Singularities of absorption and luminescence bands of free many-exciton complexes

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We consider the singularities in the profiles of the absorption and luminescence bands of free many-exciton complexes in semiconductors.

At low temperatures and high crystal-excitation levels, the interaction between excitons leads to the appearance of new luminescence bands. Exciton physics has featured in recent years intensive studies of biexcitons[1] and electron-hole drops,[2] and many-exciton complexes bound to impurities were recently observed in experiments.[3,4] In luminescence spectra, these complexes are manifest by a "picket fence" of narrow lines of different intensity and of variable distance between them. Complexes containing up to 10 excitons were observed on an Li impurity in[3]. The emission-line broadening of bound many-exciton complexes is due to participation of photons in the emission process.

It is quite obvious that owing to the attraction forces between the free excitons the latter can also become bound and form free many-exciton complexes (FMEC). The simplest example of such a complex is in essence the biexciton. Another limiting case is an exciton (dielectric) drop. The gravity centers of FMEC should have definite wave vectors of translational motion. Owing to the low binding energy, such a complex can exist at very low temperatures.

Let us discuss the shapes of the luminescence and absorption lines of FMEC. As a result of radiative recombination of one of the excitons, an $(N+1)$-exciton complex can turn into an n-exciton complex. This recombination can continue until the last exciton is annihilated. The distance between the successive emission lines will then vary, since the per-unit binding energy I_n (the binding energy per exciton of the complex) is different for different values of n. Thus, for example, for the biexciton the per-unit binding energy I_2 differs from the binding energy I_{1s} of the $1s$ exciton by an amount $I_m/2$, where I_m is the binding energy of two excitons into a biexciton. In fact, complexes with different numbers of excitons can coexist in the crystal. Their luminescence leads to the appearance of a "picket fence" of narrow lines, the position and half-width of each of them corresponds to a definite value of n.

To determine the shape of the luminescence band it is necessary to know the wave function of the complex. However, as shown in[5], the shape of the luminescence band is determined not by the biexciton wave function but by the biexciton momentum distribution function. This is due to the low binding energy of the biexciton, which determines in turn the upper temperature limit of its existence. We assume that the free $(n+1)$-exciton complexes are thermalized and are calculated by a Maxwellian momentum distribution function with temperature T. We consider a semiconductor with direct allowed optical transitions, and obtain for the shape of the luminescence band $f(\omega)$ with transformation of an $(n+1)$-exciton complex into an n-exciton complex

$$f(\omega) \sim G_{n+1,n}^{1/2} \exp\left(-n\frac{G_{n+1,n}}{k_0 T}\right), \tag{1}$$

where

$$G_{n+1,n} = \hbar(\omega_0 - \omega), \quad \hbar\omega_0 = E_g + nI_n - (n+1)I_{n+1}, \tag{2}$$

E_g is the width of the forbidden band.

It is seen from (1) and (2) that the luminescence of the complex occurs only in the long-wave region of the end-point frequency ω_0. The latter is shifted relative to the exciton-absorption line into the long-wave region by an amount $\Delta = (n+1)I_{n+1} - nI_n - I_{1s}$. With decreasing number of excitons in the complex during the course of recombination, the end-point frequency shifts towards the shorter wavelengths, if it is assumed that I_n increases monotonically with increasing n and tends to a definite limit. The significant difference between the FMEC luminescence and that of bound many-exciton complexes is that the emission band has a width governed by the kinetic energy of motion of the center of gravity of the complex. The maximum of the band is shifted towards longer wavelengths away from the end-point frequency by an amount $\Delta(\hbar\omega) = k_0 T/2n$. The emission-line half-width is also inversely proportional to n. With increasing n, the maximum of the band shifts more and more towards the end-point frequency, and its half-width decreases and tends to the "natural" line width. The last phenomenon is analogous to the Mössbauer effect on drops.[6] The presence of a gently sloping long-wave tail is connected with the band structure of the translational motion of the complex in the initial and final states. With decreasing temperature, the maximum of the band increases and shifts towards shorter wavelengths, and the half-width decreases. As $T \to 0$, the wave form of the luminescence band acquires the character of a δ-function. Just as for biexcitons,[5] the process of radiative recombination of FMEC should be characterized by a large oscillator strength.

If we consider the inverse process, namely absorption of light with transformation of a free n-exciton complex into an $(n+1)$-exciton complex, then we obtain for the shape of the absorption band $g(\omega)$ the expression

$$g(\omega) \sim G_{n+1,n}^{1/2} \exp\left[-(n+1)\frac{G_{n+1,n}}{k_0 T}\right] \qquad (3)$$

The maximum of the absorption band is shifted towards the long-wave region away from the end-point frequency ω_0 by an amount $\Delta(\hbar\omega) = k_0 T/2(n+1)$. Comparing (3) with (1) we can conclude that the behavior of the absorption band is analogous to the behavior of the luminescence band.

The regularities noted here become manifest in the case when the "natural" half-width due to scattering by phonons does not exceed the half-width due to the motion of the center of gravity of the complex. To observe FMEC in luminescence spectra it is necessary that the exciton line be very narrow, for example as narrow as the $n=1$ line of the yellow series in Cu_2O.

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