Exciton diffusion and the mechanism of exciton momentum scattering in semiconductors

N. N. Zinov'ev, L. P. Ivanov, I. G. Lang, S. T. Pavlov, A. V. Prokaznikov, and
I. D. Yaroshetskiĭ

A. F. Ioffe Physicotechnical Institute, USSR Academy of Sciences

Nonstationary diffusion of excitons in the semiconductor CdS is investigated. The mechanisms responsible for relaxation of the exciton momentum are determined by comparing the experimentally obtained temperature dependence of the momentum relaxation time with the theory, developed in the present work, of interaction between excitons and acoustic phonons (piezoelectric interaction, deformation potential), optical phonons, and impurity centers, with allowance for the internal structure of the excitons. The cross section for exciton formation by binding of free carriers and the temperature dependence of the cross section are estimated.

PACS numbers: 71.35. + z, 72.10.Di, 72.80.Ey

1. INTRODUCTION

The production of streams of quasiparticles in a condensed medium, as well as the development of methods of experimentally determining the characteristics of these streams and methods of controlling them, is one of the fundamental problems of the physics of the condensed state. The progress reached in the solution of this problem is the basis of numerous technical applications of liquids and solids. Streams of free carriers in semiconductors, in particular, have been intensively investigated during the last few decades. Interest in this question is due primarily to the fact that the production of a stream of charged particles in the medium leads to the appearance of electric current. An investigation of the characteristics that determine the current and, in particular, the mobility (or diffusion coefficient) of the particle, and the uniquely connected with them momentum relaxation times, play an exceedingly important role in this problem. On the basis of such investigations it is possible to obtain information on interactions of elementary excitations in a system, as well as on the possible methods of controlling the properties of various technical devices. Besides the investigation of the behavior of streams of charged particles, considerable interest attaches to the motion of streams of neutral excitations and in particular, excitons. The point is that excitons, in contrast to free electrons and holes, are carriers of stored energy, and their transport leads to transport of excitation energy (energy $\hbar\omega \sim E_g$, i.e., a quantum emitted as a result of recombination of the exciton, where E_g is the band gap which amounts to 1–3 eV for typical semiconductors). It is clear, therefore, that excitons exert a definite influence both on the distribution of the energy obtained from the outside by optical activation, and on its transport in the crystal. On the other hand, an investigation of transport phenomena in an exciton system can be useful also for additional identification of the mechanisms that determine the mobility of the free carriers, and particularly in those semiconductors for which there is as yet no clear understanding of the nature of the interactions that control its magnitude

(for example in III–V, II–VI materials and others). So far, however, the production of controllable streams of free excitons in semiconductors and the investigation of their characteristics was hardly considered by the researchers. This situation differs somewhat from the situation that evolved in the physics of molecular crystals.[1] Naturally, in the case of excitons, since they are electrically neutral, it is impossible to set them in motion by applying an external electromagnetic field, but there are possibilities of producing exciton-density or temperature gradients, of applying a nonuniform strain field, and of other nonelectric actions that play the role of a drawing force. The production of exciton streams by such forces, and the promise of controlling them, is in our opinion one of the ways of using such phenomena in technical applications. It is possible that investigations of this kind will be useful for experimental identification of Bose condensation of free excitons, and consequently for the observation of the superfluidity effect, as a result of which energy transport without loss would be ensured in the crystal.

At present there are practically no reported investigations of momentum relaxation of excitons in semiconductors (other than Ref. 2, where exciton motion was investigated in the field of nonuniform strain in Si in the temperature interval 1.5–20 K).

We report here the first systematic experimental and theoretical investigations of the temperature dependence of the characteristics of a stream of free excitons in semiconducors (CdS), a stream produced as a result of a density gradient in the crystals. The most important characteristic of such a crystal, as indicated above, is the diffusion coefficient, which is uniquely connected with the relaxation time of the exciton momentum. In Sec. 2 are described experimental investigations of nonstationary diffusion in a wide temperature interval 10–300 K. In Sec. 3 we consider theoretically the mechanisms of exciton-momentum scattering. In Sec. 4 is determined the temperature dependence of the cross section for binding electrons and holes into excitons. In the last Sec. 5 of the article the experimental data are compared with the conclusions of the theory, and it is deduced on this basis

that various interaction mechanisms in the elementary-particle system contribute to the relaxation of the exciton momentum.

2. EXPERIMENTAL RESULTS

Among the first studies of nonequilibrium carrier transport were the experiments, by now classics, of Haynes and Shockely on the temporal and spatial evolution of particle distribution in a sample after their injection stops. When particles (in our case, excitons) are injected in a sample at an instant of time $t = 0$ at a point $x = 0$, their density $n(x,t)$ at an arbitrary point x and at a time t is determined by the solution of the diffusion equation

$$\partial n/\partial t = D\nabla^2 n - n/\tau, \tag{1}$$

where D is the diffusion coefficient of the excitons and τ is their lifetime. Substitution of the boundary and initial conditions for (1) and the procedure of solution, with allowance for the real singularities of the investigated samples (for example, the presence, near the crystal surface, of the region in which the lifetime τ_S of the excitons differs from its value τ_V in the volume, with $\tau_V \approx 10\,\tau_S$), were carried out in Ref. 3. It can be shown that the exciton density at an arbitrary point $x > d$ at the instant of time $t > t_0$, where t_0 is the duration of the exciting pulse, is described by the expression

$$n(x,t) = \frac{n(x,t_0)L_0^2 x}{2\pi^{1/2}(Dt)^{3/2}}\exp\left(-\frac{t}{\tau_V} - \frac{x^2}{4Dt}\right), \tag{2}$$

where $L_0 = (Dt_0)^{1/2}$.

Our experiments on the determination of D were based on the idea of investigating the time dependence of the exciton density $n(x,t)$ at fixed values of x. This was accomplished in the experiment by recording the temporal characteristic of the exciton radiation in a zero-phonon luminescence line whose intensity is proportional to the exciton density in a region with thickness d_X^{-1} near the surface, where d_X is the light-absorption coefficient. We investigated the kinetics (see Fig. 1) of the radiation from the region of the excitation A ($x = 0$, observation geometry $\mathbf{k}_I \| -\mathbf{k}_L$) and in region B ($x = L$, where L is the thickness of the sample, observation geometry $\mathbf{k}_I \| \mathbf{k}_L$), where $\mathbf{k}_I$ and $\mathbf{k}_L$ are wave vectors of the exciting and recombination radiation, respectively. It is important to emphasize that the light absorption coefficient in a zero-phonon luminescence line of the exciton is $d_X \sim 10^5$ cm^{-1}, and the thickness of the investigated samples was
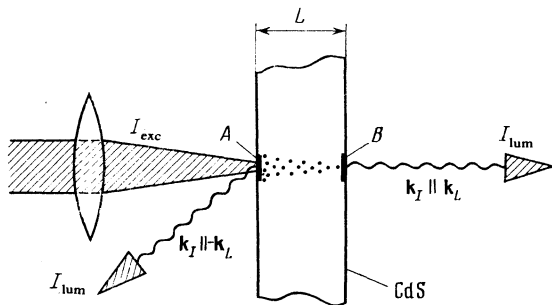

FIG. 1. Geometry of the investigation of the diffusion of excitons in CdS samples by analyzing the temporal kinetics of exciton luminescence.

