Photoluminescence spectrum in plastically deformed semiconductors and electronic states in dissociated dislocations

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An analysis of the features of the photoluminescence spectra of plastically deformed crystals of Ge and Si provides a basis for a physical picture of the emission process as the recombination of excitons bound to dissociated dislocations. These act on electrons through periodic potentials along the dislocation lines and potentials localized in the transverse directions, as well as through the potential of the packing defect, which is localized in the plane of the latter. Equations for determining the energies of the bound states are derived, and a modified version of the Koster–Slater approximation, which permits the use of the effective-mass approximation in the analysis of deep levels, is proposed. The situation for the case of the d series in Ge, which contains 13 clearly distinguishable lines and a short-wavelength limit in the emission spectrum, is examined. An alternative description of a bound state, which the roots of the dispersion equation for excitonic energies can be successfully reconciled with all the energies of the d lines in Ge using two fitting parameters (there is an independent experimental estimate for one of them), is proposed. The possibilities of revealing the one-dimensional details of the electronic states are discussed. © *1995 American Institute of Physics.*

1. INTRODUCTION

The photoluminescence of plastically deformed samples of silicon and germanium (dislocation photoluminescence) is characterized by a rich emission spectrum having several interesting features. The lines in this spectrum cover a broad range of frequencies and are very bright for the case of emission in indirect-gap semiconductors. Mechanical action and thermal treatment make it possible to significantly alter dislocation photoluminescence. It then becomes possible to purposefully order the dislocation structure and to promote the display of specific properties of one-dimensional electronic states belonging to long straight segments of dislocations. A large amount of experimental data has been accumulated, so that the physical picture of dislocation photoluminescence can be described in great detail and a description of the electronic states which are bound to dislocations and participate in the corresponding optical transitions can be proposed.

Investigations of the luminescence of silicon and germanium crystals subjected to a two-step deformation procedure (during which fairly extensive portions of the dislocation line are straightened in the second step[1]) revealed the fine structure of the known broad dislocation photoluminescence bands[2,3] appearing after the first deformation step. It was discovered that the dislocation photoluminescence spectra consist of a set of narrow lines.[4-6] The experiments showed that individual lines and even whole groups of lines can be caused to appear or disappear by varying the deformation conditions, as well as by annealing. It is significant that the spectral positions of the observed dislocation photoluminescence lines practically never changed. The superposition of dislocation photoluminescence spectra obtained under differ-

ent conditions makes it possible to obtain a rich set of lines and reveals bunching and convergence at a limiting emission energy on the short-wavelength side. It was also shown (for the dislocation photoluminescence in Ge) that the intensities of the lines from this set depend in approximately the same manner on the excitation level and on the temperature.

The data obtained provide some basis to regard the entire set of dislocation photoluminescence lines as the result of a series of transitions between quantum states of a common physical nature. In the investigation of the dislocation photoluminescence in Si in Ref. 4, the individual lines were numbered with integers, it was postulated that radiative transitions of pairs of point centers participate in the processes, and the distance between the centers in such pairs was proposed as the discrete parameter influencing the spectral frequency of the radiation. The thorough investigations of the dislocation photoluminescence in Ge crystals in Refs. 7 and 8 led to a more detailed picture of the origin of the spectral series. The importance of the dissociation of dislocations into partial dislocations (or partials) separated by packing defects with a set of discrete widths

$$R_\nu = a_\perp \nu \qquad (1.1)$$

(ν are integers, and $a_\perp$ is an elementary step in the glide plane in the direction perpendicular to the dislocation lines) was revealed. Actual direct experimental evidence of this was obtained in Ref. 8 by applying a specially oriented additional load, which caused either an increase or a decrease in the dissociation of the dislocations producing mostly short-wavelength or long-wavelength regions of the dislocation photoluminescence spectrum, respectively. The simulta-

neous appearance of several lines should thus be a consequence of the presence of several different dissociation widths in the collection of dislocations.

If we accept the established fact that the packing-defect width (1.1) has a decisive influence on the position of the emission lines, we can move forward in ascertaining the nature of dislocation photoluminescence. First of all, this fact means that at least one of the states participating in each optical transition is essentially bound to a dissociated dislocation and forms under the action of a potential which depends on R_ν. There are experimental data indicating the insensitivity of dislocation photoluminescence spectra to doping with various impurities.[7] Therefore, it may be assumed that the local potentials are created by the dislocations themselves, i.e., by the structural differences in the arrangement of the atoms in the dislocation cores from the position in an ideal lattice. In such a case potentials which are periodic along the dislocation lines and are localized in the transverse directions should be assigned to the straight segments. The isolated point centers can be associated with features on the dislocation lines themselves (jogs, kinks, intersections). An arrangement of these features in pairs on the two lines of a dissociated dislocation with separation width (1.1), i.e., along a perpendicular to the direction of the dislocation lines, was not identified among the other possible relative positions; therefore, the observed dislocation photoluminescence spectral series should most probably not be attributed to point centers. In this paper we shall discuss the situation in which dislocations create a potential which is extended along their lines and localized transversely to them.[1)]

The spectral composition of the dislocation photoluminescence makes it possible to draw some conclusions which pertain to the nature of the radiative transition and the degree of influence of the dislocation potential on the binding of carriers and are important for formulating the physical picture. The convergence of the series at a short-wavelength limit as the dissociation width of the dislocations increases points out the recombinational nature of the luminescence. In fact, when there is a two-center potential, the lowest energy level of the bound states determined by it should become deeper with increasing R_ν, so that the spectral line corresponding to the radiative capture of a carrier from a band state in that level should be shifted to a longer wavelength. In the case of the recombination of a carrier trapped in a dislocation with, for example, a band carrier of opposite sign, the progression of lines for increasing values of R_ν will correspond to the experimentally observed progression. In this case the recombination picture can also be detailed. It is assumed that a potential which is periodic along a dislocation line allows the formation of a one-dimensional electronic band (several experimental observations shows that this happens). Optical transitions between band states should produce broad (relative to the width of these bands) bands with corresponding energy thresholds. Nevertheless, the dislocation photoluminescence spectra of Ge and Si consist of narrow (~ 1 meV) lines. To explain this fact, it is natural to call upon the properties of radiative exciton recombination and to examine the case of the excitonic binding of an electron and a hole under conditions such that at least one of these particles is trapped in a level of the dislocation potential (a dislocation exciton).[2)] Here it is important to stress that the energy position of the state under consideration must be determined mainly by the dislocation potential. In fact, the pure excitonic (Coulomb) interaction in atomic semiconductors is weak (the binding energy is far smaller than the width of the band gap E_g). At the same time, under the proposed scheme of a recombinational emission process, the frequencies of the dislocation photoluminescence lines correspond to liberation of the binding energy, which is fully noticeable on the scale of E_g. The bulk of this energy should, therefore, be utilized for dislocation binding and should correspond to fairly deep dislocation levels.

