Polariton kinetics and luminescence

V. V. Travnikov and V. V. Krivolapchuk

The polariton luminescence spectra of CdS and ZnSe crystals with different exciton lifetimes τ were investigated at $T = 2$ K. A set of polariton luminescence spectra of different forms was observed for the first time for samples of the same type and the dependence of the form of the polariton luminescence spectrum on the value of τ was determined. An analysis and a simplified quantitative calculation were made of the polariton luminescence spectra allowing both for "structural" factors governed by the dispersion of the polariton energy bands (density of states, group velocity of polaritons, coefficient of polariton transmission by a boundary of a crystal) and for the dynamic factors governed by the polariton kinetics (populations of polariton states in the energy and coordinate spaces, probability of conversion of a polariton formed in the interior of a crystal into external luminescence). It was found that the kinetics of the space-energy relaxation had the dominant influence on the form of the photoluminescence spectra. The kinetics determined largely the relative role of the interaction between various factors on the form of the polariton luminescence spectrum. A quantitative calculation ensured for the first time a good agreement between the theoretical and experimental luminescence spectra.

PACS numbers: 71.36. + c, 78.55.Hx

1. INTRODUCTION

It is well known[1] that the photon–exciton interaction alters considerably the spectrum of elementary excitations of a crystal, which are excitons and photons (dashed curve in Fig. 1) if an allowance is made for the Coulomb interaction in a crystal. New excitations represent a superposition of excitons and photons and are known as polaritons. In the vicinity of an exciton resonance with an isotropic effective mass the dispersion curve of transverse polaritons consists of two branches: a lower polariton branch and an upper one (curves 1 and 2 in Fig. 1, respectively); the dispersion curve is then described by

$$\left(\frac{\hbar ck}{E}\right)^2 = \varepsilon_0 + \frac{\varepsilon_0 E_{LT}}{E_0(k) - E - ih\Gamma/2}, \qquad (1)$$

where ε_0 is the "background" permittivity; c is the velocity of light; E and k are the energy and wave vector of a polariton; $E_{LT} = E_L - E_T$ is the longitudinal–transverse splitting (E_L and E_T are the energies at the bottoms of the energy bands of the longitudinal and transverse mechanical excitons, respectively); $E_0(k) = E_T + \hbar^2 k^2/2M$ is the energy of a mechanical exciton with a wave vector k; Γ is the polariton damping. The upper polariton branch begins at the energy E_L (the band of longitudinal excitons is not shown in Fig. 1).

If the photon-exciton interaction is ignored, it follows from the laws of conservation of energy and momentum that resonance luminescence is due to conversion of an exciton into a photon at the point of intersection of the exciton parabola and the photon line (point r in Fig. 1).

According to the polariton model, the observed luminescence can be regarded as the result of conversion of a polariton and the boundary of a crystal into an external photon.[2-4] The dispersion curve of polaritons has no specific "luminescence point" so that any occupied state on the branch 1 or 2 (Fig. 1) can contribute to the polariton luminescence. The polariton luminescence spectrum is given by the expression[5]

$$I(E) = \sum_{r=1,2} T_r(E)\,v_r(E)\,F_r(x=0,E)\,\rho_r(E)\,\Delta\Omega_r(E)\,\Delta E, \qquad (2)$$

where $T_r(E)$ is the transmission coefficient of a polariton of branch r by a crystal boundary; $v_r(E)$ is the group velocity of polaritons [$v(E) = h^{-1}\partial E(k)/\partial k$]; $F_r(x, E)$ is the distribution function of polaritons belonging to the branch r at the point x; $\rho_r(E)$ is the density of states; $\Delta\Omega_r(E)$ is a solid angle through which luminescence is emitted. Since, in principle, all states can contribute to the luminescence (including states with the same values of E but different wave vectors k), the problem of determination of the polariton luminescence spectrum reduces largely to the kinetic problem, i.e., we have to determine the energy and coordinate distribution functions of polaritons belonging to different branches.

Among the theoretical treatments of the polariton luminescence spectra one should mention Refs. 5–7 (see also Refs. 8 and 9). However, it is difficult to use the results of these papers in comparing the calculations with experiments. It is assumed in Refs. 5 and 6 that an equilibrium energy distribution of polaritons is established, although it is known that this is not justified if an allowance is made for the characteristic features of the polariton kinetics.[4,7,10] The in-
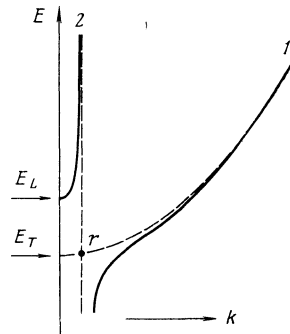

FIG. 1. Dispersion curve of polaritons in the vicinity of a specific exciton resonance.

0038-5646/83/121210-13$04.00

fluence of the kinetics of the energy distribution function of polaritons is considered in Ref. 7, but no allowance is made for the coordinate distribution function.

The need to use the polariton model even in a qualitative explanation of the experimental features of resonance exciton luminescence was first demonstrated in Refs. 11–14. A characteristic feature of the manifestation of the polariton effects in most crystals is the doublet profile of the resonance exciton luminescence lines at low temperatures. Doublet polariton luminescence lines were observed, for example, in crystals of CdS (Refs. 11, 13, 15, and 16), GaAs (Ref. 14), HgI$_2$ (Ref. 17), CdTe (Refs. 18 and 19), CuCl, CuBr, CuI (Ref. 19), LiH, LiD, NaI (Ref. 20), ZnSe (Refs. 21–23), KI (Ref. 24), and Xe (Ref. 25). The characteristics of the polariton luminescence due to resonance excitation of polaritons were investigated in Refs. 26 and 27.

Different forms of the polariton luminescence spectra were obtained in different investigations. Moreover, different qualitative explanations were put forward to account for the characteristics of the observed spectra. For example, an investigation of GaAs crystals[14] showed that the short-wavelength maximum of the polariton luminescence line was located above E_L, so that this maximum was attributed to the upper polariton branch, whereas the long-wavelength luminescence was attributed to the lower polariton branch. A similar explanation was put forward later to describe the spectra reported in Refs. 18–21. Other investigators[13,17] found both polariton luminescence maxima to be located below E_L and attributed the luminescence to the lower polariton branch. The existence of a short-wavelength maximum was attributed to a maximum of the transmission coefficient $T_1(E)$ (see also Refs. 15 and 16). The characteristics of the polariton luminescence spectra were explained in Refs. 22–24 and Refs. 26 and 27 by a minimum of the function $F(x = 0, E)$, which appeared because of a reduction in the probability that a polariton with a high value of the absorption coefficient will reach the boundary of a crystal. Therefore, a qualitative analysis of the experimental spectra revealed the influence of various factors on these spectra. All the factors governing the polariton luminescence have not yet been considered simultaneously.

We shall report investigations of the polariton luminescence spectra of CdS and ZnSe crystals characterized by different exciton lifetimes τ. A set of different profiles of the polariton luminescence lines was observed and some of them were reported earlier.[11–27] The polariton luminescence line profiles were analyzed allowing for all the factors governing the polariton luminescence spectrum [see Eq. (2)]. It was established that the general form of the polariton luminescence spectra was influenced decisively by the kinetics of the space–energy relaxation of polaritons. A quantitative calculation described well the experimental spectra. Preliminary results of the present study were published briefly elsewhere.[28]

2. EXPERIMENTAL RESULTS

We investigated the polariton luminescence spectra of the $n = 1A$ exciton states in CdS and ZnSe crystals at $T = 2$
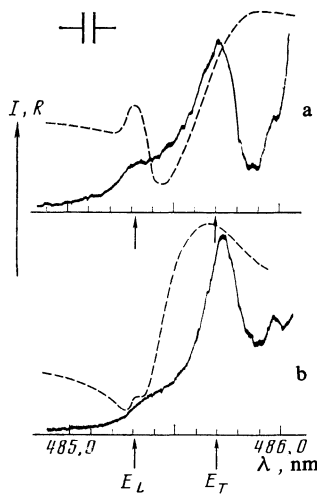

FIG. 2. Polariton luminescence spectra of CdS samples of the first type ($T = 2$ K): a) sample No. 2; b) sample No. 1.

K using samples characterized by different exciton lifetimes τ. Observations were made at right-angles to the plane of the samples.