$L \sim 10^{-3}$ cm. Under these conditions the radiation entering the recording apparatus, from the exciton generation region, when working in a $\mathbf{k}_I \| \mathbf{k}_L$ observation geometry, is reduced to a minimum. By virtue of the foregoing, crystal surface regions of thickness $d_X^{-1} \sim 10^{-5}$ cm are unique detectors of excitons, with high temporal and spatial resolution. According to (2) the temporal kinetics of exciton radiation of a zero-phonon luminescence line at $x = 0$ is determined in the geometry $\mathbf{k}_I \| -\mathbf{k}_L$ by the expression

$$I_x(t)\,|_{x=0} \propto I_0(Dt)^{-3/2}\exp(-t/\tau_S), \tag{3}$$

and in the geometry $\mathbf{k}_I \| \mathbf{k}_L$

$$I_x(t)\,|_{x=L} \propto I_0(Dt)^{-3/2}\exp\left(-\frac{t}{\tau_V} - \frac{L^2}{4Dt}\right). \tag{4}$$

It can be seen from (3) and (4) that D can be determined, if τ_S, τ_V and τ_L are known, from the condition of best agreement between the experimental dependence $I_x(t)$ and calculation in accordance with (4).

The luminescence was analyzed with a DFS-24 double monochromator and a stroboscopic system for recording the radiation signal; the system operating speed was not worse than 10^{-9} sec. The exciton radiation was recorded in accordance with the known selection rules[3] for CdS crystals. The samples were excited by radiation from an N_2 laser ($\lambda_{\text{exc}} \approx 0.337$ nm) with pulse duration $t_0 \sim 10^{-8}$ sec and with peak power $\leqslant 10$ W. The excitation intensity used in the experiment should be lower than that at which the drift motion of the exitons becomes effective. An indication of the transition from the diffusion regime of exciton motion to the drift regime (due to dragging of the excitons by the phonons) is the appearance of changes in the shape of the exciton-luminescence pulse when the pump is varied.[4] The temporal kinetics of the recombination radiation were fed to an x-y plotter and simultaneously recorded on the screen of a memory oscilloscope S8-12. The monochromator separated both the fundamental exciton emission line and the lines of its phonon replicas, whose temperature dependence was registered. In the experiment we used perfect CdS crystals with residual-donor density $N_D \leqslant 10^{15}$ cm^{-3}, grown from the gas phase. The samples were placed in the chamber of a temperature-controlled cryostat, and the accuracy at which the temperature was maintained in the investigated range was not worse than 0.01 K.

Figure 2 shows the experimental temporal kinetics of the exciton radiation at the exciton frequency in the two indicated observation geometries. As seen from the experimental data, with increasing temperature the exciton-radiation pulse is broadened at $\mathbf{k}_I \| \mathbf{k}_L$ and the time delay of the signal maximum relative to the instant t_{in} corresponding to the initial excitation pulse increases. Starting from (4), it can be shown that

$$D = \frac{1}{4}L^2\tau_V(t_M^2 + \frac{3}{2}t_M\tau_V)^{-1}, \tag{5}$$

where t_M is the time delay between the instant t_{in} and the time corresponding to the maximum of the exciton radiation at $\mathbf{k}_I \| \mathbf{k}_L$. On the other hand, it is known that
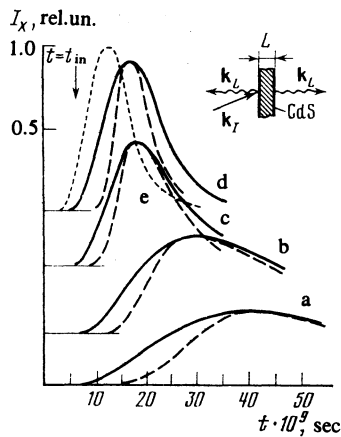
$$D = \tau_p T/m_0, \tag{6}$$

FIG. 2. Temporal kinetics of exciton luminescence in transmission geometry— a($T = 70$ K), b ($T = 60$ K), c ($T = 40$ K), d ($T = 20$ K), and in reflection geometry—e; solid lines—experiment, dashed—theory in accordance with Eq. (4).
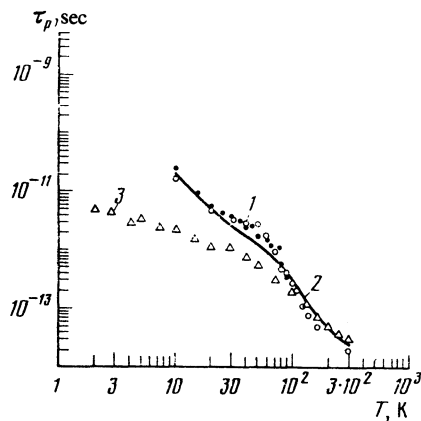

FIG. 3. Dependence of the momentum relaxation time on the temperature. For excitons: points 1) experiment; curve 2) theoretical dependence with allowance for the action of the scattering mechanisms on the acoustic and optical phonons; For electrons: points 3 from Ref. 6.

where τ_p is the exciton momentum relaxation time, T is the temperature in energy units, $m_e = m_1 + m_2$ is the effective mass of the exciton, m_1 and m_2 are the effective masses of the electron and of the hole. Taking (5) into account, we obtain then

$$\tau_p = {}^1/_4 L^2 \tau_V m_e T^{-1} (t_M{}^2 + {}^3/_2 t_M \tau_V)^{-1}. \qquad (7)$$

It can be seen from (7) that to determine the value of D from the data of Fig. 2 it is necessary to measure L, τ_V, t_M and T. The position of the instant of time t_{in} was chosen by approximating the real bell-shaped excitation pulse by a rectangular pulse of duration t_0 and having an energy (area) equal to the energy of the real pulse; the exciton of radiation pulse at $k_I \parallel - k_L$ practically duplicated the shape of the excitation pulse. The sample thickness was measured with an MBI-15 microscope capable of measuring the thickness L accurate to $\pm 2 \mu$m, and was also determined from the Fabre-Perot interference pattern (in the case of plane-parallel samples in the region of weak dispersion of the refractive index. The temperature was measured with a resistor made of compensated Ge. The value of τ_V was measured by the following three independent methods: by determining the damping constant of the exciton luminescence on the photon replica line X-LO in single-photon and two-photon excitation, and by analysis of the behavior of the damping of the exciton luminescence on the fundamental line (Fig. 2) as $t \to \infty$. Indeed, recognizing that the absorption coefficient d_{X-LO} of the light on the X-LO line is of the order of 10^2 cm^{-1}, we find from (2) that the density on the line

$$I_{X-LO}(t) \infty \int_V n(x,t) \, dr \infty I_0 e^{-t/\tau_V}, \qquad (8)$$

i.e., the emission from this luminescence line yields integral information on the total number of excitons in the sample and on its time variation. In the case of two-photon excitation, however, uniform volume generation of excitons takes place. We note that the values of τ_V determined by the two indicated methods differed at a given temperature by not more than 5%. On the other hand, analysis of the experimental data of Fig. 2 in accordance with (4) as $t \to \infty$, when