We next note that the differences in the recombination energies of the successive lines in a series are considerable, from a few to tens of meV.[7] This means that the binding power of the dislocation potential varies appreciably when R_ν varies by a unit step and that these changes occur over a great range of distances. Therefore, when the energy level is deep, the electron cloud should span the two partials and penetrate through extensive portions of the packing defect. This combination of dislocation wells of considerable depth and easy tunneling between them attests to the highly localized nature of the potentials. Consequently, the expanse of the wave function should be determined mainly by the behavior of its asymptote beyond the range of influence of the potential and, in principle, can be considerable.

The physical conclusions following from the foregoing analysis of the experimental data were used in this study to construct a theoretical model of dislocation luminescence. It is assumed that the potentials acting near dislocations are localized in directions transverse to their axes and form the deep states of the carriers trapped in them. The potential of a packing defect, which can facilitate transitions between states in the separate wells (for example, by lowering the obstacle between the holes under which tunneling must occur) and enhance the dependence of the energy level on the dissociation of the dislocations into partials, can also be utilized. A carrier trapped by such a field also interacts with a band carrier of opposite sign, forming an exciton, which is localized transversely to the dislocation lines and free along them. The excitonic binding is assumed to be far stronger than the binding with the local potential; therefore, the analysis refers mainly to the one-particle states at the dislocations. Here we employ the known approach to the problem of deep levels based on a zero-radius potential,[10,11] in which the potentials are not specifically modelled, the corresponding matrix elements are assigned phenomenologically, and the binding energies are taken from experiment. In our case, owing to the appearance of a whole series of energy levels in the dislocation photoluminescence spectra, there is an additional possibility for a theoretical analysis, which is significant in our opinion: a comparison of the dispersion equations specifying the energies of the electronic states for a fixed packing-defect width and infinite dissociation lines (the point of convergence of the dislocation photoluminescence series) permits the use of a calculation scheme in which the effective-mass approximation is permissible (in a deep-level problem). As is shown below, in the case of the dislocation

photoluminescence in Ge crystals, a fairly simple alternative can be chosen, in which the entire set of experimentally observed dislocation photoluminescence lines forming the spectral series can be reconciled with the results of the calculations with good accuracy using a minimal number of phenomenological parameters.

2. DESCRIPTION OF THE STATE OF AN ELECTRON BOUND TO A DISLOCATION

We begin by posing a specific one-electron problem. We consider the case in which a long straight segment of a complete dislocation line parallel to the $[1\bar{1}0]$ direction is split by a (111) glide plane into two partials separated from one another along the $[11\bar{2}]$ direction by the packing-defect width R_ν (1.1). We assume that this entire structural defect (the two partials and the packing defect) supplements the crystal potential of the ideal lattice with an additional potential having a fairly small radius of action (on the order of the lattice constant), which is capable of creating deep local levels in the band gap. We write this part of the defect potential in the form

$$V(\mathbf{r}) = V_{1d}(\mathbf{r}) + V_{2d}(\mathbf{r}) + V_s(\mathbf{r}) = \sum_{l_\zeta} \left[v_{1d}(\mathbf{r} - \mathbf{R}_{00l_\zeta}) \right.$$

$$\left. + v_{2d}(\mathbf{r} - \mathbf{R}_{0\nu l_\zeta}) + \sum_{l_\eta} v_s(\mathbf{r} - \mathbf{R}_{0l_\eta l_\zeta}) \right], \quad (2.1)$$

where $\mathbf{R}_{l_\xi l_\eta l_\zeta}$ denotes the coordinates of the centers of the individual potentials, which are distributed periodically along the dislocation lines (v_{1d} and v_{2d}) and in the plane of the packing defect (v_s). The unit vectors taken are the directions

$$\xi = [111], \quad \eta = [\bar{1}\bar{1}2], \quad \zeta = [1\bar{1}0], \quad (2.2)$$

and l_α are integer indices. The smooth parts of the potential of the defect (the deformation potentials, etc.) are omitted. We use (2.1) in the Schrödinger equation

$$[\hat{H}_0(\mathbf{r}) + V(\mathbf{r})]\Psi_d(\mathbf{r}) = E_d \Psi_d(\mathbf{r}) \quad (2.3)$$

and expand the Ψ function in the complete system of Bloch functions corresponding to the Hamiltonian $\hat{H}_0$:

$$\hat{H}_0 \psi_{\mathbf{k}q}^n = \varepsilon_{\mathbf{k}q}^n \psi_{\mathbf{k}q}^n, \quad \psi_{\mathbf{k}q}^n(r) = \frac{e^{i(\mathbf{k}\mathbf{r}+q\zeta)}}{\sqrt{\Omega}} u_{\mathbf{k}q}^n(\mathbf{r}),$$

$$\Psi_d(\mathbf{r}) = \sum_{n\mathbf{k}q} C_{\mathbf{k}q}^n \psi_{\mathbf{k}q}^n(\mathbf{r}), \quad (2.4)$$

