Delta,\ \beta)=-\Delta\beta+(\varkappa_0^2/\nu)\,[\tau_{bf}-(-\nu)^{-1/2}\ \mathrm{th}\ ((-\nu)^{1/2}\tau_{bf})], \qquad (36)$$

in which the time of the transition, τ_{bf}, is found from the equation

$$\text{th}\,(\tau_{bf}-\beta/2)=(-\nu)^{-1/2}\,\text{tg}\,((-\nu)^{1/2}\tau_{bf}).$$

Since the term E is not involved in the tunneling, the deficiency does not appear in the path equations; as a result, activation is involved in the dependence of the absorption on the deficiency.

With a further increase in Δ the temperature range in which regime *EBF* is optimum becomes wider. As the deficiency is increased to $\Delta \geqslant \Delta_3$, the involvement of term E in the tunneling disappears from the diagram, as does regime *EBF*.

Transitions between all regimes occur in a hard fashion (in our model). A transition between regimes *BF* and *A* at large deficiencies is depicted by the horizontal line since the term E does not participate in the tunneling. The absence from this diagram of a regime in which the tunneling occurs exclusively along the single bound term, *B*, is explained by the exceedingly harmonic nature of the bound term (more on this below). In the second mechanism, which involves a transition of an exciton to a self-trapping state, only the terms E and B can participate in the tunneling. In the region $\Delta > \Delta_1$, the regime *EB* is the only one in this channel. It is described by expression (33), in which the other branch of the tangent must be taken. In the region $\Delta < \Delta_1$ there is again an activation regime with action (35).

The absorption of light in systems with self-trapping occurs by two mechanisms simultaneously at any values of the deficiency Δ and the temperature β. At small deficiencies, absorption to a free state is predominant; at large deficiencies, absorption to a self-trapping state is predominant.

7. EFFECT OF ANHARMONICITY OF THE BOUND TERM

As was pointed out in Sec. 3, the model which we are using has one fundamental shortcoming when applied to the case of strong coupling of an exciton with an ideal lattice: Its bound term for values $\varkappa_0 < 0$ and $\nu < 0$ is purely parabolic and has no minimum corresponding to a self-trapping exciton state. For this reason, at large deficiencies the point of the transition from the free term to the bound term moves monotonically down the energy scale with respect to the bottom of the free term. We will discuss qualitatively the situation in which there is a minimum on the bound term in a model with a single degree of freedom. In this case the lowering of the point at which the free and bound terms cross with respect to the free term must give way to a rising as the deficiency increases. In the mechanism of absorption to a self-trapped state, the horizontal tunneling turns to ascending tunneling at this time. In the mechanism of absorption to a free state doubling tunneling arises as the deficiency is increased further. As the point at which terms E and B cross rises above the barrier, there is the possibility (at high temperatures) that the tunneling paths in the two absorption mechanisms will coincide. It is not difficult to see that this entire picture originates from the positive curvature of the bound term near the self-trapping minimum; thereafter the situation is completely analogous in this sense to the absorption of light by an impurity center with $\varkappa_0 < 0$ and $\nu > 0$ at large deficiencies. This region is not shown in Fig. 9.

In addition to the absence of a self-trapping minimum, the parabolic shape of the bound term in the case $\varkappa_0 < 0, \nu < 0$ has another, and subtler, consequence, which stems from the fact that the vibration frequency of a harmonic oscillator is independent of the energy. This property of a parabolic potential is important for that absorption mechanism whose tunneling path passes through the crest of the self-trapping barrier. For this mechanism there exists a region of energies near the crest of the barrier for which the tunneling occurs exclusively along the bound term and constitutes a strictly harmonic vibration with an energy-independent period $\tau(\varepsilon) \equiv 2\pi(-\nu)^{-1/2}$. At the critical temperature $T = T_c = (-\nu)^{1/2}/2\pi$ all the paths in this region are optimal. The absorption regime (tunneling along a bound term) which corresponds to these paths lies entirely at the single point T_c along the temperature scale. Clearly, such a situation is degenerate, and it should disappear in the presence of the anharmonicities which are unavoidable in any, even just slightly more realistic, model. The various possible versions of the effect of anharmonicities on the results derived in the single-mode model can be analyzed easily by the approach which has been taken in an analysis of self-trapping on the basis of the same mode.[30] We will describe here only the changes which occur in the diagram of regimes when a slight anharmonicity is taken into account.

If the anharmonicities increase the period $\tau(\varepsilon)$ as the energy moves away from the crest of the barrier, the boundary between regimes *A* and *BF* in the mechanism of absorption to a free state in the region $\Delta > \Delta_3$ splits in two, and a regime *B* arises between the two resulting boundaries. At a temperature which corresponds to the period of a path near the crest of the barrier there is a soft transition between regimes *A* and *B*. A soft transition from tunneling along a *B* term to the *BF* regime occurs at a lower temperature, corresponding to the period of a path at the height of the point at which the *B* and *F* cross. Both of the boundaries which result are horizontal since the temperatures of the transitions depend only on the relative positions of the bound and free terms. In the mechanism of absorption to a self-trapped state, the *B* regime arises in a small region of small deficiencies; this region becomes smaller as the anharmonicities become weaker. A horizontal boundary between regimes *A* and *B* (a soft transition) arises here, as does a sloping boundary between regimes *B* and *EB*, with a hard transition. As the deficiency Δ is increased, the temperature region in which regime *B* is predominant shrinks and disappears; thereafter, regimes *A* and *EB* border on each other directly.