$I_X(t)$ at $x = L$ varies like $\exp(-t/\tau_V)$, yields somewhat larger values of τ_V than in the preceding two cases (the differences do not exceed 15%). The indicated methods were used to determine the value of τ_V for each of the investigated temperatures in the range 10–300 K. Taking the foregoing into account, we determined the value of D and next also τ_p from (5) and (7). These parameters were determined also by comparing the waveform of the radiation pulse (Fig. 2) with calculation in accordance with (4). The obtained values of τ_p in the investigated temperature range are plotted in Fig. 3. From an analysis of the behavior of the experimental values of $\tau_p(T)$ one can clearly distinguish two segments with different temperature dependences. To determine the character of the interaction processes that cause the momentum relaxation in the exciton system, we proceed to consider different types of interaction between the excitons and the scatterers.

3. THEORY

A change in the exciton momentum takes place when the exciton interacts with different scatterers such as impurities, phonons (acoustic or optical) and others. Recognizing that in the case of free carriers at low and high temperatures scattering by phonons is predominant,[5,6] we calculate the value of τ_p corresponding to the interaction of the excitons with the acoustic (A) and longitudinal optical (LO) lattice vibrations. It can be assumed beforehand that scattering by A phonons is substantial at low crystal temperatures, and scattering by LO phonons at sufficiently high ones.

Since CdS is a piezoelectric, the acoustic vibrations of the lattice act on the charged carriers and on the excitons in two ways: by producing piezoelectric fields and deformation potentials. Let us calculate the value of τ_p^{PA} due to action of piezoelectric fields on the excitons.

The operator of the piezoelectric interaction of the exciton with the phonons is of the form

$$\mathcal{H}_{int}^{PA} = \sum_{j,v,q} (C_{jvq} e^{iqr_j} b_{vq} + C_{jvq}^* e^{-iqr_j} b_{vq}^+), \qquad (9)$$

where the index $j = 1$ corresponds to the electron, $j = 2$ to the hole, r_j is the radius vector of the electron or the hole,

TABLE I CDS crystal parameters used in the calculations

[26] $\dfrac{m_1}{m_0}$	[26] $\dfrac{m_2}{m_0}$	[27] $\varkappa_0$	[28] $\varkappa_\infty$	[7] v_l, cm/sec	[7] v_s, cm/c	[7] $\beta_{33}{}^*$, ch.un. CGS/cm^3
0.2	1	9	5,86	$4{,}3 \cdot 10^5$	$1.8 \cdot 10^5$	$1{,}47 \cdot 10^5$

[7] $\beta_{31}{}^*$, ch.un. CGS/cm^3	[7] $\beta_{15}{}^*$, ch.un. CGS/cm^3	[29] $|E_1 - E_2|$, eV	[30] ρ, g/cm^3	[4, 31] $\hbar\omega_{LO}$, eV	[26] ΔE, eV
$-0{,}75 \cdot 10^5$	$-0.63 \cdot 10^5$	2	4.82	0.038	0.028

* $\beta_{33} = \beta_{3,33};\quad \beta_{31} = \beta_{3,11} = \beta_{3,22};\quad \beta_{15} = \beta_{1,13} = \beta_{1,31} = \beta_{2,23} = \beta_{2,32}.$

$b_{\nu q}$ and $b_{\nu q}^+$ are the operators of annihilation and creation of an acoustic phonon of the branch ν with wave vector $\mathbf{q}$; next, according to Ref. 7

$$C_{j\nu q} = (-1)^{j+1} \frac{2\pi e \beta_{\alpha,\mu\lambda}}{\varkappa_{mn} q_m q_n} \left[\frac{\hbar}{2V_0 \rho \omega_\nu(\mathbf{q})} \right]^{1/2} q_\alpha \left(e_{\nu\mu}(\mathbf{q}) q_\lambda + e_{\nu\lambda}(\mathbf{q}) q_\mu \right),$$

where e is the electron charge, $\beta_{\alpha,\mu\lambda}$ is the tensor of the piezoelectric moduli, $\varkappa_{mn}$ is the dielectric-constant tensor, V_0 is the normalization volume, and ρ is the density of the crystal; $\omega_\nu(\mathbf{q})$ and $e_\nu(\mathbf{q})$ are the frequency and the polarization vector of the phonon branch ν with wave vector $\mathbf{q}$. The exciton momentum relaxation time τ_p^{PA} can be calculated by a method used, for example, in Ref. 8 to calculate the exciton-scattering probability. As a result we obtain

$$(\tau_p^{PA})^{-1} = \frac{e^2 T m_3{}^{1/2}}{2^{1/2} \pi \hbar^2 E^{1/2}} \overline{Y} \mathcal{K}(Ka), \tag{10}$$

where $E = \hbar^2 K^2/2m_e$ is the kinetic energy of the exciton, $\mathbf{K}$ is the wave vector of the exciton,

$$\mathcal{K}(Ka) = 2 \int_0^1 dy \, y F(Kay), \tag{11}$$

$$F(z) = \left\{ \left[1 + \left(\frac{m_2}{m_e} z \right)^2 \right]^{-2} - \left[1 + \left(\frac{m_1}{m_3} z \right)^2 \right]^{-2} \right\}^2, \tag{12}$$

$a = \hbar^2 \varkappa_0/\mu e^2$ is the exciton radius, μ is the reduced mass of the exciton, and $\varkappa_0$ is the low-frequency dielectric constant of the crystal.

The dimensionless factor Y from the right-hand side of (10) was obtained as a result of averaging over the angles that determine the direction of $\mathbf{q}$ relative to the crystallographic axis, the sum

$$\sum_\nu Y_{\nu q} = \sum_\nu \lim_{q \to 0} \frac{1}{\rho v_\nu^2(\mathbf{q})} \left| \frac{2\pi \beta_{\alpha,\mu\lambda}}{\varkappa_{mn} q_m q_n} q_\alpha [e_{\nu\mu}(\mathbf{q}) q_\lambda + e_{\nu\lambda}(\mathbf{q}) q_\mu] \right|^2,$$

$v_\nu(\mathbf{q})$ is the sound velocity of the branch ν. Replacing this sum by the average value, we use the same approximation as in Ref. 7 for the calculation of the mobility of electrons in CdS. Calculating $\overline{Y}$ by the same method as in Ref. 7 and using the parameters of the table, we obtain $\overline{Y} = 2.68 \cdot 10^{-2}$.