(n is the band index, $\mathbf{k}$ is the two-dimensional wave vector in the plane perpendicular to the dislocations, q is the projection of the wave vector onto the dislocation axis ζ, and Ω is the normalized volume). For the coefficients C, which characterize the contribution of the band states $\psi_{\mathbf{k}q}^n$ to the wave function Ψ_d of a state generated by the defect, we have

$$C_{\mathbf{k}q}^n = \frac{1}{E_d - \varepsilon_{\mathbf{k}q}^n} \int d\Omega\, \psi_{\mathbf{k}q}^{n*} V \Psi_d \quad (2.5)$$

or

$$C_{\mathbf{k}q}^n = \frac{\Omega}{(2\pi)^3 (E_d - \varepsilon_{\mathbf{k}q}^n)} \sum_{n_1} \int d^2 k_1 dq_1 C_{\mathbf{k}_1 q_1}^{n_1}$$

$$\times \sum_{l_\zeta} \exp[i(q_1 - q)a_\zeta l_\zeta]$$

$$\times \left[\int_{\Omega_0} d\Omega\, \psi_{\mathbf{k}q}^{n*}(\mathbf{r}) v_{1d}(\mathbf{r}) \psi_{\mathbf{k}_1 q_1}^{n_1}(\mathbf{r}) + \exp[i(\mathbf{k}_1 - \mathbf{k})_\eta R_\nu] \right.$$

$$\times \int_{\Omega_0} d\Omega\, \psi_{\mathbf{k}q}^{n*}(\mathbf{r}) v_{2d}(\mathbf{r}) \psi_{\mathbf{k}_1 q_1}^{n_1}(\mathbf{r}) + \sum_{l_\eta} \exp[i(\mathbf{k}_1$$

$$\left. - \mathbf{k})_\eta a_\eta l_\eta] \int_{\Omega_0} d\Omega\, \psi_{\mathbf{k}q}^{n*}(\mathbf{r}) v_s(\mathbf{r}) \psi_{\mathbf{k}_1 q_1}^{n_1}(\mathbf{r}) \right]. \quad (2.6)$$

In (2.6) a transition has been made from summation to integration over the Brillouin zone, and the integration in the matrix elements is carried out over the volume of the Wigner–Seitz cell Ω_0. For sufficiently long segments of straight dislocations (the lengths actually reach hundreds of interatomic distances) the sum over l_ζ in (2.6) is replaced by $(2\pi/a_\zeta)\delta(q - q_1)$. In this case identical values of the projection of the wave vector onto the ζ axis will appear everywhere in Eq. (2.6), so that q is a quantum parameter of the state. This means that the independent q states with energies $E_d = E_d(q)$ and the wave functions Ψ_{dq}

$$\Psi_{dq}(\mathbf{r}) = \frac{e^{iq\zeta}}{\sqrt{L_\zeta}} \psi_q^d(\mathbf{r}), \quad \psi_q^d(\mathbf{r}) = \sum_{n\mathbf{k}} C_{\mathbf{k}q}^n \frac{e^{i\mathbf{k}\mathbf{r}}}{\sqrt{S_\zeta}} u_{\mathbf{k}q}^n(\mathbf{r}), \quad (2.7)$$

which are individual terms in the sum over q in (2.4) (the functions ψ_q^d are periodic along the ζ axis, L_ζ is the normalized length, and $L_\zeta S_\zeta = \Omega$), should be considered. We replace the function and the sum over l_η in the last term in (2.6) by δ (this approximation is permissible when the packing-defect width is equal to tens of steps; the matching of the phases in the narrower packing defects and the matrix is then somewhat overestimated, but this is of nearly no significance for the rest of the calculation, which relies on the decisive role of v_{1d} and v_{2d} in the formation of the deep levels). After such replacements, (2.6) takes the form

$$C_{\mathbf{k}}^n = \frac{1}{E_d - \varepsilon_{\mathbf{k}}^n} \sum_{n_1} [v_{1d}^{nn_1} d^{n_1}(0)$$

$$+ \exp(-2\pi i\nu\kappa_\eta) v_{2d}^{nn_1} d^{n_1}(\nu) + v_s^{nn_1} d_{\kappa_\eta}^{n_1}]. \quad (2.8)$$

To write the expressions in a less cumbersome form, the subscript q, which is common to all the terms, is omitted, and the following notation is introduced:

$$d_{\kappa_\eta}^n = \int d\kappa_\xi C_{\mathbf{k}}^n, \quad d^n(\alpha) = \int d\kappa_\xi d\kappa_\eta C_{\mathbf{k}}^n \exp(2\pi i\alpha\kappa_\eta),$$

$$v_\beta^{nn_1} = \frac{1}{\Omega_0} \int d\Omega u_{\mathbf{k}q}^{n*}(\mathbf{r}) v_\beta(\mathbf{r}) u_{\mathbf{k}_1 q}^{n_1}(\mathbf{r}) \exp[i(\mathbf{k}_1 - \mathbf{k})\mathbf{r}],$$

$$\kappa = \frac{1}{2\pi}(a_\xi k_\xi \mathbf{e}_\xi + a_\eta k_\eta \mathbf{e}_\eta), \quad \alpha = 0, \nu, \quad \beta = 1_d, 2_d, s, \quad (2.9)$$

where e_ξ and e_η are unit vectors along the ξ and η directions. The expressions in (2.9) take into account the local character of the potentials v_β stipulated above, which permits assuming that the matrix elements are not dependent on the wave vectors (to test this an expansion in Wannier functions must be used, keeping only the one-center integrals).

Since we are interested in the states E_d within the band gap and since the gaps E_g in atomic semiconductors are far narrower than the electronic bands, only the contributions from the bands closest to this gap (the conduction band c and the valence band v) can be retained in the system (2.8).

We take into account the evidence following from the experimental data that the energy of a bound state becomes deeper as the dislocations are approached, i.e., as the regions where the potentials V_{1d} and V_{2d} act, are approached. In analogy to the usual problem of an electron in a two-center potential, it should be expected that the energy of the lowest level decreases only when V_{1d} and V_{2d} have the same sign. Then for negative V_d (attraction of an electron) the levels created within the gap split off from the conduction band, and for positive potentials (repulsion of an electron, i.e., binding of a hole) these levels split off from the valence band. (When V_{1d} and V_{2d} have different signs, the levels split off from both the conduction band and the valence band, but a decrease in the difference between the potentials should then be accompanied by displacement of the levels toward the edges of the bands which produced them due to the effective weakening of the total field.