In the opposite case, in which the period $\tau(\varepsilon)$ decreases with decreasing energy ε, regime *B* does not occur. In the mechanism of absorption to a free state the transition between regimes *A* and *BF* becomes an ordinary hard transition. The boundary between these regimes remains horizontal, but the transition temperature no longer corresponds to the period of a path close to the crest of the barrier.

In the self-trapping mechanism, changes analogous to those described above occur with a transition between regimes *A* and *EB* in the region $\Delta < \Delta_1$.

8. ELIMINATION OF THE LATTICE COORDINATES

The quasiclassical approach starts from the adiabatic approximation. In its most general form this approximation means that one first solves a Schrödinger equation for an exciton in a lattice deformed in some arbitrary way, and then one solves an equation of motion of the lattice in which part

of the potential energy is the binding energy of the exciton in the potential of the arbitrary lattice deformation. We have taken this approach directly in the present study since the Schrödinger equation is trivial in our model, and the equation of motion of the sole lattice degree of freedom can be solved analytically. Specifically, this approach clearly demonstrates the various versions of the optimum paths describing the process by which the light is absorbed.

In the continuum theory of self-trapping (Refs. 21 and 28, for example) and in research on edge absorption in specific models,[25,27] a slightly different version of the quasiclassical approach is usually employed. That version assumes that the effective-mass method and the harmonic approximation for the elastic energy of the lattice, $U_E(\mathbf{X})$, are applicable, and it also assumes that the potential in the Schrödinger equation for the exciton is linear in the deformation $\mathbf{X}$:

$$\left[-\frac{\hbar^2}{2m}\Delta+V(\mathbf{r},t)\right]\Psi(\mathbf{r},t)=E_{ex}(t)\Psi(\mathbf{r},t); \tag{37}$$

$$V(\mathbf{r},t)=\sum_j V_j(\mathbf{r})X_j(t),$$

where m and $\mathbf{r}$ are the mass and coordinate of the exciton. Writing the binding energy E_{ex}, of the exciton as a variational minimum of the functional

$$E_{ex}(t)=\min\int\left[\frac{\hbar^2}{2m}(\nabla\Psi)^2+V(\mathbf{r},t)\Psi^2\right]d^3r, \tag{38}$$

we can incorporate it in this form in the elastic energy. Since the elastic energy is quadratic in the lattice coordinates, we can minimize the action S with respect to the lattice path $\mathbf{X}(t)$ for a fixed arbitrary functional dependence $\Psi(\mathbf{r},t)$ in a general form. A subsequent variation of the resulting functional $S[\Psi(\mathbf{r},t)]$ leads to a time-dependent nonlinear Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\Delta+\int D(\mathbf{r},t;\mathbf{r}',t')\Psi^2(\mathbf{r}',t')\,dt'\,d^3r'\right]\Psi(\mathbf{r},t)$$

$$=E_{ex}(t)\Psi(\mathbf{r},t), \tag{39}$$

in which the phonon Green's function is the kernel:

$$D(\mathbf{r},t;\mathbf{r}',t')=\sum_{jj'}X_{jj'}(t,t')V_j(\mathbf{r})V_{j'}(\mathbf{r}'). \tag{40}$$

Here $X_{ij},(t,t')$ is the solution of the elastic equations of motion of the lattice (5), with a term $\delta_{jj'}\delta(t-t')$ on the right side. The solution $\Psi(\mathbf{r},t)$ must have a period $-i\hbar\beta$. The integration over t in (39) is carried out in the region in which a bound state exists, i.e., at $T_{ex}(t)<0$.

Equation (39) is directly applicable only in those cases in which the lattice coordinates $\mathbf{X}(t)$ are single-valued functions of the time on the optimum path. In our problem, only the mechanism of absorption to a self-trapped state corresponds to such cases. In other cases, there is retrograde motion in time, which renders the path multivalued, so this approach requires generalization.