We note that the reciprocal exciton momentum relaxation time (10) differs from the probability of scattering of the exciton as a whole in that account is taken of the arrival processes in the kinetic equation (see, e.g., Ref. 9, p. 466). For

comparison, we present the result of Ref. 7 for the reciprocal time of electron relaxation

$$(\tau_{pe}^{PA})^{-1} = \frac{e^2 T m_1{}^{1/2}}{2^{1/2} \pi \hbar^2 E^{1/2}} \overline{Y}. \tag{13}$$

For the case of thermodynamic equilibrium of the excitons (or electrons) with the lattice, which we consider here, we shall assume

$$E = {}^3\!/_2 T. \tag{14}$$

For electrons we then find from (13) that $\tau_{pe}^{PA} \propto T^{-1/2}$. The line 5 in Fig. 4 corresponds to Eq. (13) with substitution of (14). Expression (10) contains the exciton factor $\mathcal{K}(Ka)$, which depends on two parameters, Ka and m_2/m_1. Under the condition $m_2 = m_1$ we have $\mathcal{K}(Ka) = 0$, i.e., complete cancellation of the interactions of the electron and of the hole with the piezoelectric field. The parameter Ka can be treated as the ratio of the exciton radius to the characteristic
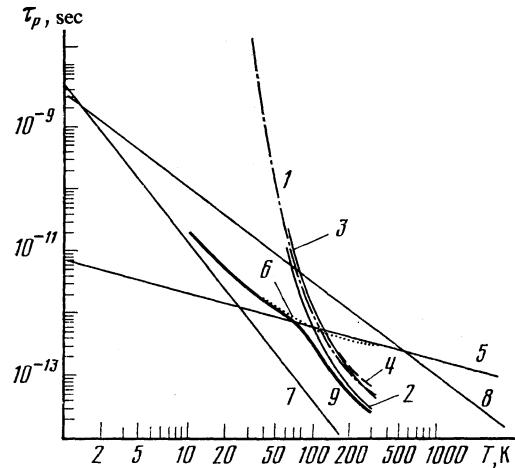

FIG. 4. Results of theoretical analysis of the momentum relaxation of excitons: 1) scattering of excitons by LO phonons in accordance with (23); 2) summary curve for momentum relaxation on optical phonons [with allowance for scattering (20) and decay (27)]; 3) exciton momentum scattering due to decay in accordance with (27); 4) scattering by LO phonons in accordance with (20); 5) electron momentum scattering by A phonons, due to interaction via the piezoelectric field (13); 6) exciton scattering by A phonons, due to interaction via the piezoelectric field (10); 7) asymptotic curve for the scattering of excitons by A phonons (piezoelectric interaction) (17); 8) exciton scattering by A phonons, due to interaction via the deformation potential (19); 9) resultant dependence of the exciton momentum relaxation (28).

wavelength of the acoustic oscillations that interact with the exciton (indeed, the wave vector of the acoustic phonons interacting with the excitons varies in the range from 0 to 2 K). We note that $\mathcal{K}(Ka)$ is, according to (11), always smaller than unity.

Calculating the integral in the right-hand side of (11), we obtain

$$\mathcal{K}(Ka) = (Ka)^{-2}[\Phi(Ka) - \Phi(0)], \tag{15}$$

where

$$\Phi(z) = -\frac{\eta_1^4}{(\eta_1+z^2)^3} - \frac{\eta_2^4}{(\eta_2+z^2)^3} - 2\eta_1^2\eta_2^2$$
$$\times\left\{\frac{2}{(\eta_2-\eta_1)^3}\ln\frac{\eta_2+z^2}{\eta_1+z^2} - \frac{1}{(\eta_2-\eta_1)^2}\left[\frac{1}{\eta_1+z^2} - \frac{1}{\eta_2+z^2}\right]\right\} \tag{16}$$

$$\eta_1 = (m_e/m_1)^2, \quad \eta_2 = (m_e/m_2)^2.$$

In Fig. 4, curve 6 describes the $\tau_p^{PA}(T)$ dependence obtained with the aid of (10) and (15) with substitution of (14) and using the parameters of the table. In the limiting case $Ka \ll 1$, which corresponds to the case of lower temperatures,[1] we have

$$(\tau_p^{PA})^{-1} \approx \frac{\sqrt{2}}{3\pi}\overline{Y}\frac{e^2 m_e}{\hbar^2}\left(\frac{m_2-m_1}{\mu}\right)^2\frac{TE^{\frac{1}{2}}}{\Delta E}, \tag{17}$$

where $\Delta E = \mu e^4/2\hbar^2\varkappa_0^2$. Thus, at low temperatures we obtain $\tau_p^{PA} \sim T^{-5/2}$ for excitons that are in thermodynamic equilibrium with the lattice. In Fig. 4, this dependence corresponds to the line 7 plotted with account taken of (17) and (14). Comparing (10) and (13), we obtain

$$\tau_{pe}^{PA}/\tau_p^{PA} = (m_e/m_1)^{\frac{1}{2}}\mathcal{K}(Ka). \tag{18}$$

At $Ka \ll 1$ we have $\mathcal{K}(Ka) \ll 1$ [see (11)], i.e., the scattering of the excitons is much weaker than the scattering of the electrons. The physical cause of this is obvious: if the wavelength of the lattice vibratations exceeds greatly the exciton radius, the exciton reacts to the piezoelectric field of the lattice as an almost pointlike particle with zero charge and zero dipole moment. At a certain value of the parameter Ka, of the order of unity, the factor $\mathcal{K}(Ka)$ reaches a maximum of the order of unity, and relation (18) can even exceed unity somewhat, as is in the fact case for CdS (see Fig. 4), since $(m_e/m_1)^{1/2} \approx 2.46$. With further increase of the parameter Ka, the value of $\mathcal{K}(Ka)$ again begins to decrease. However, the region $Ka \gg 1$ corresponds to relatively high temperatures such that the interaction of the excitons with the LO vibrations of the lattice predominates.

The exciton-momentum-relaxation time τ_p^{DA} due to the action of the deformation potentials was first calculated in Ref. 10. The value obtained for the condition $Ka \ll 1$ was

$$(\tau_p^{DA})^{-1} \approx \frac{\sqrt{2}(E_1-E_2)^2 Tm_e^{\frac{1}{2}}E^{\frac{1}{2}}}{\pi\rho v_l^2\hbar^4}, \tag{19}$$

where E_1 and E_2 are the constants of the deformation potential for the electrons and holes, and v_l is the speed of the longitudinal sound. The line 8 in Fig. 4 corresponds to the results (19) with substitution of (14) (see the table). Equation (19) is applicable in the case of low temperatures (see footnote 1). It is possible in principle to determine the exact

$\tau_p^{DA}(T)$ dependence for any temperature, but this calls for knowledge of the values of E_1 and E_2 separately, and not only of the modulus $|E_1 - E_2|$, which enters in (19). To our knowledge, the constants E_1 and E_2 have not been determined experimentally to this day. In addition, the construction of the exact plot of $\tau_p^{DA}(T)$ is not essential, since the action of the piezoelectric fields on the exciton is much stronger in the entire temperature region where scattering by acoustic phonons predominates (compare line 8 and the curve 6 in Fig. 4).