Let us next treat the situation in which both potentials have identical signs. We consider the simplest case of the one-band Koster–Slater approximation, i.e., the possibility of omitting the off-diagonal matrix elements of the potentials in Eqs. (2.8) (since we are concerned with selecting a simple uniform description of the entire rich series of dislocation photoluminescence lines, we are still not seeking the basis for such an approximation, for example a symmetry basis). After integrating both sides of Eq. (2.8) with respect to κ_ξ and determining d_{κ_η}, we then find a system of equations for $d(0)$ and $d(\nu)$ and the condition for solvability of that system, which is the dispersion equation for the energy of a state bound in a dissociated dislocation:

$$\left[P_0(E_d) - \frac{1}{v_{1d}} \right]\left[P_0(E_d) - \frac{1}{v_{2d}} \right] = |P_\nu(E_d)|^2. \qquad (2.10)$$

Here

$$P_\alpha(E_d) = \int d\kappa_\eta = \frac{S_{\kappa_\eta}(E_d)\exp(2\pi i \alpha \kappa_\eta)}{1 - v_s S_{\kappa_\eta}(E_d)},$$

$$S_{\kappa_\eta}(E_d) = \int \frac{d\kappa_\xi}{E_d - \varepsilon_k}, \qquad (2.11)$$

and the v_β are the matrix elements of potentials (2.9) (the band indices have been omitted). We are interested in the smallest of the roots of Eq. (2.10), which corresponds to the packing-defect width R_ν (1.1). We add the subscript ν to this value of the binding energy ν. $E_d = E_{d\nu}$. It is obvious that as ν increases the roots of (2.10) under consideration should

increase and shift toward the corresponding band edge, converging at a certain limiting value $E_{d\infty}$ which satisfies the equation

$$P_0(E_{d\infty}) = \frac{1}{v_{\max}}, \qquad |v_{\max}| = \max|v_\beta|, \qquad (2.12)$$

i.e., is determined by the largest potential. Using the expression for $P_0(E_{d\nu})$ from Eq. (2.10), we write the difference $P_0(E_{d\nu}) - P_0(E_{d\infty})$ in the form

$$P_0(E_{d\nu}) - P_0(E_{d\infty}) = \pm\left[\sqrt{|P_\nu(E_{d\nu})|^2 + \frac{1}{4}\left(\frac{1}{v_{1d}} - \frac{1}{v_{1d}} \right)^2} \right.$$
$$\left. - \frac{1}{2}\left| \frac{1}{v_{1d}} - \frac{1}{v_{2d}} \right| \right] \qquad (2.13)$$

(the $\pm$ sign corresponds to positive and negative potentials). Writing the dispersion equation in the form (2.13) makes further calculations much more specific. This possibility is associated with the fact that the value of the difference $P_0(E_{d\nu}) - P_0(E_{d\infty})$ is mainly determined by the integration regions with respect to k near the energy extrema ε_k. In fact, the parts of the integrals determined by the integration regions which are distant from the energy extrema depend weakly on $E_{d\nu}$ and $E_{d\infty}$, which are located in the band gap. Therefore, these parts of the integrals compensate one another in the difference $P_0(E_{d\nu}) - P_0(E_{d\infty})$. The value of $P_\nu(E_{d\nu})$ is also determined by the region of k near an extremum, since sign-reversing oscillations of the phase exponent, which suppress the corresponding contribution to the integral, are included at large k. Therefore, only the regions of the band spectrum near the extrema ε_k where the effective-mass approximation is applicable, are important in (2.13).

For concreteness, we restrict ourselves to calculations for Ge crystals (it is easier to select an adequate alternative for analysis in this case). Since at least 13 clearly distinguishable lines of the dislocation photoluminescence series are observed experimentally in Ge, we have evidence that the contribution from the overlapping of the states at individual dislocations, which is described by P_ν in (2.10) and (2.13), to the shaping of the energy level is significant over a broad range of distances between the local potentials. The characteristic length parameter δ_ν which determines the variation of this addition with R_ν, clearly has the form

$$\delta_\nu = \hbar[2m^*(E_{d\nu} - E_{k_0})]^{-1/2}, \qquad (2.14)$$

where m^* is the effective mass along η given by (2.2) and ε_{k0} is the extremum energy (the potential of the packing defect is not yet taken into account here). To realize the largest possible value of δ_ν, band states at the extrema with a small effective mass must play the decisive role in the dispersion equation. In the case of Ge, a selection based on this characteristic yields three groups of candidates: light holes, the electronic minimum at the Γ point of the Brillouin zone, and the electronic valleys at the L points on the [111] axes (in the first two cases the masses are minimal and similar: $m^*/m_0 \approx 0.04$; the transverse masses for the latter are small: $m_\perp^*/m_0 = 0.08$). The situation in which the

dislocation-bound state of a carrier taking part in the dislocation photoluminescence is determined by the surroundings of the electronic Γ minimum will be analyzed next. Omitting the details of the trial calculations, we present the qualitative basis for this choice.

In dispersion equation (2.13), which specifies the energy of a bound state, the "two-center" term P_ν, which depends on R_ν, appears along with the "one-center" term P_0, which corresponds to the contribution of the isolated potential of one partial. The values of these terms depend on the densities of states, i.e., are proportional to the effective mass. Since at the Γ point the representations according to which the Bloch amplitudes for light and heavy holes transform are identical, there is no basis to assume that the matrix elements of the potentials v_d in the functions of light and heavy holes differ significantly. This means that in the case of a dislocation level split off from the valence band, both branches of the hole band spectrum should be taken into account. However, the density-of-states mass for heavy holes is almost an order of magnitude greater than that for light holes, and thus the contributions for heavy holes should be predominant. Consequently, the bound state is characterized by a shorter tunneling distance δ_ν and cannot provide for differences in the energies $E_{d\nu}$ as ν varies that are large enough to reconcile these levels with the series of dislocation photoluminescence lines in Ge. The portion of the electronic band state with a minimum at the Γ point seems more suitable from this standpoint. This minimum is somewhat higher than the c valley at the L point, but is characterized by an effective mass two times smaller and, therefore, by a larger value of δ_ν. This situation (together with the additional possibility of facilitating tunneling by altering the potential of the packing defect) ultimately allowed for successful reconciliation with experiment.