The spectra of CdS crystals were investigated in the $\mathbf{E}\perp\mathbf{c}$, $\mathbf{k}\perp\mathbf{c}$ geometry ($\mathbf{E}$ and $\mathbf{k}$ are, respectively, the polarization vector and the wave vector of the observed luminescence, $\mathbf{c}$ is the optic axis of a crystal) and excitation was provided by an argon laser line at 476.5 nm. An investigation of a large number of samples (about 30) of different quality revealed the multiplicity of the forms of the polariton luminescence spectra. Figures 2–4 show the polariton luminescence spectra of some of the investigated samples. The dashed curves represent the reflection spectra. The position of the energy E_L was deduced from the luminescence spectrum obtained in the $\mathbf{E}\|\mathbf{c}$ geometry. It was found that E_L varied within a narrow range (up to 0.2 meV) from one sample to another. For convenience of comparison, the spectra of all the samples were plotted on the same energy scale es-
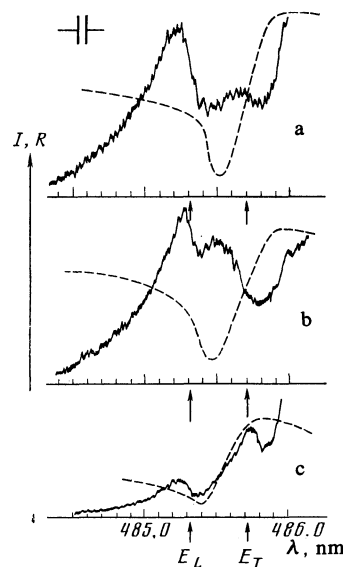

FIG. 3. Polariton luminescence spectra of CdS samples of the second type ($T = 2$ K): a) sample No. 5; b) sample No. 4; c) sample No. 3.
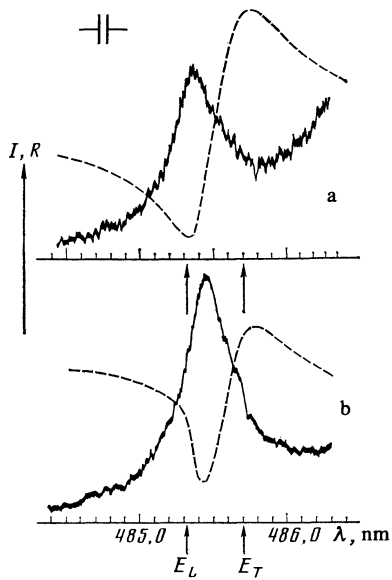
FIG. 4. Polariton luminescence spectra of CdS samples of the third type $(T = 2$ K): a) sample No. 7; b) sample No. 6.
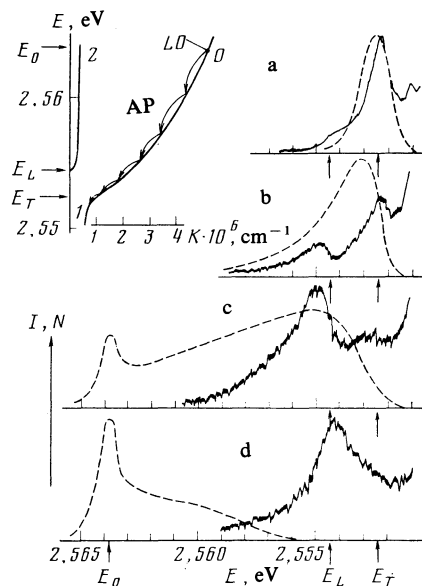

FIG. 5. Comparison of the spectra of different CdS samples (a—sample No. 1, b—No. 3, c—No. 5, d—No. 7) with the population functions $N(E)$ (dashed curves) corresponding to the excitations of these samples with the 476.5 nm line. The inset shows schematically the processes that appear in the polariton energy band on excitation with the 476.5 nm line.

tablished by reference to the energy E_L, which was taken to be 2.5544 eV (485.32 nm); the energy E_T was assumed to be 2.5524 eV (485.70 nm), as reported in Refs. 13 and 29.

The form of the polariton luminescence spectra was used to divide the samples arbitrarily into three types. In the case of samples of the first type (Fig. 2) the spectra had the main long-wavelength maximum and a weaker short-wavelength maximum which appeared in the form of a shoulder and was located below the energy E_L. The difference between the forms of the polariton luminescence spectra of samples of this type reduced mainly to different ratios of the intensities of the doublet components. Similar spectra were observed earlier not only for CdS crystals,[13,16] but also for crystals of HgI_2 (Ref. 17), CuCl, CuI (Refs. 18 and 19), LiH, LiD (Ref. 20), and Xe (Ref. 25).

The luminescence spectra of samples of the second type (Fig. 3) were characterized by a clear doublet structure with a highly pronounced short-wavelength maximum located below the energy E_L. The luminescence spectra of these samples exhibited a great variety. They differed in respect of the positions of the maxima in a doublet and in respect of the ratios of the intensities of these components. Such polariton luminescence spectra were observed earlier at helium temperatures for crystals of GaAs (Ref. 14), CdTe (Ref. 19), and ZnSe (Refs. 21–23). In the case of CdS crystals this form of the polariton luminescence spectra was observed for the first time.

In samples of the third type (Fig. 4) the polariton luminescence appeared in the form of single maxima at positions practically identical with the minima in the reflection spectra. Such polariton luminescence spectra had never been seen before.

This division of the samples in accordance with the form of the polariton luminescence spectra was correlated with the quality of the samples and with the value of τ, both of which increased on going from samples of the third type to samples of the first type. Samples of the first type were plate-

lets with very few defects and they exhibited a bright luminescence; samples of the third type were bulk crystals with the highest concentration of defects and they emitted a very weak luminescence. The quality and the luminescence intensity in the case of samples of the second type were intermediate between the two other groups. They included both bulk and platelet samples.

The lifetime had a considerable influence on the energy relaxation kinetics. The inset in Fig. 5 shows schematically the processs occurring in CdS crystals on excitation with the 476.5 nm line.[30] As a result of the scattering of the exciting light by longitudinal optical (LO) phonons, polaritons appeared at the point O on the branch 1. The subsequent scattering on acoustic phonons (AP) populated other points of the lower polariton branch. The form of the resultant function describing the population of the polariton states on the energy scale $N(E)$ depended strongly on τ, governed by the probability of nonradiative transitions. The form of the function $N(E)$ and the value of τ could be found from the $2LO$ luminescence spectra representing the radiation that appeared after the scattering of polaritons from the resonance region by two LO phonons.[30] We used this circumstance to find the functions $N(E)$ shown in Fig. 5 and to estimate τ. For samples of the third type we found that $\tau \lesssim \tau^A$ $(\tau^A = 5 \times 10^{-12}$ sec is the lifetime in the case of scattering of polaritons by AP from the point O—Ref. 30) and the majority of the polaritons did not reach resonance but were lost in the direct vicinity of the point O (Fig. 5b). For samples of the second type the value of τ was of the order of $(10–100) \times 10^{-12}$ sec and the polaritons reached the resonance region. In spite of the considerable difference between the form of $N(E)$ for different samples (Figs. 5b and 5c), a common feature was a considerable population of the states both below and above the energy E_L. In the case of samples of the

first type the lifetime as $\tau \sim (2-3) \times 10^{-9}$ sec (Refs. 10, 30, and 31) and the polaritons were scattered repeatedly by AP and became accumulated near the energy E_T (Fig. 5a). In this case the majority of the populated states was below the energy E_L.

Correlation between the form of the polariton luminescence spectrum and τ was observed in the case of ZnSe crystals. Figure 6 shows the polariton luminescence spectra obtained on excitation with a DRSh-250 lamp for two samples with different values of τ. The dotted curves are the functions $N(E)$ obtained on excitation with the 441.6 nm line of a cadmium laser. In the case of a sample with a small value of τ the population function $N(E)$ was of strongly nonequilibrium nature (Fig. 6b) and the form of the polariton luminescence was, as in the case of CdS, of the third type (the luminescence maximum coincided with the minimum in the reflection spectrum). Samples with large values of τ exhibited polariton luminescence spectrum and distributions $N(E)$ of the first type (Fig. 6a).

3. POLARITON DISTRIBUTION FUNCTION F(x, E)

The main difficulty in describing the polariton luminescence spectrum lies in finding the polariton distribution function. It is necessary to solve the Boltzmann equation which in the simplest one-dimensional case (with the x axis perpendicular to the surface of a sample) can be written as follows (see also Ref. 5):

$$[1+F_r(x,E)] W_r(x,E) + g_r(x,E) - \Gamma_r(x,E) F_r(x,E)$$

$$-v_r(E) \frac{\partial}{\partial x} F_r(x,E) = 0, \quad (3)$$

where $W_r(x, E)$ is the probability of formation at a point x of a polariton from a branch r with an energy E because of transitions from other polariton states; $g_r(x, E)$ is the term
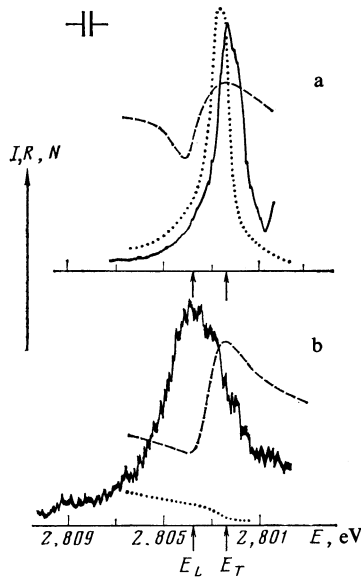

FIG. 6. Polariton luminescence spectra of ZnSe samples of the first (a) and third (b) types. The dotted curves represent the population functions $N(E)$ corresponding to the excitation of these samples with the 441.6 nm laser line.
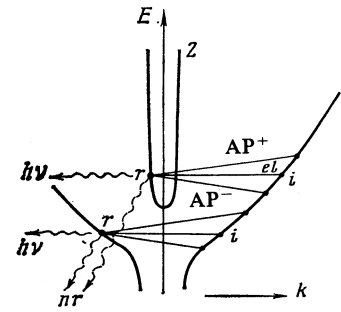

FIG. 7. Schematic representation of the processes that govern the formation and loss of polaritons in a radiation-emitting state r. A polariton in a state r appears because of arrival from other points i on the polariton branches as a result of el scattering and scattering with the participation of acoustic phonons (AP). Loss from a state is due to processes which are the inverse of the two just stated and also due to nonradiative capture of polaritons by impurities. (The processes involving LO phonons are not shown.)

describing generation of polaritons by the remaining processes (for example, by direct optical generation or because of binding of free electrons and holes directly in the observed state); $\Gamma_r(x, E)$ is the total probability of loss from a given state.