It is important to emphasize that when calculating the exciton momentum relaxation time it is necessary, generally speaking, to take into account not only the process of exciton scattering without change of their internal state (analogous to the processes of scattering of electrons and holes), but also decay processes, i.e., transitions of excitons into states belonging to the continuous energy spectrum, as well as processes of scattering with transition into the excited states of the discrete spectrum. Just as the scattering of the exciton as a whole, transitions with change of the internal state lead to relaxation of the exciton momentum, since they are accompanied by absorption or emission of acoustic[8,11,12] or optical[13-15] phonons.

Decay by the action of acoustic phonons is possible only under the condition $E \gg \Delta E$, inasmuch as in exciton decay, just as in scattering by A phonons, the energy transferred to the exciton from the lattice vibrations is very low. The condition $T \gg \Delta E$ for CdS means $T \gg 325$ K. At such temperatures, the interaction of excitons with LO photons predominates (see below), so that decay processes due to interaction with A phonons are inessential in our case.

For scattering by A-phonons with transition of the excitons into excited states, the energy threshold[12] is somewhat lower $(E \gg (3/4)\Delta E)$, but in the case of CdS it also corresponds to the temperature regions where the interaction with the A phonons is not at all significant.

Let us calculate the relaxation time τ_p^{LO} of the excitons as they interact with longitudinal optical (LO) lattice vibrations. The scattering of an exciton by LO phonons was first considered in Ref. 16. In Ref. 17, when calculating the probability of exciton scattering by LO phonons use was made of the Fröhlich interaction[18] and the case considered as $\Delta E \gg \hbar\omega_{LO}$, where ω_{LO} is the maximum frequency of the long-wave LO vibrations. We use the results of Ref. 15, where the probabilities of scattering and decay of excitons on LO phonons were calculated at arbitrary temperatures and at an arbitrary ratio of $\hbar\omega_{LO}$ to ΔE. For the probability of scattering with absorption of an LO phonon we have[15]

$$W_a^{LO} = \frac{\alpha_e\omega_{LO}}{2\zeta^{\frac{1}{2}}}N_0\varphi(\lambda,\beta)\,|_{\lambda-(\zeta)}^{\lambda+(\zeta)} \tag{20}$$

where

$$\alpha_e = \frac{e^2}{2\hbar\omega_{LO}l_e}(\varkappa_\infty^{-1} - \varkappa_0^{-1}) \tag{21}$$

is the coupling constant of the excitons with the LO phonons, $\varkappa_\infty$ is the high-frequency dielectric constant, $l_e = (\hbar/2m_e\omega_{LO})^{1/2}$ is the characteristic length, which can be treated as the reciprocal wave vector of an exciton with kinetic ener-

gy $E = \hbar\omega_{LO}$,

$$\zeta = E/\hbar\omega_{LO}, \quad N_0 = (e^{\hbar\omega_{LO}/T} - 1)^{-1},$$

$$\lambda_{\pm}(\zeta) = \Lambda(\zeta^{1/2} \pm (\zeta+1)^{1/2})^2,$$

$$\Lambda = \frac{m_1 \hbar\omega_{LO}}{4m_2 \Delta E}, \quad \beta = (m_2/m_1)^2,$$

and $\varphi(\lambda,\beta)$ is a function defined in Ref. 13. Curve 4 of Fig. 4 describes the dependence of $(W_s^{LO})^{-1}$ on T in accordance with (20), with substitution of (14) and using the data in the table. For the case of low temperatures

$$T \ll \hbar\omega_{LO}, \tag{22}$$

we obtain from (20)

$$W_s^{LO} \approx 2\alpha_e \omega_{LO} e^{-\hbar\omega_{LO}/T} F(a/2l_e). \tag{23}$$

At temperatures (22) we have for electrons and holes[18]

$$W_{sj}^{LO} = 2\alpha_j \omega_{LO} e^{-\hbar\omega_{LO}/T}; \quad j=1, 2, \tag{24}$$

where α_j is the Fröhlich constant for the electrons or holes and differs from α_e (21) in that m_e is replaced by m_j. The quantity F in (23) depends on the parameters m_2/m_1 and $a/2l_e = (m_e\hbar\omega_{LO}/4\mu\Delta E)^{1/2}$. At temperatures (22), the wave vector of the LO phonons that interacts with the excitons lies in a narrow interval near l_e^{-1} (Ref. 15). Therefore the parameter $a/2l_e$ is of the order of the ratio of the exciton radius to the wavelength of the LO phonon that interacts with the exciton. If $m_2 \approx m_1$ or $a/2l_e \ll 1$, we get $F \ll 1$ because the action of the electric field produced by the LO vibrations on the electron is almost completely cancelled by the action of the same field on the hole.[2)] In the case of CdS, however, the values of m_1 and m_2 differ strongly enough, and the parameter $a/2l_e \approx 1.56$, so that F is of the order of unity. Using the table, we find $F = 0.545$. Curve 1 of Fig. 4 is a plot of $(W_s^{LO})^{-1}$ vs T in accordance with the approximate formula (23). Comparing the theoretical curves 4 and 1, we see that the approximate expression for the case of low temperatures describes well the dependence of $(W_s^{LO})^{-1}$ on T up to 300 K, where $T/\hbar\omega_{LO} \approx 0.67$, and

$$\zeta = E/\hbar\omega_{LO} \approx 3T/2\hbar\omega_{LO} \sim 1.$$

It is shown in Fig. 18 that at the value of T from (22) the arrival processes do not influence the electron relaxation time τ_{pe}^{LO} i.e., that $\tau_{pe}^{LO} = (W_{s1}^{LO})^{-1}$ apart from small corrections (a similar result was essentially obtained even earlier in Ref. 19). The same proof of the small influence of the arrival processes is valid also in the case of exciton scattering at the value of T from (22). Since the approximation (23) yields good results in the entire investigated temperature range, we assume that the arrival processes, which are the inverse of the scattering of the exciton as a whole, have little effect on τ_p^{LO} at $T \leqslant 300$ K.