The following concomitant qualitative argument also seems very important. The matrix element specifying the probability of the radiative decay of a dislocation exciton contains an integral of the momentum operator $\hat{p}$ and one-electron functions for the electronic and hole "seed" states. If an electronic state is bound to the Γ minimum, the symmetry properties of the Γ states and $\hat{p}$ allow direct recombination with a hole Γ state.[12] In the case of potentials which attract electrons and repel holes under consideration here, it is natural to use a hole state which "emerges" at the Γ maximum of the valence band to construct a dislocation exciton (which will be done below). This situation corresponds to direct recombination luminescence and a large luminescence quantum yield, which are apparently manifested experimentally. Finally, after more elaborate construction of a dislocation bound state (involving both the Γ and L band extrema), direct collapse of a dislocation exciton can occur in indirect-gap Ge, but only to the extent of the mixing of the electronic Γ minimum.

Let us thus examine the energy levels split off by the dislocation potential from the states bound to the minimum of the conduction band at the Γ point, while disregarding the influence of the other band edges. The dispersion law ε_{kq}^c in the conduction band of Ge near the Γ point is isotropic:[13,14]

$$\varepsilon_{kq}^c = \varepsilon_0^c + \frac{\hbar^2}{2m_c}(k^2 + q^2). \tag{2.15}$$

Then the integrals (2.11) are

$$S_{\kappa_\eta} = -\frac{1}{E_0^* \sqrt{\kappa_\eta^2 + \Delta_{d\nu}}},$$

$$P_\alpha = \frac{1}{E_0^*} \int_{-\kappa_m}^{\kappa_m} d\kappa_\eta \frac{\exp(2\pi i \alpha \kappa_\eta)}{\sqrt{\kappa_\eta^2 + \Delta_{d\nu} + \bar{v}_s}}, \tag{2.16}$$

where

$$\Delta_{d\nu} = \frac{1}{E_1^*}\left(\varepsilon_0^c + \frac{\hbar^2 q^2}{2m_c} - E_{d\nu}\right), \quad \bar{v}_s = \frac{v_s}{E_0^*},$$

$$E_0^* = \frac{2\pi\hbar^2}{m_c a_\xi a_\eta}, \quad E_1^* = \frac{(2\pi\hbar)^2}{2m_c a_\eta^2}. \tag{2.17}$$

The limiting cut-off value κ_m, for which we assumed $\kappa_m > 2\sqrt{\Delta_{d\nu}}$, was introduced into the integral in (2.16); it drops out from the left-hand side of Eq. (2.13), and on the right-hand side, in P_ν, it can be replaced by ∞. The role of the potential of the packing defect v_s has not yet been discussed. The calculations which we present here showed that the case of $v_s < 0$ is most suitable and that for the deep levels of interest to us, it is sufficient to consider the situation of a "weak" packing defect, in which $\Delta_{d\nu} > \bar{v}_s^2$. In this case the integral P_α in (2.16) does not have any singularities on the real axis. To calculate P_ν we pass to the complex plane with cuts from the branch points $\kappa_\eta = \pm i\sqrt{\Delta_{d\nu}}$ to infinite limits along imaginary semiaxes, select a contour which passes the point $\kappa_\eta = i\sqrt{\Delta_{d\nu}}$ along a cut, and obtain

$$P_\nu = -\frac{2}{E_0^*}\left(\frac{\pi\gamma_\nu}{\lambda_\nu}\exp(-2\pi\nu\lambda_\nu\sqrt{\Delta_{d\nu}}) + F_\nu\right),$$

$$F_\nu = K_0(2\pi\nu\sqrt{\Delta_{d\nu}}) - \gamma_\nu^2\int_0^\infty dt \frac{\exp(-2\pi\nu\sqrt{\Delta_{d\nu}})\,\mathrm{ch}\,t}{\mathrm{sh}^2 t + \gamma_\nu^2}. \tag{2.18}$$

Here

$$\gamma_\nu^2 = \frac{\bar{v}_s^2}{\Delta_{d\nu}}(<1), \quad \lambda_\nu = \sqrt{1 - \gamma_\nu^2}, \tag{2.19}$$

and K_0 is the modified Bessel function. The first term in (2.18) corresponds to the contribution from the pole $\kappa_\eta = i\sqrt{\Delta_{d\nu} - \bar{v}_s^2}$, and the function F_ν appears as a result of circumventing branch point. The influence of the potential of the packing defect caused the appearance of the first term in P_ν [see Eq. (2.18)] with an exponential function, whose exponent is smaller than in the asymptotic (for $2\pi\nu\sqrt{\Delta_{d\nu}} > 1$ expression for F_ν.[3)]

For $P_0(E_{d\nu})$ with logarithmic accuracy we have

$$P_0(E_{d\nu}) = -\frac{2}{E_0^*}\left[\ln\frac{2\kappa_m}{\sqrt{\Delta_{d\nu}}} + \frac{2\gamma_\nu}{\lambda_\nu}\mathrm{arctg}\sqrt{\frac{1 + \gamma_\nu}{1 - \gamma_\nu}}\right]. \tag{2.20}$$

At this point we can take advantage of another simplification, which is not of fundamental significance, and set $v_{1d} = v_{2d}$. In this case a single free parameter $\bar{v}_s$ remains in

