Broadening of an exciton line in solid solutions with a degenerate valence band

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The broadening of an exciton line in a solid solution with a degenerate valence band is shown to be anomalously large if the translational mass of the exciton is negative. This broadening is determined by the scattering of the exciton by composition fluctuations with a large momentum transfer.

Several experimental studies[1–4] have been carried out on the composition dependence of the broadening of the exciton reflection and absorption lines in solid solutions. This broadening has been linked with fluctuations in the position of the edge of the valence band and of the conduction band which result from composition fluctuations. For a solid solution with composition x, the quantity $\xi(\mathbf{r})$, which is the deviation of the concentration of the substitutional atoms from its average value, is a random function of the coordinates with a correlation function

$$\langle \xi(\mathbf{r})\,\xi(\mathbf{r}')\rangle = Nx\,(1-x)\,\delta(\mathbf{r}-\mathbf{r}'), \tag{1}$$

where N is the concentration of sublattice sites that are filled by substitutional atoms, and the angle brackets mean a configurational average. The random potential acting on an electron is $V_e(\mathbf{r}) = \alpha_e \xi(\mathbf{r})/N$, while that acting on a hole is $V_h(\mathbf{r}) = \alpha_h \xi(\mathbf{r})/N$, where $\alpha_e = d\epsilon_c/dx$, and $\alpha_h = d\epsilon_v/dx$ are the rates of change of the position of the bottom of the conduction band and of the position of the top of the valence band as the composition varies. The following expression was derived in Ref. 5 for the width of an exciton absorption line:

$$\Delta = 0.08\,\frac{x^2(1-x)^2\,(\alpha_e+\alpha_h)^4\,(m_e+m_h)^3}{\hbar^6 N^2}, \tag{2}$$

where m_e and m_h are the masses of the electron and hole. Expression (2) was derived for the case of nondegenerate valence and conduction band. The experiments of Refs. 1–4 also correspond to this case.

It might be expected that the width of an exciton line in a solid solution with a degenerate valence band would be less than that calculated from (2). Actually, as was shown in Ref. 6, if the mass ratio of the heavy and light holes is large ($m_{hh} \gg m_{lh}$), the state density in the valence band in the solid solution, $\rho_h(\epsilon)$, falls off with distance into the band gap in a manner $\rho_h(\epsilon) \sim \exp[-19,\ 4(\epsilon/\Delta_h)^{1/2}]$, where Δ_h is found from (2) with $m_h = m_{hh}$ and $a_e = 0$, $m_e = 0$. In the case of a nondegenerate valence band, on the other hand, this decay is described by the expression[5] $\rho_h(\epsilon) \sim \exp[-3.7(\epsilon/\Delta_h)^{1/2}]$; i.e., it is far slower.

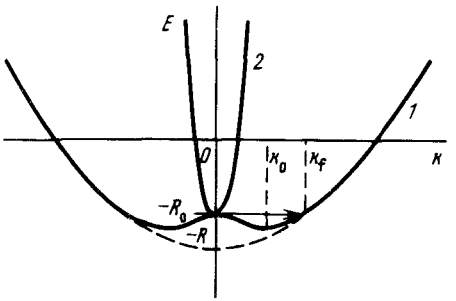

FIG. 1. Exciton dispersion law in a semiconductor with a degenerate valence band in the case $m_{hh} \gg m_{lh}$, m_e. Branches 1 and 2 correspond to bound states of an electron with a heavy hole and a light hole, respectively. The dashed curve shows the dispersion of an exciton in the case of a nondegenerate valence band.

In the present study we have shown that in the case of a degenerate valence band, the broadening of an exciton line can be far greater than that predicted by (2), because of a negative translational mass of the exciton. As was shown in Ref. 7, the dispersion law for an exciton in a semiconductor with a degenerate valence band has the form shown in Fig. 1; at quasimomenta $k \gg 1/a_B$, where $a_B = \hbar^2\kappa/m_e e^2$ is the first Bohr radius of the exciton and κ is the dielectric constant, the dispersion is decribed by

$$\epsilon(k) = -R + \frac{\hbar^2 k^2}{2m_{hh}} + \frac{4R^2 m_e}{\hbar^2 k^2}, \tag{3}$$

where $R = e^2/2\kappa a_B$ is the exciton Rydberg. Expression (3) holds under the conditions $m_{hh} \gg m_{lh}, m_e$ and has a maximum at $k = k_0 = 1/a_B(2m_{hh}/m_e)^{1/4}$; here $\epsilon(k_0) = -R\,[1 - 2^{3/2}(m_e/m_{hh})^{1/2}]$. It was shown in Ref. 7 that the inequality $\epsilon(k_0) < -R_0$, where R_0 is the exciton binding energy at $k = 0$; this inequality means that the translational mass is negative. As was shown in Ref. 8, we can describe R_0 by the expression $R_0 = R\theta$, where $\theta = 2m_{lh}/(m_e + 2m_{lh}) < 1$. The broadening of an exciton line in the case of a negative translational mass is determined by the scattering of an exciton which is created by light in a state with $k = 0$ by the random potential which is set up by composition fluctuations. The role of intermediate states is played by states with $|k| = k_f$ (Fig. 1). Since the density of intermediate states is high, the broadening of the exciton line due to this process is large. It can be shown that the shape of an absorption line, $K(E)$, is Lorentzian in this case