In the calculation of τ_p^{LO} it is necessary to take into account the exciton-decay processes.[15] We shall assume (without proof) that the arrival processes, inverse to decay (i.e., binding of electrons and holes into excitons), have likewise little effect on τ_p^{LO}, just as the arival processes inverse to exciton scattering as a whole. We therefore assume

$$(\tau_p^{LO})^{-1} \approx W_s^{LO} + W_d^{LO}, \tag{25}$$

where W_d^{LO} is the probability of the transition of an exciton from the ground state $n = 1$ to states belonging to the continuous energy spectrum of the relative motion of the electrons and holes. In the right-hand side of (25) we have discarded the sum $\Sigma_{n>2} W^{(n)}$, where $W^{(n)}$ is the probability of exciton scattering with transition from the ground state ($n = 1$) into an excited state ($n = 2,3,...$) belonging to the discrete spectrum of the internal energy of the exciton (see Refs. 12 and 14). We assume that the discarded sum is small compared with $W_s^{LO} + W_d^{LO}$ (cf. the results obtained in Ref. 14 for the case $m_2/m_1 = 5$, which pertains to transmissions with emission of LO phonons). By disregarding in the right-hand side of (25) the probabilities of scattering with transitions into excited states of the discrete spectrum, we overestimate somewhat the theoretical values of τ_p.

In Ref. 15 there was obtained the expression

$$W_d^{LO} = \alpha_e \omega_{LO} N_0 w_1^{abs}(\zeta), \tag{26}$$

where $w_1^{abs}(\zeta)$ is expressed in the form of a sum of double and triple integrals (the latter corresponds to the interference contribution to W_d^{LO}). Since these integrals were not accurately calculated for the values of ζ in the interval from 0 to 1 (this can apparently be done only with a computer), the probability W_d^{LO} as a function of T was determined theoretically less accurately than $W_s^{LO}(T)$. To estimate the integrals we used an approximation that is valid at $\zeta \ll 1$. In the upshot we obtain the result for CdS

$$W_d^{LO} \approx 0.92\alpha_e \omega_{LO} (e^{\hbar\omega_{LO}/T} - 1)^{-1}, \tag{27}$$

corresponding to curves 3 of Fig. 4.

Summing the contributions of the scattering (20) and the decay (27), we obtain curve 2 of Fig. 4. Finally, curve 9 of Fig. 4 describes the resultant theoretical temperature dependence of τ_p with allowance for scattering (due to piezoelectric fields) by A phonons, and for scattering and decay on LO phonons, i.e., the quantities

$$\tau_p = [(\tau_p^{PA})^{-1} + (\tau_p^{LO})^{-1}]^{-1}, \tag{28}$$

with $(\tau_p^{PA})^{-1}$ calculated in accordance with (10) and $(\tau_p^{LO})^{-1}$ in accordance with (25) using (20) and (27).

Scattering of excitons by charged impurities yields the following contribution to the reciprocal exciton momentum relaxation time, calculated in the Born approximation:

$$(\tau_p^N)^{-1} = \frac{2\pi Ne^4 E^{-3/2}}{\varkappa_0^2 \sqrt{2m_e}} \int_0^1 dy \frac{y^3 F(Kay)}{[y^2 + (2Kr_0)^{-2}]^2}, \tag{29}$$

where N is the impurity density, $r_0 = (\varkappa_0 T/4\pi n_0 e^2)^{1/2}$ is the screening radius, n_0 is the carrier density, and $F(z)$ the function defined in (12). The density of the charged impurities in the investigated samples apparently does not exceed $N = 10^{15}$ cm^{-3}. If we put $n_0 = N = 10^{15}$ cm^{-3}, the parameter that characterizes the degree of screening of the charged impurities is $(2Kr_0)^{-2} \ll 1$ even at 10 K, so that the screening can be neglected. In the limiting case of low temperature under the conditions $Ka \ll 1$ (see footnote 2), we obtain from

(29)

$$(\tau_p{}^N)^{-1} \approx \frac{2\pi N e^4 E^{1/2}}{\varkappa_0{}^2 (2m_e)^{1/2}(\Delta E)^2}\left(\frac{m_1-m_2}{\mu}\right)^2. \qquad (30)$$

Substituting (14) and using $N = 10^{15}$ cm^{-3} and the data in the table, we obtain at 10 K, according to (29), $\tau_p^N \approx 3.3 \cdot 10^{-11}$ sec. Thus, owing to the cancellation of the interactions of the electrons and the holes that make up the excitons by the charged centers, the exciton scattering by the impurities becomes considerably weaker precisely at low temperatures, where the interaction of the carriers with the charged impurities can be substantial. Since the quantity $\tau_p^N \approx 3.3 \cdot 10^{-11}$ sec exceeds the experimental value of τ_p at 10 K, we conclude that the interaction of the excitons with the impurities does not influence significantly $\tau_p(T)$ in the investigated CdS samples.

4. DETERMINATION OF THE CROSS SECTION FOR BINDING ELECTRONS AND HOLES INTO EXCITONS

At sufficiently high temperatures, when the exciton decay probability exceeds their reciprocal lifetime, a thermodynamic equilibrium is established in the crystal between the systems of the excitons and the free electrons and holes. Under equilibrium conditions, the following relation is valid[3]

$$\sigma = \frac{(2\pi)^{1/2}\hbar^3 W_d}{3^{1/2}\mu T^2}e^{\Delta E/T}, \qquad (31)$$

where σ is the mean-temperature cross section for binding of electrons and holes into excitons. Using the experimental data for W_d, we determine in accordance with (31) the binding cross sections as functions of temperature.

The experimental values W_d^{exp} are obtained by subtracting from the experimentally obtained $(\tau_p^{-1})^{exp}$ the theoretically calculated contributions of the scattering processes, i.e.,

$$W_d{}^{exp} = (\tau_p{}^{-1})^{exp} - \tau_{ps}{}^{-1}, \quad \tau_{ps}{}^{-1} = (\tau_p{}^{PA})^{-1} + (\tau_{ps}{}^{LO})^{-1},$$

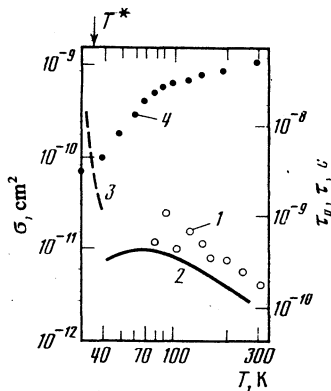where $(\tau_p^{PA})^{-1}$ is defined in (10), and $(\tau_{ps}^{LO})^{-1} = W_s^{LO}$ is defined in (20). The experimental $\sigma(T)$ dependence is shown by curve 1 of Fig. 5. It was plotted for the temperature range from 80 to 300 K, inasmuch as at lower temperatures the contributions of the decay processes to the total value of τ_p^{-1} are small (see Figs. 3 and 4) and cannot be separated. The theoretical curve 2 of Fig. 5 is a plot of Eq. (31), in the right-hand side of which we substituted the theoretical values of W_d^{LO} calculated in accordance with (27).