Eq. (2.13). The other parameters (the bottom energy ε_0^c, the mass m_c, and the lattice constants a_ξ and a_η are known. The overall form of Eq. (2.13) for the binding energies included in γ_ν [see (2.19)] is

$$\ln\gamma_\nu + \frac{2\gamma_\nu}{\lambda_\nu}\,\mathrm{arctg}\,\sqrt{\frac{1+\gamma_\nu}{1-\gamma_\nu}} + \frac{\pi\gamma_\nu}{\lambda_\nu}\exp(-2\pi\nu\lambda_\nu\sqrt{\Delta_{d\nu}}) + F_\nu$$

$$= \ln\gamma_\infty + \frac{2\gamma_\infty}{\lambda_\infty}\,\mathrm{arctg}\,\sqrt{\frac{1+\gamma_\infty}{1-\gamma_\infty}}. \qquad (2.21)$$

The quantity $\Delta_{d\nu}$ defines the eigenvalue of the energy of the bound state $E_{d\nu}$ measured from the energy of a free electron with a wave vector q. Finding $\Delta_{d\nu}$ as the root of the dispersion equation (2.21), which does not depend on q, we also find $E_{d\nu}$, which has a one-dimensional band spectrum beginning from the level $\varepsilon_0^c - E_1^*\Delta_{d\nu}$:

$$E_{d\nu} = E_{d\nu}(q) = \varepsilon_0^c - E_1^*\Delta_{d\nu} + \frac{\hbar^2 q^2}{2m_c}. \qquad (2.22)$$

The comparison with experiment is confined to converting the emission energies into $\Delta_{d\nu}$ [see Eq. (2.17)] (with consideration of the excitonic binding) and verifying that they satisfy the dispersion equation for all the lines of the dislocation photoluminescence series in Ge [this procedure requires one more parameter: the point of reference for the number ν, i.e., matching of the number of each line in the series to the corresponding packing-defect width R_ν of (1.1)].

3. EXCITON BOUND TO A DISSOCIATED DISLOCATION

To describe a dislocation exciton we use the two-particle Schrödinger equation

$$\left[\hat{H}^c(\mathbf{r}_1) - \hat{H}^v(\mathbf{r}_2) - \frac{e^2}{\kappa_0 r_{12}}\right]\Psi_{dex}(\mathbf{r}_1,\mathbf{r}_2) = E_{dex}\Psi_{dex}(\mathbf{r}_1,\mathbf{r}_2). \qquad (3.1)$$

The procedure for passing from the many-particle treatment to Eq. (3.1) can be performed in the usual manner (see, for example, Ref. 15) and is omitted here. Equation (3.1) contains the effective Hamiltonian corresponding to an excited state of the crystal, in which an electron from the valance band has been transferred to a dislocation level [this corresponds to $\hat{H}^c(\mathbf{r}_1)$, which coincides with the Hamiltonian in (2.3)] and a hole was left in the valence band [the Hamiltonian $-\hat{H}^v(\mathbf{r}_2)$]. The situation with an electron-attracting dislocation potential V is considered; therefore, the state released in the valence band should correspond to the emergence of a newly formed hole and is described by a Hamiltonian in which $V(\mathbf{r}_2)$ can be omitted. On this basis we have $\hat{H}^v(\mathbf{r}_2) = \hat{H}_0^v(\mathbf{r}_2)$ and the Schrödinger equation (2.4) can be used for states in the valence band. The electron–hole interaction in (3.1) is given by Coulomb attraction with the dielectric constant κ_0.

The conceptual problem is similar to the familiar problem of a direct exciton in Ge (see, for example, Ref. 12, Sec. 27); one difference is the localized nature of the electronic state in directions transverse to the dislocation lines, which should not significantly alter the result regarding the weakness of the binding in the electron–hole pair. Therefore, we

can use one-particle functions in the Luttinger–Kohn basis,[12] where the periodic parts $\psi_q^d(\mathbf{r}_1)$ and $u_{\mathbf{k}q}^v(\mathbf{r}_2)$ are taken at the Γ point:

$$\varphi_{q_1}^d(\mathbf{r}_1) = \frac{\exp(iq_1\zeta_1)}{\sqrt{L_\zeta}}\psi_0^d(\mathbf{r}_1),$$

$$\varphi_{q_2\mathbf{k}_2}^v(\mathbf{r}_2) = \frac{\exp[i(q_2\zeta_2 + \mathbf{k}_2\mathbf{r}_2)]}{\sqrt{\Omega}}u_0^v(\mathbf{r}_2). \qquad (3.2)$$

The effective-mass approximation is permissible for the energy spectrum: for simplicity we shall disregard the degeneracy of the hole spectrum at the Γ point, replacing it by an isotropic spectrum with a certain mean effective mass m_v:

$$\varepsilon_{\mathbf{k}q}^v = \varepsilon_0^v - \frac{\hbar^2}{2m_v}(k^2 + q^2) \qquad (3.3)$$

(this simplification is of no consequence for subsequent quantitative evaluations).

Thus, we represent the function Ψ_{dex} in the form of a superposition

$$\Psi_{dex} = \sum_{q_1 q_2 \mathbf{k}_2} \beta_{q_1 q_2 \mathbf{k}_2}\varphi_{q_1}^d(\mathbf{r}_1)\varphi_{q_2\mathbf{k}_2}^v(\mathbf{r}_2)$$

$$= \frac{1}{\sqrt{\Omega L_\zeta}}\Phi_{dex}(\zeta_1,\mathbf{r}_2)\psi_0^d(\mathbf{r}_1)u_0^v(\mathbf{r}_2), \qquad (3.4)$$

where

$$\Phi_{dex}(\zeta_1,\mathbf{r}_2) = \sum_{q_1 q_2 \mathbf{k}_2}\exp[i(q_1\zeta_1 + q_2\zeta_2 + \mathbf{k}_2\mathbf{r}_2)]\beta_{q_1 q_2 \mathbf{k}_2} \qquad (3.5)$$

is the envelope of the function. Plugging (3.4) into (3.1), multiplying by $\varphi_{q_1'}^{d*}(\mathbf{r}_1)\varphi_{q_2'\mathbf{k}_2'}^{v*}(\mathbf{r}_2)$, and integrating with respect to $d\Omega_1 d\Omega_2$, we obtain an equation for a dislocation exciton in the usual manner:

$$\left[-\frac{\hbar^2}{2m_c}\frac{\partial^2}{\partial\zeta_1^2} - \frac{\hbar^2}{2m_v}\left(\frac{\partial^2}{\partial\zeta_2^2} + \frac{\partial^2}{\partial\xi_2^2} + \frac{\partial^2}{\partial\eta_2^2}\right)\right.$$

$$\left.-\frac{e^2}{\kappa_0}\int\frac{d\xi_1 d\eta_1|\psi_0^d(\xi_1,\eta_1)|^2}{\sqrt{(\zeta_1-\zeta_2)^2 + (\xi_1-\xi_2)^2 + (\eta_1-\eta_2)^2}}\right]$$

$$\times\Phi_{dex}(\zeta_1,\mathbf{r}_2) = [E_{dex} + \varepsilon_0^v - E_{d\nu}]\Phi_{dex}(\zeta_1,\mathbf{r}_2). \qquad (3.6)$$

