Exciton luminescence from fluctuation-induced tails in the density of states of disordered solid solutions

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(Submitted January 14, 1997)

Fiz. Tverd. Tela (St. Petersburg) 39, 1170–1182 (July 1997)

The shape of the luminescence spectra of excitons localized by composition fluctuations in a disordered solid solution, is calculated by a theoretical model that takes into account two different aspects of the electron-phonon interaction: 1) the lifetimes of localized states are limited because of transitions (tunneling) between states of the tail with emission of phonons. This implies that only a relatively small fraction of the states in the tail - those which have no access to such transitions - are populated long enough to emit radiation; 2) the luminescence spectra from these long-lived radiating states is also caused by the simultaneous emission of phonons. It is shown that both these aspects are important in explaining the observed shift in the maximum of the luminescence band relative to the maximum of the exciton absorption line. The shape of the short-wavelength edge of the luminescence band is determined primarily by the dependence of the number of clusters of minimum size on the localization energy, in particular its rapid decrease in the neighborhood of the mobility edge, whereas the spectrum of recombination with emission of phonons determines the shape of the long-wavelength tail of the primary emission band. The calculated shape of the emission spectrum is compared with spectra obtained experimentally for luminescence from the solid solution CdS_{(1-c)}Se_{c}. It turns out that a satisfactory description of the experimental spectra of CdS_{(1-c)}Se_{c} over a wide range of compositions requires two models of the localized exciton: localization of the exciton as a whole (model I) or localization of the hole with the electron bound to it by the Coulomb interaction (model II). © 1997 American Institute of Physics. [S1063-7834(97)00507-8]

The intrinsic luminescence of many disordered systems\textsuperscript{1–10} including II-VI solid solutions,\textsuperscript{1–8} arises from the recombination of excitons localized in wells of the potential profile. A common feature of such systems is a considerable red shift of the luminescence with respect to the maximum of the exciton absorption, so that the fundamental emission band lies in a wavelength range where absorption coefficient and the density of fluctuation-induced states are both small.

If we are to understand the physical processes occurring in disordered systems, it is important to understand the origin of this red shift in the luminescence band and the relation between the luminescence and absorption spectra. The large value of this shift for amorphous systems,\textsuperscript{10} which are characterized by a strong exciton-phonon interaction, is well known. In a number of II-VI solid solutions, the exciton-phonon interaction broadens the fundamental luminescence band and produces LO-phonon replicas of this band.\textsuperscript{12}

The goal of this paper is to construct a theoretical model of fluctuation-induced states that can predict where the band of intrinsic luminescence from these states is located with respect to their absorption spectrum, to justify qualitatively the approach used via continuum percolation theory, and to compare the theoretical and experimental results for II-VI solid solutions.

In Sec. 1 of this paper, we obtain a general expression for the density of fluctuation states in the tail for a single-band model of the solid solution with weak diagonal disorder. We then give a simplified solution to the problem in the energy range where the states of the tail can be treated as isolated from one another to a zero-order approximation. The approach we have developed includes a modified variational method for calculating the dependence of the density of states on localization energy. This dependence contains an additional parameter that lets us describe the experimental data not only in the region where the density of states varies exponentially, but also in the neighborhood of the mobility edge, where the exponential dependence changes to a power law. Next, we carry out a parallel calculation for the total number of localized states that is unrelated to the variational procedure, which allows us to normalize the density of fluctuation states obtained from the previous calculation. The calculation of the number of states is based on the assumption that the exciton states are localized in fluctuations that are essentially simply-connected potential wells. These potential wells form in regions where atoms of the narrow-gap component cluster, i.e., where there is an excess of these atoms compared to their average concentration. In the limit of weak scattering, the requirement that each well be simply connected, and that the excess concentration in its volume be minimized, leads to an answer that follows from the theory of percolation on a lattice of a disordered sublattice: the

lower bound on the excess concentration is the critical concentration in the percolation problem along the sites of the sublattice. In the weak scattering limit, the fluctuation wells are large in size, and a cluster of excess atoms in such a well is structurally a fractal of finite size. The densities of states in the tail obtained from these arguments are in agreement with experimental data over a wide range of concentrations. Later in this section we derive the basic relations between the density and the spectral density of fluctuation states, and calculate the spectrum for exciton absorption in the region of fluctuation states without taking into account interactions with lattice vibrations.

In Sec. 2 of the paper we calculate the shape of the zero-phonon luminescence band. Since within the framework of this problem the possibility of optical recombination is limited by the lifetime of an exciton with respect to transitions (tunneling) to lower-lying states in the tail of localized states accompanied by emission of phonons,1–3 in order to describe the luminescence it is first necessary to find the energy distribution of those states for which channels for a nonradiative exit are absent or strongly limited.