We note that expression (31) with substitution (27) describes the cross section for binding accompanied by emission of an LO phonon, since this process is the inverse of decay with absorption of an LO phonons. Since $W_d \propto N_0$, the right-hand side of (31), following substitution of (27), is proportional to

$$N_0 \exp (\Delta E/T) = (N_0+1)\exp [-(\hbar\omega_{LO}-\Delta E)/T],$$

which corresponds to the mean-temperature probability of binding with emission of an LO phonon, which has an energy threshold $E \geqslant \hbar\omega_{LO} - \Delta E$ (Ref. 20). Thus, the theoretical curve 2, which has a maximum, corresponds to the temperature dependence

$$\sigma \infty T^{-2}(N_0+1)\exp\left(-\frac{\hbar\omega_{LO}-\Delta E}{T}\right). \qquad (32)$$

The contribution of processes of binding with emission or absorption of A phonons to σ is relatively small, at any rate in the interval from 80 to 300 K, and possibly also at lower temperatures. Binding into an exciton in the case of interaction with A phonons calls for multiple interaction until the pair energy becomes lower than T (Ref. 21). This process is effective in materials with low energy of carrier binding into an exciton (for example, in Ge, Ref. 22). If the binding energy is such that

$$\hbar\omega_{LO} - T \approx \Delta E/n^2,$$

$n = 1,2,...$ (as in the case of CdS), the interaction with the LO phonons becomes decisive in the carrier binding into an exciton. A similar picture is apparently typical also of the situation where an electron is trapped by a deep attracting center, with emission of an optical phonon.[23] The reason is the following.

The interaction of excitons with LO phonons in CdS is very strong, since $\alpha_e \approx 1.24$; the exciton radius is comparable with the wavelength of the absorbed phonons, and the difference $\hbar\omega_{LO} - \Delta E$ is small—it corresponds to a temperature 116 K. Scattering of excitons by A phonons can predominate only at temperatures so low that the number of LO phonons is exponentially small (see Figs. 3 and 4). In the case of binding of electrons and holes on LO phonons, however, the factor

$$\exp(-\hbar\omega_{LO}/T)$$

is replaced by the factor

$$\exp[-(\hbar\omega_{LO}-\Delta E)/T]$$

[see (32)], therefore the limiting temperature, cooling to which makes the interaction with the A phonons substantial, is lower for binding processes than for exciton-scattering processes.

FIG. 5. Dependence of the cross section for binding of free carriers into an exciton on the temperature: 1) experimental values of σ; 2) theoretical $\sigma(T)$ dependence; 3) lifetime of exciton relative to its decay into a free electron and a free hole upon absorption of an LO phonons (27); 4) experimental dependence of the lifetime τ of an exciton on the temperature, T^*) boundary of temperature region $T > T^*$ in which the conditions of thermodynamic equilibrium is satisfied for the process of binding of free carriers into an exciton.

5. DISCUSSION OF RESULTS AND CONCLUSIONS

We proceed now to compare the theoretical results of Sec. 3 with the results of investigations of nonstationary diffusion of excitons in CdS at temperatures 10–300 K. The theoretical calculations show that in this temperature region, in sufficiently pure crystals, the main contribution to the exciton-momentum relaxation processes is made by the interaction with the phonons (acoustic and optical). In the region $T < 60$ K, as shown by results of the theoretical analysis, the most effective relaxation mechanism is scattering by acoustic phonons, due to the piezoelectric interaction of the excitons and phonons. At temperatures 60 K $< T < 130$ K, a characteristic region is observed, in which a mixed mechanism of scattering by piezoacoustic and optical phonons is realized. In the region $T > 130$ K, interaction of excitons with LO phonons predominates, and the scattering of the excitons as a whole and their decay give approximately equal contributions to τ_p^{-1}. Calculation of the contribution of the deformation interaction to the probability of exciton scattering by A phonons has shown that this contribution is small compared with the contribution of the piezoelectric interaction in the temperature interval from 10 to 300 K.

Comparing the interactions of the excitons with the phonons with analogous processes for free carriers (electrons and holes) we find that the former have distinctive features. First, allowance for the internal structure of the electrons calls for an analysis of the possibility of its decay when interacting with LO phonons. Second, the finite size of the exciton as a particle leads to a different temperature dependence in the limit of low and high temperatures for the scattering by A phonons. The analysis of these interaction processes leads to the resultant theoretical $\tau_p(T)$ curve shown in Fig. 3. As can be seen from a comparison of the experimental data with this curve, the agreement is on the whole satisfactory both for the functional dependence $\tau_p(T)$ and quantitative agreement of the results of the theory and the experiment. It must be emphasized that, as can be seen from (10), (20), and (27), this agreement was obtained without using any adjustable parameter (all the necessary parameters of the samples were determined directly in experiments, see the table). It is of interest to compare the results of investigations of the temperature dependence of the electron mobility in n-CdS (Refs. 5, 6) with the corresponding results for excitons. As seen from Fig. 4, at low temperatures the value of τ_p for excitons depends on the temperature like $T^{-5/2}$ (for electrons, like $T^{-1/2}$), this being due to the increase of the wavelength of the phonons interacting with the exciton when the temperature is lowered, and to the cancellation of the polar character of the interaction with the acoustic phonons (interaction via the piezoelectric field). In the region $T \geqslant 30$ K, the $\tau_p(T)$ dependence for excitons approaches that for electrons; at $T > 130$ K its character is determined by the interaction with the LO phonons [$\tau_p \propto \exp(\hbar\omega_{LO}/T)$]. It must be noted that at high temperatures, the experimental values of τ_p for the excitons are somewhat lower than the corresponding values of τ_{pe} for electrons (see Fig. 3), in agreement with the prediction of the theory. Indeed, comparing Eq. (23) for excitons with expression (24) from Ref. 18 for electrons and

holes, and using the data of the table, we have

$$W_s^{LO}/W_{sj}^{LO} = 0.545\,(m_e/m_j)^{1/2}. \qquad (33)$$

It can be seen from (33) that scattering of excitons by LO phonons is somewhat more effective than scattering of electrons, and is somewhat less effective than scattering of holes (the contribution of the exciton decay on LO phonons to τ_p^{-1} should even strengthen the inequality $\tau_p < \tau_{pe}$). From the comparison of the experimental $\tau_p(T)$ dependence with the theoretical one it can also be concluded that in interaction with LO phonons allowance for exciton decay into free electrons and holes is also important. The fact that the best agreement between theory and experiment is realized precisely when account is taken of both scattering of the exciton as a whole and of its decay leads to the conclusion that the two exciton-momentum scattering processes make approximately equal contributions to τ_p^{-1}.