Here the potential term contains the wave function of an electron bound in a dissociated dislocation averaged over the coordinate ζ_1. Separating the free motion of the center of gravity with the coordinate

$$Z = \frac{m_c\zeta_1 + m_v\zeta_2}{M}, \quad M = m_c + m_v, \qquad (3.7)$$

which can be described by the equation

$$-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial Z^2}g(Z) = \frac{\hbar^2 K^2}{2M}g(Z), \qquad (3.8)$$

we write the equation for the bound state

TABLE I.

Line	d	d	d	d	d	d	d	d	d	d	d	d	d	...	d
$\hbar\omega_n$	431	450	466	478	489	498	506	513	518	524	527	531	534	...	550
$\varepsilon_0^c - E_{dn}$	464	445	429	417	406	397	389	382	377	371	368	364	361	...	345

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial\zeta^2} - \frac{\hbar^2}{2m_v}\left(\frac{\partial^2}{\partial\xi^2} + \frac{\partial^2}{\partial\eta^2}\right) \right.$$

$$\left. -\frac{e^2}{\kappa_0}\int \frac{d\xi_1 d\eta_1 |\psi_0^d(\xi_1,\eta_1)|^2}{\sqrt{\zeta^2 + (\xi - \xi_1)^2 + (\eta - \eta_1)^2}} \right] f(\xi,\eta,\zeta)$$

$$= E_b f(\xi,\eta,\zeta), \tag{3.9}$$

whose eigenvalue E_b, which has the form

$$E_b = E_{dex} + \varepsilon_0^v + E_{dv} - \frac{\hbar^2 K^2}{2M}, \tag{3.10}$$

determines the excitonic binding energy and, therefore, E_{dex}. In (3.9) $\zeta = \zeta_1 - \zeta_2$ is the relative coordinate of the electron and hole along the dislocation axis, $\xi = \xi_2$ and $\eta = \eta_2$ are the coordinates of the exciton (hole) transverse to the axis, and $\mu^{-1} = m_c^{-1} + m_v^{-1}$. After setting the energies E_{dex} for recombination of a dislocation exciton [which are expressed in terms of E_b using (3.10)] equal to the energies $\hbar\omega_n$ of the dislocation photoluminescence spectral lines

$$E_{dex}(\nu) = E_b - \varepsilon_0^v + E_{dv} = \hbar\omega_n \tag{3.11}$$

($K = 0 - a$ direct process), we are able to compare the series of roots of the dispersion equation (2.21) to the series of the experimental frequencies ω_n. Here the relationship between the spectral number of each line n and the number ν is expressed in terms of a reference offset Δn:

$$\nu = n + \Delta n, \tag{3.12}$$

whose value is the free parameter mentioned at the end of Sec. 2. The main dependence on the number n of the line (or the packing-defect width R_ν) is determined by the electronic binding energy E_{dv}, the dependence of the excitonic binding energy E_b on ν can be disregarded in this case owing to the smallness of both E_b itself and its departure from E_{dv}, as well as the changes in them. [To evaluate E_b we take into account the localized nature of the function ψ_0^d near the partials. Consequently the potential term in (3.8) can be written in an approximation in the form

$$-\frac{e^2}{2\kappa_0}\left(\frac{1}{\sqrt{\xi^2 + \eta^2 + \zeta^2}} + \frac{1}{\sqrt{\xi^2 + (\eta - R_\nu)^2 + \zeta^2}} \right),$$

which corresponds to the problem of two Coulomb centers with charges $e/2$. In the limit $\nu \to 0$ the value of E_b should be close to the binding energy of a direct exciton in Ge. As ν increases, E_b decreases due to the separation of the charge between two wells. A comparison with the results for a direct exciton in Ge indicates that E_b has a value of order several meV.] We set $E_b = 2$ meV (in agreement with the experimental data[16]) in (3.10) for further calculations. At this point there is no need to refine the value of E_b by analyzing Eq.

(3.9): replacement by a value of the same order has practically no effect on the results following from Eq. (2.21).

Table I presents the emission energies $\hbar\omega_n$ of the dislocation photoluminescence d lines in Ge and the corresponding values of $\varepsilon_0^c - E_{dn} = E_g^0 + E_b - \hbar\omega_n$ (in meV).

The values of γ_∞ and Δn were adjusted in Eq. (2.21) to achieve agreement between its two sides when

$$\gamma_\nu = \gamma_\infty \sqrt{\frac{\varepsilon_0^c - E_{d\infty}}{\varepsilon_0^c - E_{d\nu}}}$$

for all the values taken from Table I is plugged into the left-hand side. The following parameters were used in the calculations: $E_g^0 = 897$ meV, $m_c = 0.041 m_0$, $a_\eta = \sqrt{(3/8)}a = 3.46$ Å, $a_\xi = a/\sqrt{3} = 3.36$ Å. The best agreement was achieved when the following values were chosen:

$$\gamma_\infty = 0.78, \quad \Delta n = 5. \tag{3.13}$$

In this case the accuracy (the difference between the values on the right- and left-hand sides divided by the value of the right-hand side) was at least 1–2%.