In other words, it is necessary to know the distribution of spatially isolated localized states. In general, this problem is one aspect of the quantum theory of percolation.11–22 Isolated states in lattice models were studied in Refs. 14–16. As was shown in Ref. 16, two types of isolated localized states arise in the quantum theory of percolation. The first type are those states that belong to isolated atoms14–16 (in our case, potential wells) and to relatively small complexes of these atoms (superclusters), which are formed when atoms (potential wells) are randomly distributed. The role of superclusters becomes more important close to the mobility threshold. Isolated localized states of a different kind are caused by interference effects.16,19 However, in the presence of diagonal disorder, which determines the distribution of states in energy for the problem we are studying here, we should expect a considerable suppression of interference effects. In this case the problem reduces to finding the distribution of states in the tail over the superclusters in the continuum model, i.e., it reduces to a problem that is to a considerable degree analogous to the problem of percolation through overlapping spheres.23–29 In these calculations, we use the distribution of states over the superclusters and relations that follow from the classical theory of percolation through overlapping spheres to isolate those fluctuation states with maximum lifetime, which form the zero-phonon luminescence band. Within the framework of this approach we are able to establish the position of the zero-phonon luminescence band with respect to the maximum of the phononless absorption band for the ground state of an exciton and the mobility edge.

In Sec. 3 we describe how the interactions of excitons with optical and acoustic phonons affect the absorption spectrum and the luminescence of localized excitons. We discuss two models for exciton localization that imply considerable differences in the way excitons interact with phonons. In the first model it is assumed that the electron is able to follow the motion of the hole adiabatically, while in the second model the electron interacts with a distribution of hole density averaged over the fluctuation well. Both of these limits, and also intermediate cases, are realized in the solid solution Cd$_3$S$_1$–c$_1$Se. Preliminary results in which we took into account exciton-phonon interactions were published in Ref. 3.

In the last section, the results we obtain are used to describe the luminescence spectrum of the solid solution Cd$_3$S$_1$–c$_1$Se, for which extensive experimental data are available.1–8

1. FLUCTUATION STATES IN A SOLID SOLUTION

Assume that the fluctuation potential in the case of binary solutions with anion substitution primarily affects states of the valence band. In this case, since the effective mass of a hole is as a rule considerably larger than the mass of a conduction-band electron, we can postulate two mechanisms for exciton localization: (I) localization of the center of gravity of the exciton, and (II) localization of the hole, to which the electron is bound by the Coulomb interaction. Both of these mechanisms will be discussed at the same time below. They lead to similar results when the density of localized states is calculated, but differ significantly in the analysis of the interaction with lattice vibrations.

1) Hamiltonian and density of states in a single-band model. Assume that a macroscopic volume $V$ of the solid solution consisting of $N$ sites of the crystal lattice is occupied in a random fashion by atoms of two kinds, $A$ and $B$. The average number of $A$ and $B$ atoms in the volume $V$ are respectively $N_A = cN$ and $N_B = (1-c)N$, where $c$ is the concentration of $A$ atoms. The single-band Hamiltonian of this system can be written in the form

$$H = - \sum_{n,m} \Psi_n \Psi_m \left( \Psi_{n+m} - \Psi_n \right) + \sum_n E_n \Psi_n^2,$$  \hspace{1cm} (1)

where we will assume that the $\Psi_n$ are real. The off-diagonal matrix elements $W_{nm}$ are assumed to be identical for atoms of the two kinds, while the diagonal matrix element $E_n$ takes on a value of $E_A$ if the site is occupied by an atom $A$, and $E_B$ in the opposite case. In the limiting cases $c = 0$ and $c = 1$, the Hamiltonian (1) reduces to the Hamiltonian of perfect crystals of $B$ or $A$ atoms, respectively. In this case all the $E_n$ are replaced by $E_n = E_A$ or $E_B$.

In the virtual crystal approximation, the position of the bottom of the band for the solid solution is related to the average value of $E_n$ on a site:

$$\langle E \rangle_G = cE_A + (1-c)E_B.$$  \hspace{1cm} (2)

The energy $\omega$ is also measured from the bottom of the band $E_G$, and $\omega > 0$ for localized states; then the diagonal matrix elements can be written as

$$\Delta_n = \sqrt{E_n - E_G},$$  \hspace{1cm} (3)

where the quantity $\Delta_n$ now depends on the concentration of the solid solution as well.

The problem of calculating eigenfunctions and eigenvalues of a crystal Hamiltonian with atoms of two kinds placed in a disordered fashion is a linear problem, and its solution is obtained by diagonalizing a matrix of rank $N$, each of whose columns can be written as