Analysis of the experimental and theoretical data for CdS, carried out in Sec. 4, allows us to estimate, in order of magnitude, the cross section for binding electrons and holes into excitons in the temperature interval from 80 to 300 K (see Fig. 5); this cross section turns out to be quite appreciable $(\sigma \sim 10^{-11}$ cm^2 at 80 K, which is comparable with the corresponding data of Refs. 24 and 25). It makes it also possible to show that the predominant contribution to the cross section is made by binding processes with participation of LO phonons, at least in this temperature region.

---

[1] The parameter $Ka = (Em_e/\Delta E\mu)^{1/2}$, where ΔE is the binding energy of the exciton in the ground state. Since in the case of CdS we have the ratio $m_e/\mu \approx 7.2$, the condition $Ka \lesssim 1$ corresponds to the requirement $T \lesssim 30$ K.

[2] In Ref. 17 is considered the case $a/l_c \ll 1$, so that according to that reference the probability of exciton scattering by LO phonons is less the probability of scattering by LA phonons.

[3] In the derivation of (31) we did not take into account the transition of excitons into excited states of the discrete spectrum and their inverse transitions from excited states to the ground state. It appears that these probabilities are small compared with the decay probability (see Refs. 12 and 14).

---

[1] V. M. Agranovich and M. D. Galanin, Transfer of Electronic Excitation Energy in Condensed Medial [in Russian], Nauka, 1978.

[2] M. A. Tamor and J. P. Wolfe, Phys. Rev. Lett. 44, 1703 (1980). J. P. Wolfe, Physics Today, No. 3, 46 (1982).

[3] E. Gutsche and J. Voigt, Proc. Int. Conf. on II–VI Semicond., D. G. Thomas, ed., Benjamin, 1967, p. 337.

[4] N. N. Zinov'ev, L. P. Ivanov, V. Il. Kozub, and I. D. Yaroshetskiĭ, Zh. Eksp. Teor. Fiz. 84, 1761 (1983) [Sov. Phys. JETP 57, 1027 (1983)].

[5] W. W. Piper and R. E. Holsted, Proc. Intern. Conf. Semicond. Phys. Prague, 1960, p. 1046.

[6] H. Fujita, A. Kobayashi, and T. Kawai, J. Phys. Soc. Jpn. 20, 109 (165).

[7] A. P. Hutson, Conf. on Semicond. Comp., Suppl. J. Appl. Phys. 32, 2287 (1961).

[8] C. Trallero Giner, L. I. Korovin, and S. T. Pavlov, Fiz. Tverd. Tela (Leningrad) 19, 3414 (1977) [Sov. Phys. Solid State 19, 1994 (1977)].

[9] A. I. Ansel'm, Introduction to the Theory of Semiconductors [in Russian], Nauka, 1978.

[10] A. I. Ansel'm and Yu. A. Firsov, Zh. Eksp. Teor. Fiz. 29, 151 (1955) [Sov. Phys. JETP 2, 143 (1956)].

[11] A. A. Lipnik, Fiz. Tverd. Tela (Leningrad 1, 726 (1959); 2, 2044 (1960); 3, 2322 (1961); 6, 1068 (1964) [Sov. Phys. Solid State 1, 661 (1959); 2, 1835 (1961); 3, 1683 (1962); 6, 823 (1964)].

[12]C. Trallero Giner, I. G. Lang, and S. T. Pavlov, Fiz. Tekh. Poluprov. **14**, 235 (1980) [Sov. Phys. Semicond. **14**, 138 (1980)].

[13]K. A. Aristova, C. Trallero Giner, I. G. Lang and S. T. Pavlov, Phys. Stat. Sol. (b) **85**, 351 (1978).

[14]C. Trallero Giner, I. G. Lang, and S. T. Pavlov, Fiz. Tverd. Tela (Leningrad) **21**, 2028 (1979) [Sov. Phys. Solid State **21**, 1544 (1979)].

[15]C. Trallero Giner, O. Soto-Longo Costa, I. G. Lang, and S. T. Pavlov, Fiz. Tverd. Tela (Leningrad) **24**, 2724 (1982) [Sov. Phys. Solid State **24**, 1544 (1982)].

[16]A. I. Ansel'm and Yu. A. Firsov, Zh. Eksp. Teor. Fiz. **30**, 719 (1956) [Sov. Phys. JETP **3**, 564 (1956)].

[17]T. Toyozawa, Progr. Theor. Phys. **53**, 20 (1958).

[18]H. Fröhlich, Adv. Phys. **3**, 325 (1954).

[19]B. Davydov and I. Shmushkevich, Zh. Eksp. Teor. Fiz. **10**, 1043 (1940).

[20]R. P. Alvares, C. Trallero Giner, I. G. Lang, and S. T. Pavlov, Fiz. Tverd. Tela (Leningrad) **21**, 2685 (1979) [Sov. Phys. Solid State **21**, 1544 (1979)].

[21]V. N. Abakumov, V. I. Perel', and I. N. Yassievich, Zh. Eksp. Teor. Fiz. **78**, 1240 (1980) [Sov. Phys. JETP **51**, 626 (1980)].

[22]E. M. Gershenzon, Gol'tsman V. V. Multanovskiĭ, and N. G. Ptitsyna, Pis'ma Zh. Eksp. Teor. Fiz. **33**, 590 (1981) [JETP Lett. **33**, 574 (1981)].

[23]V. N. Abakumov, Fiz. Tekh. Poluprov. **13**, 59 (1979) [Sov. Phys. Semicond. **13**, 34 (1979)].

[24]V. F. Grin', Ea. A. Sal'kov, and V. A. Khvostov, Fiz. Tverd. Tela (Leningrad) **15**, 2694 (1973) [Sov. Phys. Solid State **15**, 1792 (1974)].

[25]V. L. Broude, N. N. Tartakovskiĭ, and V. B. Timofeev, Fiz. Tverd. Tela (Leningrad) **14**, 3531 (1972) [Sov. Phys. Solid State **14**, 2971 (1973)].

[26]J. J. Hopfield and D. G. Thomas, Phys. Rev. **122**, 35 (1961).

[27]M. Balkanski, in: Optical Properties of Solids, F. Abeles, ed., Amsterdam, 1972.

[28]D. L. Rode, Semiconductors and Semimetals, Academic, 1975.

[29]J. E. Rowe, M. Cardona, and F. H. Pollak, Proc. Int. Conf. II–VI Semicond. Compounds, D. G. Thomas, ed., Providence, 1967, p. 112.

[30]D. Berlincourt, H. Jaffe, and L. R. Shiozawa, Phys. Rev. **129**, 1009 (1963). Sprav. Khimika (Chemist's Handbook), Vol. 2, Basic Properties of Inorganic and Organic Compounds. TITIKhL, 1963, p. 78.

[31]C. B. a la Guillaume, J. M. Debever, and F. Salvan, Phys. Rev. **117**, 567 (1969). J. F. Scott, T. C. Damen, R. C. C. Leite, and J. Shan, Phys. Rev. **B1**, 4330 (1970).

Translated by J. G. Adashko