The process of formation and loss of polaritons are represented schematically in Fig. 7. The function $W_r(x, E)$ is governed by transitions from the initial states i to a state r assisted by optical and acoustic phonons, and also by the processes of elastic (el) scattering of polaritons on impurities, which may be important at low temperatures.[3,32-34] Consequently, the probability $W_r(x, E)$ is governed by the expression

$$W_r(x,E) = W_r^{AP}(x,E) + W_r^{LO}(x,E) + W_r^{el}(x,E)$$

$$= \sum_p W_r^p(x,E).$$

The probability $W_r^p(x, E)$ for a transition from a state i to a specific state r because of a p-type perturbation (LO, AP, el) is

$$W_r^p(x,E) = \sum_{i=1,2} \frac{2\pi}{\hbar} \int F_i(x,E_i) |H_{ri}^p|^2 \rho_i(E_i) d\Omega_i,$$

where H_{ri}^p is the matrix element of a transition from a state i to a state r because of a perturbation p; $F_i(x, E_i)$ is the distribution function of initial states in the branch i; $\rho_i(E_i)$ is the density of the initial states given by

$$\rho_i(E_i) = \frac{1}{(2\pi)^3} \frac{k_i^2(E_i)}{hv_i(E_i)}. \quad (4)$$

The contribution to the probability $\Gamma_r(x, E)$ is made not only by the processes of loss to other polariton states, but also by the nonradiative loss of polaritons:

$$\Gamma_r(x,E) = \Gamma_r^{nr}(x,E) + \sum_p \Gamma_r^p(x,E),$$

where $\Gamma_r^{nr}(x, E)$ is the probability of nonradiative loss of polaritons and $\Gamma_r^p(x, E)$ is the probability of return from a state r to a state i because of a perturbation p. This probability is given by the expression

V. V. Travnikov and V. V. Krivolapchuk   1213

$$\Gamma_r^p(x,E) = \sum_i \frac{2\pi}{\hbar} \int |H_{ir}{}^p|^2 \rho_i(E_i) \, [1 + F_i(x,E_i)] \, d\Omega_i. \quad (5)$$

It is very difficult to solve Eq. (3) in its general form. We shall use the following approximations and simplifications in order to find the distribution function.

1. Under the excitation conditions used in our study the polaritons appear in the resonance region because of successive relaxation from higher states because of interaction with AP (Fig. 5). In this case we can ignore the generation term. However, it must be included in an analysis of the polariton luminescence with the same energy as the excitation.[26,32] Allowing for the excitation conditions we can also ignore the processes involving LO phonons. Such processes can make a significant contribution at helium temperatures only if the energy of the exciting light exceeds the energy of the investigated states by an amount equal to an integral multiple of the LO phonon energy.[5,12]

2. At low excitation intensities employed in our study we have $F(x, E) \ll 1$ and, therefore, we can assume that $[1 + F(x,E)] = 1$ and that the function $F_r(x, E)$ is independent of the coordinate.

3. In the range above E_L because $\rho_1(E) \gg \rho_2(E)$, we can calculate $W_r(x, E)$ allowing only for the processes of arrival only from the lower polariton branch and in the calculation of $\Gamma_r(E)$ an allowance is made only for the loss to the states in the lower branch.[35]

4. Processes involving AP are regarded as elastic,[35] i.e., it is assumed that $E_i = E_r$. The exciton energy bands are assumed to be isotropic. Consequently, the probabilities of arrival and loss $W_r(x,E)$ and $\Gamma_r^p(E)$ (where $p = $ AP or el) are related by the simple expression

$$W_r{}^p(x, E) = F_i(x, E)\Gamma_r{}^p(E). \quad (6)$$

5. The main simplification lies in the selection of the distribution function of polaritons in the initial states ($i = 1$). By analogy with Refs. 5 and 6, we shall assume that this function is a product of the spatial $C(x)$ and energy $f_i(E)$ distribution functions:

$$F_1(x, E) = f_1(E)C(x). \quad (7)$$

A qualitative allowance for the inhomogeneity of the spatial distribution resulting from the surface excitation used in our study can be made if $C(x)$ is given by

$$C(x) = \frac{1}{\alpha_0^2 L^2 - 1}(e^{-x/L} - e^{-\alpha_0 x}), \quad (8)$$

where α_0 is the absorption coefficient of the exciting light; L is the effective diffusion length. The selected form of the distribution function represents a special case of the spatial distribution function of excitons obtained in the diffusion approximation[36] subject to the boundary condition[1)] $C(0) = 0$.

Under the above approximations, Eq. (3) can be rewritten in the form

$$\frac{\partial}{\partial x}F_r(x,E) + \frac{\Gamma_r(E)}{v_r(E)}F_r(x,E)$$
$$-f_1(E)\frac{1}{\alpha_0^2 L^2 - 1}(e^{-x/L} - e^{-\alpha_0 x})\frac{\Gamma_r^{AP}(E) + \Gamma_r^{el}(E)}{v_r(E)} = 0. \quad (9)$$

The required solution of Eq. (9) for polaritons traveling toward the surface (corresponding to negative values of the velocity) in a semiinfinite crystal $[F(\infty, E) = 0]$ is

$$F_r(0,E) = \frac{1}{(\alpha_0 L + 1)[\alpha_r(E) + \alpha_0][\alpha_r(E)L + 1]}$$
$$\frac{\Gamma_r^{AP}(E) + \Gamma_r^{el}(E)}{v_r(E)}f_1(E), \quad (10)$$

where

$$\alpha_r(E) = \Gamma_r(E)/v_r(E) \quad (11)$$

is the absorption coefficient of a polariton in a state r (Ref. 6). In accordance with the definition (11), the absorption of a polariton is due to all the processes of loss from a state with a given energy and a given wave vector. The function $\Gamma_r(E)$ governing the probability of loss from a given state is identical to the damping occurring in Eq. (1). The use of Eq. (11) is justified in the case of weak damping. In this connection it should be pointed out that according to our estimates the maximum damping even in the case of the most defective samples $[\Gamma = 1/\tau = 2 \times 10^{11} \text{ sec}^{-1} (0.13 \text{ meV})]$ was considerably less than the critical value $[\Gamma_c = 8 \times 10^{11} \text{ sec}^{-1} (0.5 \text{ meV})]$ for which the polariton approximation becomes valid (if $\Gamma < \Gamma_c$ the dispersion curves are practically identical with those in the $\Gamma = 0$ case).[38] We calculated all the functions associated with the polariton dispersion using Eq. (1) with $\Gamma = 0$.

4. POLARITON ABSORPTION

In calculations it is usual to assume that the damping is constant. For $\Gamma(E) = $ const, the frequency dependence $\alpha_r(E)$ is governed entirely by the function $v_r(E)$ (Fig. 8). The functions in Fig. 8 and all the calculations reported below were carried out using the parameters of CdS ($\varepsilon_0 = 10$; $M = 0.9m_0$—Ref. 29), because we had a wide range of samples of these crystals so that a detailed comparison could be made between the calculations and experiments. On approach to the resonance from the low-energy side the velocity $v_1(E)$ falls strongly, reaching its minimum in the region of the longitudinal–transverse splitting (LT region) and then increases, becoming comparable with the velocity of mechanical excitons. The velocity $v_2(E)$ rises steeply from zero at E_L and reaches values typical of the velocity of propaga-
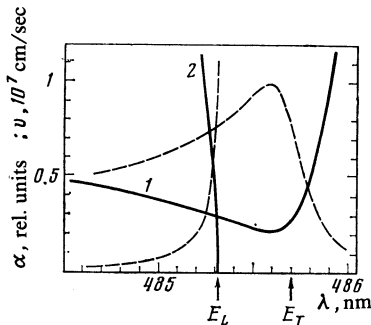

FIG. 8. Frequency (wavelength) dependences of the group velocity (continuous curves) and of the absorption coefficient (dashed curves) for the lower (1) and upper (2) polariton branches. The absorption coefficient is calculated for $\Gamma = $ const.

tion of light in matter. Consequently, $\alpha_1(E)$ has a pronounced maximum in the LT region due to a minimum of $v_1(E)$, and the coefficient $\alpha_2(E)$ decreases rapidly from infinitely high values at $E = E_L$ to much less than $\alpha_1(E)$. In reality, the polariton damping is a function of the energy which should affect the spectral dependence $\alpha_r(E)$.

Investigations of the absorption spectra of CdS crystals[39,40] have established that the main absorption maximum occurs at the wavelength 485.55–485.45 nm, i.e., much less than E_L. Since in the $E < E_L$ range the exciting light is converted mainly into polaritons belonging to the lower branch,[41] we may assume that the experimentally observed absorption maxima are due to maxima of $\alpha_1(E)$. This may be used as the criterion for the selection of $\Gamma_r(E)$.