As the formal solution of the equations of motion with a right side, the Green's function $D(\mathbf{r},t;\mathbf{r}',t')$ has a singularity at $t=t'$. The generalization which is required here is achieved by introducing some analytic functions $D^+(\mathbf{r},t;\mathbf{r}',t')$ and $D^-(\mathbf{r},t;\mathbf{r}',t')$, which coincide with $D(\mathbf{r},t;\mathbf{r}',t')$ at $it>it'$ and $it<it'$, respectively. When there is a retrograde region, it is necessary to introduce a time contour which is "folded in three," on which the times in Schrödinger equation (39) can be ordered, and the path $\mathbf{X}(t)$ can be converted into a single-valued function of the time. For times t' which precede t as the contour is traced out we must then use the function $D^+(\mathbf{r},t;\mathbf{r}',t')$ as the kernel, while for times t' which follow t we must use the function $D^-(\mathbf{r},t;\mathbf{r}',t')$. In the absence of folds on the contour, this recipe naturally yields the same result as the direct use of the function $D(\mathbf{r},t;\mathbf{r}',t')$.

CONCLUSION

We have presented in its general form the quasiclassical approach to the calculation of the exponential function in the coefficient of edge optical absorption due to multiphonon processes, and we have demonstrated this approach with a simple but not uninteresting model. The absorption below the edge of the band is treated here as a tunneling of a lattice in a potential consisting of three terms: an empty term E, a bound term B, and a free term F. The position of the first term with respect to the other two is controlled by the energy deficiency of the photon, Δ. The absorption coefficient is determined by the action along that tunneling path which is the optimum path for the given phonon frequency and the given temperature T.

We have introduced the concept of absorption mechanisms corresponding to different minima of the lattice terms. The free term always has a minimum, so in any situation there will be an absorption mechanism in which the exciton is in a free state. If there is also a minimum on the bound term, a second absorption mechanism will arise. Since the bound term may not be unique, the number of absorption mechanisms is determined by the particular system. The absorption by any mechanism occurs in a manner which is completely independent of the absorption by any other mechanism. The total absorption is actually determined by some one mechanism which is predominant in the given region of the values of the parameters Δ and T, but the absorption by other mechanisms can be distinguished (e.g., on the basis of secondary luminescence); this possibility seems to us to be an interesting field for some experiments.

We have introduced the concept of horizontal tunneling in a single-valued potential and of ascending and descending tunneling in a double-valued potential. The distinctions among them which are of fundamental importance from the theoretical point of view concern the shape of the time contour which describes the tunneling of the lattice. The presence of retrograde regions on the paths of the ascending and descending tunneling means that caution must be exercised when the standard method of eliminating lattice coordinates is used (Sec. 8). According to our results, simple horizontal tunneling is a relatively rare process during the absorption of light. It arises in the mechanism of absorption to a self-trapped state and (in a certain region of deficiencies) in the mechanism of absorption to a bound state at an impurity center. Absorption to a free state always occurs through ascending tunneling. It is easy to see that this conclusion is general and is not tied to the particular model which is used. In some previous studies[25] of edge optical absorption with a free final state of the charge carriers or excitons, retrograde motion was not considered, so the re-

sults of those studies qualify at best as crude approximation. A transition from one type of tunneling to another cannot be observed experimentally, since it is not accompanied by any deviation from analyticity in the action $S(\Delta,\beta)$.

We have introduced the concept of absorption regimes, as sequences of terms which are crossed during tunneling. A transition between regimes as the deficiency and the temperature vary may occur in a hard fashion, i.e., with a slope change on the dependence $S(\Delta,\beta)$, or in a soft fashion, i.e., with a smooth dependence of the action. Seeing these features experimentally would seem to be problematical.

We regard the diagrams showing the arrangement of the various regimes in the plane of the parameters Δ and T as the primary result of this study. The quantitative characteristics of the absorption are contained in the transcendental equations which were written in the corresponding sections of this paper and which can be studied only by numerical or asymptotic methods. Of greatest interest from the experimental standpoint is the shape of the edge absorption line, which is described by the dependence of the action $S(\Delta,\beta) = \ln[K(\omega)]$ on the deficiency $\Delta = E_g - \hbar\omega$. We do not have room here to reproduce the diagrams of $S(\Delta,\beta)$ for the various values of the parameters. Furthermore, there is no major reason to do so, because of the simplified nature of the model which we have used. We will restrict our discussion to a qualitative description of this behavior.

At large deficiencies the Δ dependence of the action is approximately linear. For absorption at impurity centers and for absorption in an ideal crystal with weak exciton-phonon coupling, this dependence becomes slightly steeper with increasing Δ. For absorption to a self-trapped state, it becomes less steep. At small deficiencies the mechanism of absorption to an exciton free state always dominates since at $\Delta = 0$ the action $S(\Delta,\beta)$ vanishes, and the absorption coefficient has only the small factor associated with the coefficient of the exponential function. A characteristic feature of absorption at an impurity center is that the action also vanishes at a value of the deficiency equal to the exciton binding energy at a center in an undeformed lattice (the absorption in this case naturally goes to an impurity state). In crystals with self-trapping, the absorption coefficient falls off monotonically with increasing deficiency Δ for both mechanisms.

For the *BF* regime and for the activation regime, the action is characteristically a purely linear function of the deficiency. This fact, however, does not bear directly on the Urbach rule, since these regimes occur only in a mechanism which is not predominant. An explanation of the Urbach rule thus requires actual analysis of specific models.

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