4. CONCLUSIONS

The problem of the energy states of a one-dimensional dislocation exciton has been considered in a simplified version of the Koster–Slater model for the local potentials (associated with the partials and the packing defect). The possibility of quantitative agreement between the excitonic energies corresponding to a set of discrete packing-defect widths and the spectral positions of 13 dislocation photoluminescence lines of the d series in Ge was demonstrated using a modified form of the dispersion equation for the energies, which permits analysis in the effective-mass approximation. It is doubtful whether an attempt should be made to increase the accuracy of this agreement: the physical model is, by any standard, highly simplified; the values of the parameters used (for example, the direct band gap E_g^0) are not very accurately known; the effect of dislocation deformation on the band characteristics was not taken into account; the form of the spectrum of the d series allows the positions of the lines to be fixed somewhat differently, i.e., with a 1–2 meV shift; etc. It is important that the spectrum can be very sensitive to variations in the distances R_ν over a very broad range when the initial distance between the partials corresponding to the first line in the series is sufficiently large. The proposed physical picture of dislocation photoluminescence is also supported by the realistic nature of the values of the two free parameters of the problem. The value $\Delta n = 5$ falls within the range discovered experimentally in Refs. 7 and 8 when a load increasing or decreasing the dissociation of the dislocations was studied; to the data in Ref.

8 imply $\Delta n = 7 \pm 2$. The effective value of the packing-defect potential obtained from (2.17) and (2.19), the value of (3.13) selected, and the data in the table is estimated to be $v_s \simeq 2.7$ eV, i.e., it has the typical scale of the electronic energy parameters in Ge (Refs. 13 and 14) and is totally permissible.[4]

In conclusion, let us discuss the question of the efficiency of the radiative processes accompanying quantum transitions involving dislocation states. For plastically deformed Ge the process of the emission of the lines of the d series may be considered direct (to the extent that the physical picture of electronic transitions considered above is correct); being an elementary event, this process should be very efficient. In the case of Si, the analogous process apparently does not occur [here the direct band gap at the Γ point is large, i.e., about 3.5 eV (Ref. 14), so that the Γ-minimum can hardly play an appreciable role in creating an electronic bound state]. Therefore, the dislocation photoluminescence in Si most probably occurs by means of indirect transitions. Of course, the real quantum yield depends not only on the value of the constant of the elementary emission event, but also on the participation of radiationless channels (we are referring to true multiphonon transitions, rather than competition with other capture centers). In this context the role of the one-dimensional nature of the electron (and exciton) states bound to long straight segments of dislocations seems very important. We recall that the occurence of a process of multiphonon energy transfer requires a lattice fluctuation in the volume occupied by the least extended state participating in the transition. The probability of a lattice fluctuation, which is exponentially dependent on that volume, is negligibly small in the case of the extended one-dimensional system under consideration (the corresponding volume is equal to about $\sim L_\xi a^2$, i.e., is a macroscopic quantity), limiting the efficiency of the radiationless process and eliminating the Stokes shift and the phonon broadening of the emission lines. However, electron localization, particularly self-trapping due to the interaction with acoustic phonons, is possible in the one-dimensional situation (this question, as applied to dislocation states, was considered in Ref. 17, and calculations show that the self-trapping energy is smaller than the excitonic binding energy E_b). Therefore, several characteristic regimes can arise in dislocation photoluminescence, in principle:

1) At very low temperatures dislocation excitons are self-trapped (or some other type of capture occurs). In this case the luminescence can be weakened as a consequence of the mechanism for radiationless losses upon recombination.

2) As the temperature rises, these trapped states are ionized, a transition is made to a one-dimensional exciton band, and the radiationless channel is eliminated, i.e., narrow exciton recombination emission lines appear.

3) When the temperature rises further, the excitonic Coulomb interaction is disrupted; the electron trapped by the dislocation can recombine with a free band hole; there are no radiationless losses, but the shape and width of the lines should vary in accordance with the form of the one-dimensional dislocation band. According to the evaluations from the present work and Ref. 17, such transformations of the dislocation photoluminescence spectrum are possible in

the case of Ge at helium temperatures. Similar effects can be caused by illumination at suitable frequencies. Alteration of the dislocation structure, which is accompanied by shortening of the straight segments of the dislocation lines, by the introduction of point defects (intersections, jogs, kinks, etc.) on them, i.e., elimination of the one-dimensional nature of the electronic states, should also have a quantitative effect on the character of the dislocation photoluminescence spectrum. Well designed experiments of this kind and determination of the characteristic temperatures or frequencies which stimulate the appearance of the one-dimensional characteristics of the electronic system would provide important data for understanding the physical properties of the interesting and complex system of electrons in plastically deformed semiconductors.

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[1] A simplified version of such an analysis was previously performed in Ref. 9.

[2] We note that an alternative excitonic interpretation of dislocation photoluminescence was previously proposed by Perel' and Yassievich in Ref. 16. They suggested that the luminescence is caused by recombination of an exciton trapped in one of the partials when its state is disturbed by the deformation potential of another dislocation at a distance R_ν. According to their hypothesis, just this disturbance creates the differences between the frequencies of the lines in the series. However, the excitonic binding energy is about 2–3 meV, according to evaluations based on temperature-induced changes in the dislocation photoluminescence spectrum,[16] while the serial differences are significantly greater, so that when the quantum state is constructed, the hierarchy of potentials should be different.

[3] Physically, the decrease in the exponent of the exponential function decreases because tunneling occurs below the bottom of the two-dimensional band of bound states created by the packing defect itself. The position of the bottom of this band is determined by the pole of the integrand in (2.16) for $\bar{v}_s < 0$ and equals $\varepsilon_c^e - E_1^* \bar{v}_s^2$.

[4] The other potential v_d from the dispersion equation (2.21) was eliminated and should be evaluated independently from Eq. (2.12), but expression (2.20) for P_0 is unsuitable here, since the integral diverges at large k and the effective-mass approximation is therefore inappropriate. If (2.20) is, nevertheless, used with the cut-off parameter $\kappa_m = 1$ and the tabulated value of $\varepsilon_c^e - E_{d\infty}$, we obtain the rough estimate $v_d \simeq 9$ eV, which could also be compared with some characteristic energies in Ge.[13,14]

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