If we assume that a crystal is ideal, then at helium temperatures the loss from a given state can only be due to transitions to other states because of the scattering on AP. We can determine the function $\Gamma_r^{AP}(E)$ by calculating the matrix elements of a polariton transition from a state r to a state i, which are governed by the products of the matrix elements of a transition of a "pure" exciton from a state with a wave vector $\mathbf{k}$ to a state with a wave vector $\mathbf{k}_i$, and the coefficients allowing for the proportion of the exciton properties in the initial and final polariton states.[6,42] Estimates indicate that in the investigated resonance region these coefficients can be assumed to be unity.[42]

In calculating the matrix elements for the scattering by longitudinal acoustic (LA) phonons we shall use an expression which describes the scattering of excitons in the range of small wave vectors[6]:

$$H_{ir}^{LA} = (\hbar q / 2\rho_L u V)^{1/2} D\delta(E_i - E_r), \qquad (12)$$

where ρ_L is the density of the investigated crystal; u is the velocity of sound; $D = (2/3)(E_v - E_c)$; $E_v - E_c$ is the difference between the deformation potentials of the valence and conduction bands; $q = |\mathbf{k}_r - \mathbf{k}_i|$ is the wave vector of an acoustic phonon participating in a transition; V is the volume of the investigated part of a crystal; the function $\delta(E_i - E_r)$ allows for the adopted approximation of "elasticity" of the transition. Since the occupation numbers of AP are low at $T = 2$ K, Eq. (12) allows only for the processes involving the transfer of a phonon to a lattice. After substitution of Eq. (12) in Eq. (5) and integration over all the states i, we obtain

$$\Gamma_i^{LA}(E) = 3D^2 k_i{}^3(E) / 2\pi\hbar\rho_L u v_i(E). \qquad (13)$$

In calculating a similar expression for polaritons of the upper branch, we shall assume that $q = |\mathbf{k}_1 - \mathbf{k}_2| = k_1$, because $k_1(E) \gg k_2(E)$. Consequently, we have

$$\Gamma_2^{LA}(E) = {}^3/_4 \Gamma_1^{LA}(E).$$

Figure 9a shows the frequency dependences of the partial absorption coefficients[2] $\alpha_r^{LA}(E)$. In calculating $\Gamma_r^{LA}(E)$ the anisotropy of CdS crystals is allowed for by averaging the value of the exciton mass $M = 1.34 m_0$ and the other parameters are taken from Ref. 6. In the range $E < E_L$ the dependence $\alpha_1^{LA}(E)$ has no maximum and the calculated values of the absorption coefficient $\alpha_1^{LA}(E)$ are smaller in the LT region than in the experiments.[39,40] In addition to the LA phonons, contributions to the polariton scattering processes
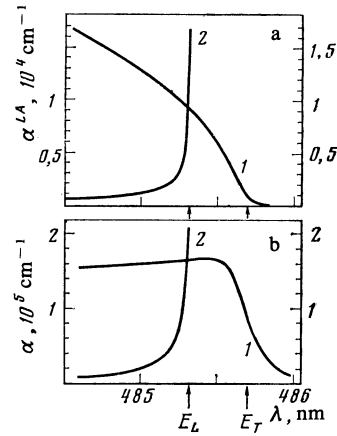

FIG. 9. Frequency (wavelength) dependences of the absorption coefficients for the lower (1) and upper (2) branches. The upper part of the figure shows the spectrum calculated allowing only for the processes involving LA phonons. The lower part shows the spectra calculated allowing not only for the participation of LA phonons but also for the contribution of extrinsic processes $(b = 10, \Gamma^{nr} = 2 \times 10^{11} \text{ sec}^{-1})$.

are made also by TA phonons,[43] but allowance for the latter cannot alter significantly the value of the absorption coefficient or the nature of its frequency dependence[3] $\alpha_1^{AP}(E)$, so that we shall allow only for the LA phonons. Therefore, an analysis of the low-temperature absorption spectra demonstrates the need to include "extrinsic" damping mechanisms, i.e., those other than the scattering by phonons.

The processes of the interaction of polaritons with defects and impurities have been ignored so far. We shall describe them by the following approximation. We shall take the quantity Γ^{nr} to be independent of energy and the same for branches 1 and 2. We shall describe the function $\Gamma^{el}(E)$ using the approximation from Refs. 32 and 44, where it has been assumed that the matrix element for the elastic scattering is independent of $|\mathbf{k}_r - \mathbf{k}_i|$. The frequency dependence $\Gamma^{el}(E)$ is governed entirely by the density of the final states $\rho_1(E)$. For the sake of convenience in comparison of the contributions of the elastic scattering processes with the scattering by AP, we shall represent $\Gamma^{el}(E)$ in the form

$$\Gamma_1^{el}(E) = \Gamma_2^{el}(E) = b\rho_1(E)\Gamma_1^{LA}(E_L)/\rho_1(E_L), \qquad (14)$$

where b is a dimensionless parameter. If $b = 1$, the probability of elastic scattering of polaritons of energy E_L is equal to the probability of their scattering by AP.

Figure 9b shows the frequency dependences of the absorption coefficients calculated using the parameters obtained by fitting the theory to the experimental polariton luminescence spectra of sample No. 3 $(b = 10, \Gamma^{nr} = 2 \times 10^{11} \text{ sec}^{-1})$. The proposed spectrum agrees much better with the experimental spectra[39,40] both in respect of the amplitude and in respect of the nature of the frequency dependence in the region $E < E_L$ than does the spectrum $\alpha^{LA}(E)$.

5. ENERGY DISTRIBUTION FUNCTION OF POLARITONS

In the adopted approximation, the quantity $f_1(E)$ is the energy distribution function independent of the coordinates. It can be approximated using the experimentally determined

1215   Sov. Phys. JETP **58** (6), December 1983

V. V. Travnikov and V. V. Krivolapchuk   1215

population functions $N(E)$, which can be described by

$$N(E) = \rho_1(E) f_1(E), \qquad (15)$$

where $\rho_1(E)$ is the density of the polariton states belonging to the lower branch and $f_1(E)$ is the distribution function of the polaritons from the lower branch averaged over the coordinate (the contribution to the $2LO$ luminescence is made by polaritons everywhere in a crystal). The expression (15) allows only for the states in the lower polariton branch, because it is these states that dominate—because of the high density—the $2LO$ luminescence. We used the experimental functions $N(E)$ and the expression (15) in the selection of the form of the function $f_1(E)$.

The polariton luminescence spectra were calculated in Refs. 5 and 6 on the assumption that $f_1(E)$ is the equilibrium Boltzmann function. Figure 10 shows the polariton population function calculated from Eq. (15) at $T = 2$ and 4 K on the assumption that a thermal equilibrium is established between polaritons and the lattice. Since below E_T there is a low but finite density of states (curve 3 in Fig. 10), the equilibrium distribution function $(e^{-E/kT})$ gives rise to an exponential increase in the population on reduction in the energy. Therefore, the hypothesis of a thermal equilibrium gives an unacceptable result.

We shall describe the population function by selecting $f_1(E)$ to be

$$f_1(E) = \text{const} \cdot \exp[-(E-E_c)/kT^*], \quad \text{if} \quad E > E_c \ (\text{region I}),$$
$$f_1(E) = \text{const}, \quad \text{if} \quad E < E_c \ (\text{region II}), \qquad (16)$$

where k is the Boltzmann constant; T^* is a temperature parameter; E_c is the energy at which the nature of the distribution function changes. The population functions determined experimentally for several CdS samples are compared in Fig. 11 with those calculated from the expression (15) using Eq. (16). We can see that a suitable selection of T^* and E_c ensures that the observed population functions are well approximated by the calculations. The question now arises what is the physical meaning of regions I and II and what quantities are represented by the energy E_c and by the parameter T^*? The lifetime in the case of the AP scattering $[\tau^A(E) = 1/\Gamma^{AP}(E)]$ decreases rapidly on increase in the energy. In fact, for any
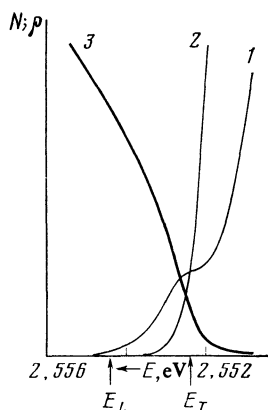

FIG. 10. Population functions $N(E)$ calculated from Eq. (15) on the assumption that an equilibrium distribution of polaritons has been established: 1) $T = 4$ K; 2) $T = 2$ K; 3) density of states in the lower polariton branch.
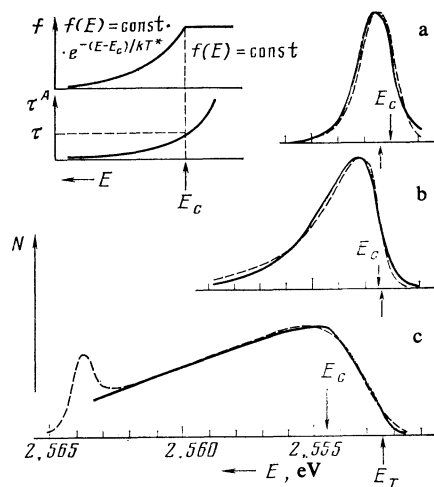

FIG. 11. Comparison of the experimental population functions $N(E)$ (dashed curves) with calculations (continuous curves) carried out using Eqs. (15) and (16) for several samples: a) sample No. 1 ($T^* = 5.3$ K); b) sample No. 3 ($T^* = 15$ K); c) sample No. 5 ($T^* = 57$ K). The inset shows schematically the nature of the energy distribution function $f(E)$. The values of the energy E_c are identified by arrows.

reasonable value of τ we can always find a point in an energy band (this is the point E_c) for which we have $\tau^A(E) = \tau$. Above this point we have region I, where $\tau^A(E) < \tau$ and polaritons are scattered several times by acoustic phonons during their lifetime. In this region the distribution is governed by the parameter T^*, which represents the effective temperature of "hot" polaritons established as a result of partial thermalization during the time τ. On increase in τ, the point E_c shifts downward on the energy scale, the number of the events of scattering by acoustic phonons increases, the degree of thermalization becomes greater, and the effective temperature falls. In the region below E_c the probability of interaction with acoustic phonons is less than the probability of polariton loss and the subsequent energy relaxation in region II is unlikely. The bulk of the polariton states become populated because of single-event processes of transfer from region I. A comparison of the calculations with the experimental results shows that the population is well described in this region by the relationship $N(E) \propto \rho_1(E)$, i.e., the probability of occupancy of the states is independent of the energy. Such a population corresponds to an extreme nonequilibrium ("infinitely hot") distribution $(T^* = \infty)$.