$$K(E) = \frac{\gamma}{2\pi\,(E^2 + \gamma^2/4)}, \tag{4}$$

where $E = \hbar\omega - \epsilon_g - R_0$, ω is the frequency of the light, and ϵ_g is the band gap. The linewidth γ is determined by the probability that an exciton will leave a state with $k = 0$ as it is scattered by composition fluctuations:

$$\gamma = 2\pi \left\langle \sum_{\mathbf{k},\,\mu=\pm 3/2} \left| \int d\mathbf{r}_e^3 \int d\mathbf{r}_h^3 \psi_0^*(\mathbf{r}_e, \mathbf{r}_h)\,[V_e(\mathbf{r}_e) + V_h(\mathbf{r}_h)]\,\psi_{k,\mu}^f(\mathbf{r}_e, \mathbf{r}_h) \right|^2 \delta(\epsilon(k) + R_0) \right\rangle, \tag{5}$$

where $\epsilon(k)$ is given by (3), and ψ_0 and $\psi_{\mathbf{k},\mu}^f$ are the wave functions of the initial and final states. In the case of a degenerate valence band, these functions are the four-

component column vectors

$$\psi_0(\mathbf{r}_e, \mathbf{r}_h) = \frac{1}{V^{1/2}} \chi_{z\mu_0} \varphi_0(\mathbf{r}_e - \mathbf{r}_h), \tag{6}$$

$$\psi^f_{\mathbf{k}\mu}(\mathbf{r}_e, \mathbf{r}_h) = \frac{e^{i\mathbf{k}\mathbf{r}_h}}{V^{1/2}} \chi_{\mathbf{k},\mu} \varphi_f(\mathbf{r}_e - \mathbf{r}_h), \tag{7}$$

where V is the normalization volume, and $\chi_{\mathbf{k},\mu}$ is an eigenfunction of the operator $(\hat{\mathbf{J}}\mathbf{k})/k$, which is the projection of the spin 3/2 (Ref. 9) onto the direction of the quasimomentum, $\mathbf{k}$: $(\hat{\mathbf{J}}\mathbf{k})/k\chi_{\mathbf{k},\mu} = \mu\chi_{\mathbf{k},\mu}$. The index μ can take on the values $\pm 1/2$, $\pm 3/2$. Branch 2 in Fig. 1 corresponds to the values $\mu = \pm 1/2$. The final states for the scattering, on the other hand, correspond to branch 1, for which we have $\mu = \pm 3/2$, so that we are left with only these terms in sum (5). The column vector $\chi_{z,\mu 0}$ is an eigenfunction of the operator $\hat{J}_z$; the index μ_0 can take on one of the values $\pm 1/2$, $\pm 3/2$, depending on the polarization of the exciting light. The functions φ_0 and φ_f describe the relative motion of the electron and hole in the initial and final states; they have the standard hydrogen-like form $\varphi_0(r) = (\pi a_B^3/\theta^3)^{1/2} \exp(-r\theta/a_B)$, $\varphi_f(r) = (\pi a_B^3)^{-1/2} \exp(-r/a_B)$. The dependence on the electron spin has been omitted from (6) and (7), since the electron spin does not change in the course of the scattering. Substituting (6) and (7) into (5) and using (1), we find

$$\gamma = \frac{32\sqrt{2}x(1-x)m_{hh}^{3/2} R^{1/2} (1-\theta)^{1/2}\theta^3}{\pi N \hbar^3 (1+\theta)^6} \left[\alpha_h + \frac{\alpha_e}{\left(1 + \frac{m_{hh}(1-\theta)}{m_e(1+\theta)^2}\right)^2}\right]^2. \tag{8}$$

In deriving (8) we used the relation

$$\frac{1}{4\pi} \int d\Omega_{\mathbf{k}} \sum_{\mu = \pm 3/2} (\chi^*_{\mathbf{k},\mu} \chi_{\mathbf{k},\mu}) = 1/2. \tag{9}$$

It can be seen from (8) that in the case of a degenerate valence band the width of an exciton line has a composition dependence $x(1-x)$, while for nondegenerate bands we would have $\Delta \sim x^2(1-x)^2$. Using (2) and (8), we can write the ratio Δ/γ as $\Delta/\gamma \sim [\Delta/R(1-\theta)]^{1/2}$. We thus have $\gamma \gg \Delta$, if the depth of the minimum in the exciton dispersion law (Fig. 1) exceeds Δ. The same condition, $R(1-\theta) \gg \Delta$, is the condition for the applicability of expression (8), since in deriving it we assume that the final state of the exciton in the scattering is not perturbed by the fluctuational potential.

We know of two experimental studies[10,11] of the broadening of an exciton line in a solid solution with a degenerate valence band. Ryabchenko *et al.*[10] reported that in the compounds $Cd_{1-x}Mn_xTe$ (they studied samples with $x < 0.05$) the broadening is more than an order of magnitude greater than that predicted by expression (2). A careful study of the composition dependence of the width of the exciton line in $CuBr_xI_{1-x}$ solutions over the entire range $0 < x < 1$ was carried out in Ref. 11; the behavior $\gamma \sim x(1-x)$ was found.

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