Using the proposed nature of the function $f_1(E)$, we can employ the energy E_c obtained on fitting $N(E)$ to estimate τ, if we assume that $\tau = \tau^{LA}(E_c) = 1/\Gamma^{LA}(E_c)$. For example, in the case of sample No. 2 we find that $\tau = 2 \times 10^{-9}$ sec, whereas for sample No. 5, we obtain $\tau = 3.7 \times 10^{-11}$ sec. The times found in this way are in good agreement with our estimates (Table I) and with the results of direct measurements carried out on high-quality CdS samples.[10,31] This justifies the use of the adopted form of the function $f_1(E)$ and the method of estimating τ from the energy E_c.

In crystals of the third type all the polaritons newly formed by the incident excitation reached the region below E_c. In this case up to the resonance region there is a negligible proportion of polaritons generated with E_0. The function

TABLE I. Values of parameters used to calculate spectra in Fig. 13.

Sample No.	T^*, K	τ, sec	L, 10^{-4} cm	b	Γ^{nr}, sec^{-1} (τ^{nr}, sec).	
№ 1	5.3	$3 \cdot 10^{-9}$	10	1,5	$3 \cdot 10^{10}$	($3.3 \cdot 10^{-11}$)
№ 2	8	$2 \cdot 10^{-9}$	6	2,5	$5 \cdot 10^{10}$	($2 \cdot 10^{-11}$)
№ 3	15	$4 \cdot 10^{-10}$	0.6	10	$2 \cdot 10^{11}$	($5 \cdot 10^{-12}$)
№ 5	57	$4 \cdot 10^{-11}$	0.25	10	$2 \cdot 10^{11}$	($5 \cdot 10^{-12}$)
№ 7	∞	$5 \cdot 10^{-12}$	0	10	$2 \cdot 10^{11}$	($5 \cdot 10^{-12}$)

$N(E)$ describing the population of the bulk of the polariton states has a definite long-wavelength edge (Fig. 5d). This edge corresponds to the energy which may be attained by polaritons from the point E_0 as a result of one or two collisions with acoustic phonons.[30] In order to describe samples of the third type throughout the range from E_0 to $\sim E_T$, we have to employ $f_1(E)$ in a form more complex than that given by Eq. (16). However, a satisfactory agreement between the calculations and experiments obtained for the majority of samples in the range $E < E_c$ demonstrates that the main factor that governs the population in the range below E_c of interest to us is the frequency dependence of the density of states. Therefore, even in the case of samples of the third type an analysis of the form of the polariton luminescence spectrum can be made assuming that $N(E) \propto \rho_1(E)$ throughout the region near the resonance.

The temperature T^* of the best samples does not drop below 5 K. It should be stressed that in this case the value of T^* is a quantity that represents not the temperature of the heated equilibrium subsystem, but is a measure of the deviation of the steady-state distribution of polaritons from a thermal equilibrium. At temperatures above those of liquid helium the populations of exciton states in perfect samples can be described satisfactorily by an equilibrium distribution.[45] The possibility of establishing an equilibrium by increasing the temperature of a sample is a consequence firstly of an increase in the probability of interaction with acoustic phonons and secondly because of an increase in τ (in the case of high-quality samples the value of τ is governed by the capture of bound excitons by shallow levels[10] and an increase in temperature increases the rate of capture because of an increase in the probability of thermal dissociation of bound excitons). However, even at high temperatures when the exciton luminescence is considered in the polariton model, it is necessary to allow for the characteristics of $f_1(E)$ in the low-energy range.

A more accurate form of $f_1(E)$ can be obtained by solving the balance equation.[7] However, in our case when the main purpose is to describe the polariton luminescence spectrum, the use of $f_1(E)$ in the form (16) is quite satisfactory for the understanding of the main features of this spectrum.

6. ANALYSIS OF POLARITON LUMINESCENCE SPECTRA

Luminescence was observed in a fixed external solid angle $\Delta\Omega_{ex}$. For normal emergence of luminescence from a crystal, we have[6]

$$\Delta\Omega_{ex} = \Delta\Omega_r(E) n_r{}^2(E), \qquad (17)$$

where $\Delta\Omega_r(E)$ is the internal solid angle that governs the set

of directions of the polariton wave vectors which may contribute to the luminescence; $n_r(E)$ is the refractive index of a state in a branch r with an energy E. After substitution of Eqs. (17) and (4) in Eq. (2), the expression for the polariton luminescence intensity simplifies greatly to

$$I(E) = \sum_{r=1,2} T_r(E) F_r(x=0, E) \frac{\Delta\Omega_{ex} E^2 \Delta E}{\hbar^3 c^2 (2\pi)^3}$$

$$\sim \sum_{r=1,2} T_r(E) F_r(x=0, E),$$

or, using Eq. (10), to

$$I(E) = \sum_{r=1,2} \frac{T_r(E)}{v_r(E)} \frac{\Gamma_r{}^{LA}(E) + \Gamma_r{}^{el}(E)}{[\alpha_r(E) + \alpha_0][\alpha_r(E) L + 1]} f_1(E). \qquad (18)$$

Figure 12 shows the frequency dependences of the various factors and terms in Eq. (18) and this is done in order to facilitate an analysis of the form of the polariton luminescence spectra. The transmission coefficients are calculated using an expression from Ref. 41 for $\Gamma = 0$ subject to the Pekar boundary condition. Figure 12a shows the frequency dependence of $T_1(E)/v_1(E)$. Below E_L we have $T_1(E)/v_1(E) = T_2(E)/v_2(E)$ (Ref. 41). In the range $E < E_L$ we find that in the adopted approximation we have $T_2(E) = 0$ and the contribution to the luminescence can only be made by the lower polariton branch. The function $T_1(E)/v_1(E)$ has
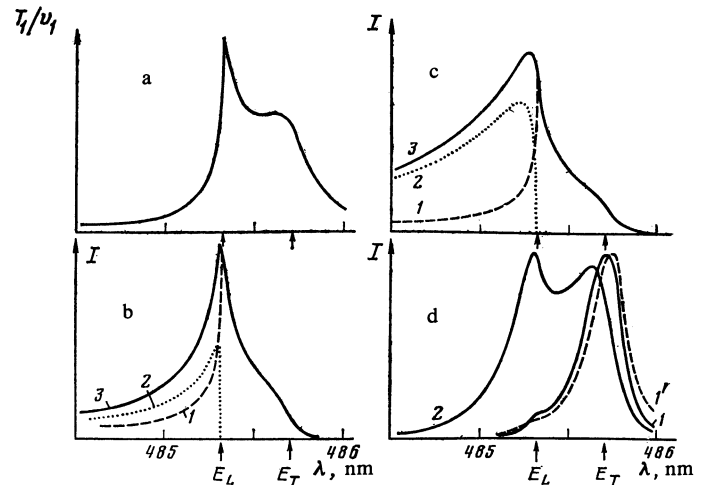

FIG. 12. Frequency (wavelength) dependences of the factors and terms in Eq. (18) governing the polariton luminescence spectrum. Parts b and c show the luminescence spectra for the lower (curves denoted by 1) and upper (curves denoted by 2) polariton branches; curves denoted by 3 represent the combined spectrum. The scales are the same for all the curves. The intensity in the spectra 1, 1', and 2 at the maxima in Fig. 12b are equalized for convenience of comparison of the forms of the polariton luminescence spectra.

two strong maxima: the short-wavelength maximum is governed by the maximum of the function $T_1(E)$, and the long-wavelength maximum is governed by the minimum of $v_1(E)$.

Figure 12b shows the spectral form of the factors

$$\frac{T_r(E)}{v_r(E)} \frac{\Gamma_r^{LA}(E)+\Gamma_r^{el}(E)}{\alpha_r(E)+\alpha_0} .$$

These factors determine the form of the polariton luminescence spectra typical of the samples with the lowest values of τ [when τ is very low, there is no diffusion ($L=0$), and $f_1(E)$ is independent of the energy]. The contributions of the lower and upper polariton branches in the range $E>E_L$ are then approximately the same. This is an unusual result since it was earlier assumed that the contribution to the luminescence in the range $E>E_L$ is made only by the upper polariton branch because $T_2(E)\gg T_1(E)$. We can gain a better understanding of the factors that determine the ratio of the contributions of the two branches to the observed luminescence by employing the approach developed in Ref. 6 which—bearing in mind the above approximations and notation— can be formulated as follows. Let $\dot{N}(E, x, \mathbf{k}_r)$ be the number of polaritons, with an energy E and with wave vectors $\mathbf{k}_r$ lying within a solid angle $\Delta\Omega_r(E)$, formed at a point x per unit time:

$$\dot{N}(E, x, \mathbf{k}_r)=W_r(x, E)\rho_r(E)\Delta\Omega_r(E)\Delta E,$$

where $W_r(x, E)$ is the probability of formation per unit time of a polariton in a state r at a point x; $\rho_r(E)\Delta\Omega_r(E)\Delta E$ is the number of polariton states in a branch r that may contribute to the luminescence. The probability that polaritons formed at the point x contribute to the luminescence is governed firstly by the probability that polaritons reached the surface of a crystal without absorption (this is governed by the function $e^{-\alpha_r(E)x}$) and, secondly, by the probability that a polariton reaching the surface is transformed into external luminescence [this is determined by the coefficients $T_r(E)$]. The polariton luminescence spectrum is found by integration over a semiinfinite crystal of contributions of polaritons formed at different points in the crystal:

$$I(E)=\sum_{r=1,2}\int_0^\infty \dot{N}(E, x, \mathbf{k}_r)e^{-\alpha_r(E)x}T_r(E)\,dx$$

$$=\sum_{r=1,2}\int_0^\infty W_r(x, E)e^{-\alpha_r(E)x}\rho_r(E)\Delta\Omega_r(E)\Delta E T_r(E)\,dx. \tag{19}$$

After integration with respect to x with the aid of Eqs. (4)–(8), we find that Eq. (19) can be reduced to the form which is fully identical with Eq. (18).[4] In addition to the function $W_r(x, E)$, the value of which is approximately the same for polaritons from the lower and upper polariton branches, the contributions to the polariton luminescence are governed— according to Eq. (19)—firstly by the value of $\alpha_r(E)$ and secondly by the factor $\rho_r(E)\Delta\Omega_r(E)\Delta E T_r(E)$, which can be reduced to the following form if use is made of Eqs. (4) and (17):

$$\rho_r(E)\Delta\Omega_r(E)\Delta E T_r(E)=\frac{\Delta\Omega_{ex}E^2}{\hbar^3 c^2(2\pi)^3}\frac{T_r(E)}{v_r(E)} . \tag{20}$$

Since $T_1(E)/v_1(E)=T_2(E)/v_2(E)$, the value of the factor

(20) is the same for both branches. Consequently, the difference between the values of $T_r(E)$ should not result in a difference between their contributions to the total luminescence intensity. According to Eq. (20), the factor by which $T_1(E)$ is less than $T_2(E)$ is exactly equal to the factor by which the number of the polariton states in the lower branch that can contribute to the luminescence is greater than the number of similar states in the upper branch. Consequently, the relative contributions of the branches is governed mainly by the ratio of the quantities $\alpha_2(E)$ and $\alpha_1(E)$, and also by the spatial distribution function.

If $L=0$, the contribution of a branch to the luminescence is governed by the factor $[\alpha_0+\alpha_r(E)]^{-1}$. In the immediate vicinity of E_L (for $E>E_L$) the contribution of the lower branch is greater than that of the upper branch because in this region we have $\alpha_1(E)<\alpha_2(E)$. On increase in the energy the value of $\alpha_2(E)$ decreases strongly and the contribution of the upper branch becomes greater than that of the lower branch. When $L=0$, the contributions of both branches are approximately the same, i.e., in the absence of diffusion the usual (photon) and additional (exciton) waves make comparable contributions to the luminescence.[1]

The spectrum shown in Fig. 12c differs from the spectrum in Fig. 12b only by allowance for the finite value of $L=5\times10^{-5}$ cm. Allowance for diffusion increases the influence of the polariton absorption processes on the polariton luminescence spectrum. The greater the depth of diffusion of polaritons into a crystal, the smaller the contribution to the luminescence by the states with higher values of $\alpha_r(E)$. Consequently, a change in the general form of the polariton luminescence spectrum on increase in L is governed by an increase in the contribution made to the luminescence by the parts of the upper polariton branch with low values of $\alpha_2(E)$. This increases the relative intensity of the short-wavelength wing and shifts the main maximum relative to E_L in the direction of shorter wavelengths. The shift is proportional to L. Therefore, if L is sufficiently large, then beginning from $\alpha_1(E)L>1$ in the region $E>E_L$, both the form and the position of the maximum in the short-wavelength part of the polariton luminescence spectrum are governed by the partial contribution of the upper-branch polaritons. The polaritons of the lower branch reach the surface subject to considerable losses because of the absorption processes. However, we must bear in mind that the energy is stored in a crystal and is concentrated in the lower polariton branch, whereas the upper branch is simply the radiative channel for the emission of the polariton energy.

Figure 12d demonstrates the influence of the change in the function $f_1(E)$ on the form of the polariton luminescence spectrum. This figure shows the spectra calculated by altering, compared with the preceding spectra, only part of the function $f_1(E)$ [$E_c=2.552$ eV(485.77 nm), $T^*=6$ K (spectrum 1) and $T^*=15$ K (spectrum 2)]. A reduction in the parameter T^* and a shift of E_c toward the range of the energy E_T corresponds to an increase in the degree of thermalization of polaritons. This increases the population of the low-energy parts in the LT region. Consequently, we find that, for example, at $T^*=15$ K the polariton luminescence

exhibits a strongly pronounced doublet structure (spectrum 2) and a further reduction in T^* shows that the calculated spectrum includes an intense long-wavelength maximum with a short-wavelength wing (spectrum 1). The difference between spectra 1 and 2 is similar to the difference between the forms of the polariton luminescence spectra observed earlier for GaAs (Ref. 14) and CdS (Ref. 13) crystals. In Refs. 13 and 14 the characteristics of the form of the spectra are explained from different points of view. In our calculations the transition from spectrum 1 to spectrum 2 is entirely due to a change in the parameter T^* (other parameters are kept constant). This demonstrates a much stronger influence of the energy distribution function on the form of the polariton luminescence spectrum than that allowed for in the earlier calculations.

An increase in the degree of thermalization is due to an increase in τ, which should also increase the value of L. For spectrum 1' (Fig. 12d) we have $L = 5 \times 10^{-4}$ cm, compared with $L = 5 \times 10^{-5}$ cm for spectrum 1 (the other parameters are the same in both cases). An increase in L by an order of magnitude produces only a small shift of the luminescence line. The general form of the polariton luminescence spectrum changes only slightly because in this case the absorption coefficient depends weakly on the energy within the line profile.

It thus follows from our analysis that the spatial and energy distribution function has a decisive influence on the form the the polariton luminescence spectrum. The function $f_1(E)$ determines the general distribution of the intensity over the line profile and the influence of $C(x)$ reduces to a redistribution of the contribution to the observed luminescence of the regions with different values of $\alpha_r(E)$. The influence of the transmission coefficients is greatest at low values of τ. As τ increases, the influence of these coefficients on the general form of the polariton luminescence spectrum decreases. The role of the transmission coefficient may become greater when luminescence is observed at large angles.[15,16]

7. COMPARISON OF THE CALCULATED POLARITON LUMINESCENCE SPECTRA WITH THE EXPERIMENTAL RESULTS

A comparison of the experimental polariton luminescence spectra of five samples with the spectra calculated from Eq. (18) is made in Fig. 13. The "intrinsic" parameters governing the dispersion curve and characterizing the interaction with acoustic phonons were the same in all the calculations. The absorption coefficient of the exciting light α_0 was assumed to be 7×10^4 cm^{-1} (Ref. 46). The spectra of each specific sample were calculated using the other parameters listed in Table I. The effective temperature T^* and the energy E_c were found by fitting to the experimental function $N(E)$. The value of τ for samples with short lifetimes was estimated from the $2LO$ luminescence spectrum.[30] In the case of samples with high values of τ such an estimate could be difficult because for the majority of samples the $2LO$ luminescence spectrum was masked by luminescence of impurity origin, which made it difficult to isolate the weak $3LO$ line.[30] This was exactly the situation in the case of samples 1
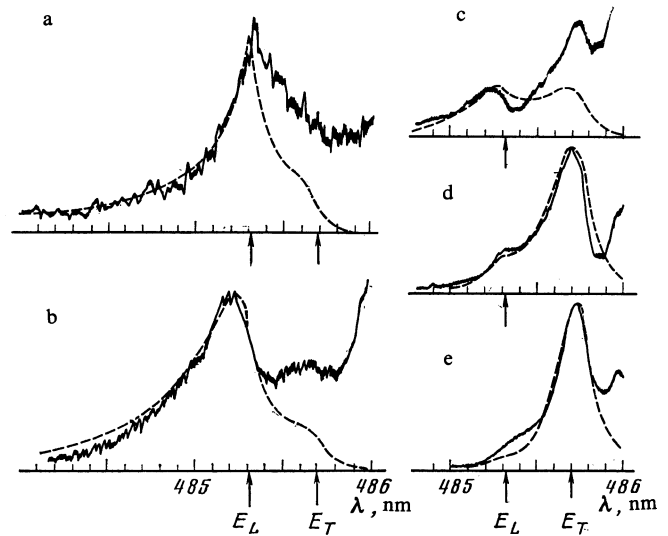

FIG. 13. Comparison of the calculated (dashed curves) with the experimental (continuous curves) spectra of different samples: a) sample No. 7; b) sample No. 5; c) sample No. 3; d) sample No. 2; e) sample No. 1.

and 2. The values of τ listed in Table I for these samples were selected on the basis of direct measurements carried out on high-quality CdS samples[10,31] allowing for the different values of the parameter T^*, which should be less for a crystal with a higher value of τ. The diffusion length was estimated from the formula $L = (1/3 \ \overline{v^2} \tau \tau_k)^{1/2}$ (Ref. 36), where $\overline{v^2}$ is the mean square value of the group velocity of polaritons from the lower branch; τ_k is the momentum relaxation time given by the expression

$$1/\tau_k = 1/\tau^A + 1/\tau^{el},$$

where $\tau^{el} = 1/\Gamma^{el}$ is the lifetime of polaritons in the case of elastic scattering processes. The value of $\overline{v^2}$ was found by averaging over the distribution $N(E)$ in region I. The time τ_k was calculated after a suitable selection of b applicable to a polariton for which the square of the group velocity amounted to $\overline{v^2}$. The parameters b and Γ^{nr} were obtained as follows. For each value of b beginning from zero we found successively the value of L and then varied Γ^{nr}. Table I gives the minimum values of b and Γ^{nr} for which the calculated polariton luminescence spectra agreed best with the experimental results. It should be pointed out that the effective diffusion parameters listed in Table I were clearly overestimated because L was obtained using a formula valid under thermodynamic equilibrium conditions.

The parameters obtained were in agreement with the qualitative characteristics of the samples. The "extrinsic" parameters b and Γ^{nr} increased on reduction in τ. It was worth noting the considerable difference between the time $\tau^{nr} = 1/\Gamma^{nr}$ and the time τ. In this connection we shall consider in somewhat greater detail the factors that govern the polariton lifetime. The low value of τ for samples of the third type was due to a high probability of nonradiative loss of polaritons.[30] An increase in τ on improvement in the quality of the samples was due to a reduction in the probability of nonradiative processes. In principle, suppression of all the nonradiative loss channels should ensure that τ is governed

only by the processes of radiative loss of polaritons from a crystal.[7,9] However, in the case of real crystals such a situation would be difficult to achieve. In the case of perfect CdS samples the value of τ is determined by the processes of capture by shallow traps.[10] The values of τ determined in Refs. 10 and 30 represent the lifetime of the bulk polaritons accumulated in the interior (in a layer of thickness of the order of L). On the other hand, the parameter τ^{nr}, appearing in our case as a result of an allowance for the influence of the structure of $\alpha_r(E)$ on the polariton luminescence formula, represents effectively the surface layer because it is this layer that dominates the resonance luminescence. In the surface layer the lifetime may be considerably less than in the bulk,[31,37] which is clearly due to a high concentration of defects on the surface.

8. DISCUSSION OF RESULTS

Figure 13 shows that there are discrepancies between the experimental results and the calculations, which is to be expected in view of the approximations and simplifications adopted by us. We shall now consider in detail some of these approximations.

The energy relaxation of polaritons, particularly below E_T, may be accompanied by a considerable change in the spatial distribution of polaritons. This imposes restrictions on the use of the approximation $E(x, E) = f(E)C(x)$. In the case of high values of τ the function $F(x, E)$ may be influenced also by the processes of surface and bulk reabsorption.[47]

In calculations of all the functions that depend on the dispersion of polaritons we assumed in Eq. (1) that $\Gamma = 0$. This simplifies greatly the calculations and makes it possible to introduce such concepts as the group velocity and density of states, which become indeterminate in the case of finite values of Γ (Ref. 48). In the case of real values of the damping (Table I) an allowance for Γ in Eq. (1) does not—as pointed out earlier—alter the dispersion curve of polaritons. Therefore, if the damping is neglected in Eq. (1), the frequency dependence of the function $\Gamma(E)$ determined mainly by the dispersion of polaritons should not be affected. On the other hand, the function $T(E)$ depends strongly on the quantity Γ (Ref. 41). Even in the case of relatively weak damping, characteristic of perfect samples, the frequency dependence $T(E)$ should differ considerably from the $\Gamma = 0$ case[41] and in the range below E_L the contribution to the luminescence for finite values of Γ should be made also by the upper branch. Neglect of the damping in the calculation of $T(E)$ may be one of the reasons for the discrepancy between the experiments and calculations, particularly in the case of crystals of the third type, for which the position of the maximum is governed by the function $T(E)$. In the calculations made on the assumption that $L = 0$ the position of the polariton luminescence maximum in fact coincides with E_L and in the case of crystals of the third type it varies from sample to sample, and in some cases it differs considerably from the energy E_L (Fig. 4).

Our analysis allows for the contribution of only the bulk polaritons to the luminescence, but the influence of damping

raises the question whether surface polaritons contribute to the luminescence spectra because an increase in the spatial damping of bulk polaritons may have the effect that the surface region where these polaritons are deexcited may become comparable with the region of existence of surface polaritons.[49] It is also important to discuss the role of surface polaritons because in recent reports the observed features of the polariton luminescence spectra are attributed to surface polaritons.

Inclusion of surface polaritons in the interpretation of the observed spectra is clearly necessary because the energy range of existence of surface polaritons largely overlaps the polariton luminescence region. The dispersion curve of surface polaritons [i.e., the dependence $E(k_\parallel)$, where $k_\parallel$ is the component of the wave vector along the crystal boundary] in the absence of the spatial dispersion fits completely in the LT region between the energy E_T and the energy $E_s[\varepsilon(E_s) = -1]$, located below the energy E_L (in the case of CdS crystals, we have $E_L - E_s \approx 0.2$ meV). If an allowance is made for the spatial dispersion, then $E(k_\parallel)$ may extend from the energy E_T continuously to the region above E_L (Ref. 50).

Surface polaritons have been observed in the exciton resonance region for several compounds by the attenuated total internal reflection (ATIR) method.[50] Surface polaritons cannot contribute to the luminescence in the case of an ideally flat boundary because of the law of conservation of the wave vectors. Conversion into external luminescence is possible in the case of surface polaritons only when they are scattered by deviations from the ideal flatness of the boundary. A calculation of the probability of conversion of surface polaritons into external luminescence because of scattering by acoustic phonons and surface roughness is given in Ref. 49. It is shown there that the scattering of surface polaritons may give rise to two maxima in the luminescence spectrum and these maxima should be located between the energies E_T and E_L.

The results of Ref. 49 were used to interpret the experimental luminescence spectra of ZnTe (Ref. 51) and Xe (Ref. 25) crystals. In Ref. 51 a qualitative interpretation of the reflection and luminescence spectra was used to find the values of the energies E_T and E_L. Two lines in the spectrum, observed between the values of E_T and E_L found in this way, were attributed—in accordance with Ref. 49—to the surface polariton luminescence. The proposed interpretation was criticized in Ref. 52, where the values of E_T and E_L were obtained by a theoretical analysis of the specular reflection spectra and of ATIR spectra of ZnTe crystals. It was shown there that both luminescence maxima attributed in Ref. 51 to surface polaritons are located on the long-wavelength side of the energy E_T, so that they must represent impurity luminescence. The positions of the maxima attributed to surface polaritons in the luminescence spectrum of Xe crystals are quite close to those expected on the basis of the results of Ref. 49.

Our analysis demonstrates that the characteristic features observed in the LT region may be due to bulk polaritons arising because of the maxima of the functions $T(E)$ and $N(E)$ or because of the characteristics of the structure of the

absorption coefficients. It should also be pointed out that the calculations made in Ref. 49 were made ignoring the spatial dispersion on condition that the Debye frequency ω_D satisfies the inequality $\hbar\omega_D < E_L - E_T$. An allowance for the finite mass of excitons and for the actual form of the dispersion of acoustic phonons may, in principle, alter the calculated spectral position of the short-wavelength maximum of surface polaritons. Therefore, the question of participation of surface polaritons in the luminescence spectra is still unanswered. The main contribution to the polariton luminescence spectra observed under the usual conditions is made by bulk polaritons. Surface polaritons may be responsible for some features of the spectra; in principle, the absence of an allowance for surface polaritons in our study may be one of the reasons for the discrepancies between the calculations and experiments. However, a reliable proof of the participation of surface polaritons in the luminescence spectra would require further studies. Special attention should be given to an active controlled surface treatment.

In spite of the approximations and assumptions made above, our approach can account for all the main features of the observed spectra. The nature of changes in the general form of the theoretical spectra is in good agreement with the experiments. Therefore, the proposed approach provides a correct description of the general physical phenomena underlying polariton luminescence.

9. CONCLUSIONS

We analyzed and calculated the polariton luminescence spectra including all the factors that determine the form of these spectra. We demonstrated the dominant influence of the kinetics of the space-energy relaxation of polaritons, governing the relative importance of the effects of various factors on the polariton luminescence spectra. The characteristics of the kinetics account for the observed multiplicity of the experimental polariton luminescence spectra.

The proposed approach provides a unified explanation of the main features of all the doublet polariton luminescence spectra observed so far for semiconductor crystal,[11-18,21-23] insulators,[21-24] and cryocrystals.[25] The multiplicity and the difference between the observed spectra are clearly due to the fact that samples of different quality were investigated. In the case of molecular crystals characterized by large oscillator strengths (for example, anthracene) the polariton luminescence spectrum may be affected considerably by the characteristics of the polariton kinetics due to the large effective mass of excitons.[9] This results in a departure of the general form of the polariton luminescence spectra of these crystals from those mentioned above. An analysis of the polariton luminescence spectra of molecular crystals may be made by the approach employed above if an allowance is made for the finite energy of the phonons participating in the formation of the polariton luminescence spectra.

The dependences of the form of the polariton luminescence on the lifetime and diffusion length of excitons demonstrate the possibility of investigating the features of the space-energy kinetics of excitations appearing in a crystal on the basis of the recorded polariton luminescence spectra.

[1)]When $C(x)$ is described by an expression from Ref. 36 the frequency dependence of the final expression for $F_r(0, E)$ depends weakly on the selected boundary conditions. The case when $C(0) = 0$ corresponds to a high surface annihilation rate γ. If $\gamma = 0$, the boundary condition reduces to the form $dC/dx|_{x=0} = 0$. In this case the expression for $F_r(0, E)$ differs from Eq. (10) by the factor $[1 + \alpha_0 L + \alpha_r(E)L]$, which has a weak frequency dependence within the polariton luminescence profile. Bearing in mind that on the surface of a crystal the value of τ can be considerably less than in the bulk,[31,37] we find that the condition $C(0) = 0$ is clearly more realistic.

[2)]A similar calculation was first carried out in Ref. 35. The authors attempted to explain the experimental values of the low-temperature absorption coefficients by allowing only for the "intrinsic" processes of scattering by LA phonons and they used overestimated values of the deformation potential constant $(D = 30$ eV$)$. In our calculations it was assumed that $D = 5$ eV (Ref. 6).

[3)]In the investigations of resonance Brillouin scattering[43] it was shown that in the case of CdS the polariton scattering lines along certain directions $(k \perp c)$ are of comparable intensity for LA and TA phonons. Since the anisotropy of the piezoelectric scattering, responsible for the appearance of the TA lines, is considerably stronger than the deformation scattering anisotropy (the scattering by TA phonons vanishes along certain directions[43]), it follows that the contribution of the TA phonons to the value of $\Gamma(E)$ is at least comparable with the contribution for the LA phonons. The frequency dependence $\alpha_1^{TA}(E)$ is even steeper within the LT region than for the LA phonons $[\Gamma_1^{TA}(E) \propto k_1^5(E)$, as shown in Ref. 43.

[4)]In Ref. 6 the final formula differs from Eq. (18) because the authors ignored the "extrinsic" processes and used a different expression for the function $C(x)$ which $[C(x) = e^{-x/L}]$ gives a nonphysical result in the absence of diffusion.

[1]S. I. Pekar, Kristallooptika i dobavochnye svetovye volny (Crystal Optics and Additional Light Waves), Naukova Dumka, Kiev, 1982.
[2]Y. Toyozawa, Prog. Theor. Phys. Suppl. No. 12, 111 (1959).
[3]V. M. Agranovich, Usp. Fiz. Nauk 71, 141 (1960) [Sov. Phys. Usp. 3, 427 (1960)].
[4]J. J. Hopfield, Proc. Eighth Intern. Conf. on Physics of Semiconductors, Kyoto, 1966, in: J. Phys. Soc. Jpn. 21, Suppl., 77 (1966).
[5]A. Bonnot and C. Benoit à la Guillaume, in: Polaritons (Proc. First Taormina Research Conf. on Structure of Matter, Taormina, Italy, 1972, ed. by E. Burstein and F. DeMartini), Pergamon Press, New York (1974), p. 197.
[6]W. C. Tait and R. L. Weiher, Phys. Rev. 178, 1404 (1969).
[7]H. Sumi, J. Phys. Soc. Jpn. 41, 526 (1976).
[8]V. M. Agranovich and M. D. Galanin, Perenos énergii élektronnogo vozbuzhdeniya v kondensirovannykh sredakh (Transfer of Electron Excitation Energy in Condensed Media), Nauka, M., 1978.
[9]M. S. Brodin, S. V. Marisova, and É. N. Myasnikov, Ukr. Fiz. Zh. 27, 801 (1982).
[10]P. Weisner and U. Heim, Phys. Rev. B 11, 3071 (1975).
[11]C. Benoit à la Guillaume, A. Bonnot, and J. M. Debever, Phys. Rev. Lett. 24, 1235 (1970).
[12]E. F. Gross, S. A. Permogorov, V. V. Travnikov, and A. V. Sel'kin, Fiz. Tverd. Tela (Leningrad) 13, 699 (1971) [Sov. Phys. Solid State 13, 578 (1971)].
[13]E. Gross, S. Permogorov, V. Travnikov, and A. Selkin, Solid State Commun. 10, 1071 (1972).
[14]D. D. Sell, R. Dingle, S. E. Stokowski, and J. V. DiLorenzo, Phys. Rev. B 7, 4568 (1973).
[15]S. A. Permogorov and A. V. Sel'kin, Fiz. Tverd. Tela (Leningrad) 15, 3025 (1973) [Sov. Phys. Solid State 15, 2015 (1974)].
[16]I. Broser and R. Broser, J. Lumin. 12-13, 201 (1976).
[17]I. Akopyan, B. Novikov, S. Permogorov, A. Selkin, and V. Travnikov, Phys. Status Solidi B 70, 353 (1975).
[18]P. Hiesinger, S. Suga, F. Willmann, and W. Dreybrodt, Phys. Status Solidi B 67, 641 (1975).
[19]S. Suga, K. Cho, P. Hiesinger, and T. Koda, J. Lumin. 12-13, 109 (1976).

[20]V. G. Plekhanov and A. A. O'Connell-Bronin, Fiz. Tverd. Tela (Leningrad) **20**, 2078 (1978) [Sov. Phys. Solid State **20**, 1200 (1978)]; Phys. Status Solidi B **86**, K123 (1978).

[21]P. S. Kosobutskiĭ, Ukr. Fiz. Zh. **22**, 980 (1977).

[22]B. V. Novikov, A. B. Pavlov, and V. G. Talalaev, Fiz. Tverd. Tela (Leningrad) **23**, 207 (1981) [Sov. Phys. Solid State **23**, 116 (1981)].

[23]B. Sermage and M. Voos, Phys. Rev. B **15**, 3935 (1977).

[24]Truong van Khiem and A. Nouailhat, J. Phys. Soc. Jpn. **50**, 121 (1981).

[25]I. Ya. Fugol', O. N. Grigorashchenko, A. M. Ratner, and E. V. Savchenko, Solid State Commun. **38**, 1031 (1981); I. Ya. Fugol', O. N. Grigorashchenko, and E. V. Savchenko, Phys. Status Solidi B **111**, 397 (1982).

[26]C. Weisbuch and R. G. Ulbrich, Phys. Rev. Lett. **39**, 654 (1977).

[27]C. Weisbuch and R. G. Ulbrich, J. Lumin. **18-19**, 27 (1979).

[28]V. V. Travnikov and V. V. Krivolapchuk, Pis'ma Zh. Eksp. Teor. Fiz. **36**, 196 (1982) [JETP Lett. **36**, 242 (1982)].

[29]A. B. Pevtsov, S. A. Permogorov, Sh. R. Saĭfullaev, and A. V. Sel'kin, Fiz. Tverd. Tela (Leningrad) **22**, 2400 (1980) [Sov. Phys. Solid State **22**, 1396 (1980)].

[30]S. A. Permogorov and V. V. Travnikov, Fiz. Tverd. Tela (Leningrad) **22**, 2651 (1980) [Sov. Phys. Solid State **22**, 1547 (1980)].

[31]N. N. Zinov'ev, Kand. diss. (Thesis for Candidate's Degree), Leningrad, 1983.

[32]A. B. Pevtsov, S. A. Permogorov, and A. V. Sel'kin, Pis'ma Zh. Eksp. Teor. Fiz. **33**, 419 (1981) [JETP Lett. **33**, 402 (1981)].

[33]C. Hermann and P. Y. Yu, Phys. Rev. B **21**, 3675 (1980).

[34]A. A. Gogolin and E. I. Rashba, Solid State Commun. **19**, 1177 (1976).

[35]W. C. Tait and R. L. Weiher, Phys. Rev. **166**, 769 (1968).

[36]V. M. Agranovich, Teoriya éksitonov (Theory of Excitons), Nauka, M., 1968.

[37]J. Lagois, Phys. Rev. B **23**, 5511 (1981).

[38]W. C. Tait, Phys. Rev. B **5**, 648 (1972).

[39]J. Voigt, Phys. Status Solidi B **64**, 549 (1974).

[40]S. I. Pekar and M. I. Strashnikova, Zh. Eksp. Teor. Fiz. **68**, 2047 (1975) [Sov. Phys. JETP **41**, 1024 (1975)].

[41]A. V. Sel'kin, Kand. diss. (Thesis for Candidate's Degree), Leningrad, 1974; Phys. Status Solidi B **83**, 47 (1977).

[42]J. J. Hopfield, Phys. Rev. **182**, 945 (1969).

[43]E. S. Koteles, in: Excitons (ed. by E. I. Rashba and M. D. Sturge), North-Holland, Amsterdam, 1982, p. 83.

[44]E. L. Ivchenko, G. E. Pikus, and N. Kh. Yuldashev, Zh. Eksp. Teor. Fiz. **80**, 1228 (1981) [Sov. Phys. JETP **80**, 629 (1981)].

[45]E. F. Gross, S. A. Permogorov, and B. S. Razbirin, Usp. Fiz. Nauk **103**, 431 (1971) [Sov. Phys. Usp. **14**, 104 (1971)].

[46]M. S. Brodin and M. I. Strashnikova, Fiz. Tverd. Tela (Leningrad) **8**, 684 (1966) [Sov. Phys. Solid State **8**, 549 (1966)].

[47]V. M. Agranovich, S. A. Darmanyan, and V. I. Rupasov, Zh. Eksp. Teor. Fiz. **78**, 656 (1980) [Sov. Phys. JETP **51**, 332 (1980)].

[48]V. M. Agranovich and V. L. Ginzburg, Kristallooptika s uchetom prostranstvennoĭ dispersii i teoriya éksitonov, Nauka, M., 1979 (Spatial Dispersion in Crystal Optics and the Theory of Excitons, Wiley, New York, 1967).

[49]V. M. Agranovich and T. A. Leskova, Pis'ma Zh. Eksp. Teor. Fiz. **29**, 151 (1979) [JETP Lett. **29**, 135 (1979)]; V. M. Agranovich, S. A. Darmanyan, T. A. Leskova, and V. I. Rupasov, Izv. Akad. Nauk SSSR Ser. Fiz. **43**, 1284 (1979).

[50]J. Lagois and B. Fischer, Festkoerperprobleme **18**, 197 (1978).

[51]M. S. Brodin and M. G. Matsko, Pis'ma Zh. Eksp. Teor. Fiz. **30**, 571 (1979) [JETP Lett. **30**, 538 (1979); Solid State Commun. **35**, 375 (1980)].

[52]L. Schultheis and J. Lagois, Solid State Commun. **44**, 1557 (1982).

Translated by A. Tybulewicz