Luminescence Process

The absorption and the emission are related to each other and they are described by two terms which are complex conjugate of each other in the interaction Hamiltonian (H_{eR}). In an absorption process energy is removed from an incident e.m. wave while electron-hole pairs are created. Emission is the inverse of this process, i.e. an electron-hole pair inside the medium is destroyed with the emission of e.m. radiation (radiative recombination).

In a luminescence experiment one excites initially a nonequilibrium distribution of electron and hole (e-h) pairs in a semiconductor. In most cases the electrons and holes will thermalize among themselves and they reach quasi-thermal equilibrium in a short time compared to the time it takes for electrons and holes to recombine.
In the final step the e-h pairs recombine radiatively, producing the spontaneous emission. Thus a luminescence process involves three separate steps:

- Excitation: e-h pairs have to be excited by an external source of energy.
- Thermalization: the excited e-h pairs relax towards quasi-thermal equlibrium distributions.
- Recombination: the thermalized e-pairs recombine radiatively to produce the emission.

When the external excitation source is the e.m. radiation the process is called photoluminescence.

Direct vs Indirect Bandgap Materials

In a perfect semiconductor e-h pairs will thermalize and accumulate at the conduction and valence band extrema, where they tend to recombine.
If this semiconductor has a direct bandgap the e-h pairs will recombine radiatively with high probability. As a result, high quality direct-bandgap semiconductors, such as GaAs, are strongly emitters of bandgap radiation. They are important material for optoelectronic devices (lasers, LEDs).

In indirect bandgap semiconductors, such as Si and Ge, e-h pairs can recombine radiatively only via phonon-assisted transitions. Since the probability of these transitions is smaller than for competing nonradiative process, these materials are not efficient emitters. The indirect bandgap semiconductor GaP is an exception. In GaP the radiative transition can be enhanced by localizing the e-h pairs at defects such as isovalent N.

There is much ongoing effort to make Si a more efficient emitter of light fabricating Si in the form of nanometer-size crystallites known as nanocrystals. It is argued that by physically confining electrons and holes one can enhance their radiative recombination rate. One technique involves the electrolysis to produce a spongy form of Si known as porous Si. Unlike bulk Si, porous Si has been shown to produce efficient visible photoluminescence and electroluminescence (reasons are not clear)

Band-to-Band Transitions

In photoluminescence (PL) experiments one always excites equal numbers of electrons and holes. Since the intrinsic carrier concentrations n_i and p_i are usually very low, it is relatively easy to excite optically in an intrinsic semiconductor enough carriers that $n_e=n_h >> n_i=p_i$. In addition to radiative recombination decay processes, the photoexcited e-h pairs can also recombine nonradiatively. The total decay rate of the photoexcited polulation of e-h pairs is given by:

$$(1/\tau_{tot}) = (1/\tau_{rad}) + (1/\tau_{nonrad})$$

In nonradiative processes the energy of the e-h pair is dissipated as heat via excitation of phonons.

To calculate the shape of the band-to-band PL spectra, we shall assume a direct bandgap semiconductor with a gap E_g and joint density of states:

$$D_j \propto (E - E_g)^{1/2}$$

Let f_e and f_h represent the quasi-equilibrium energy distribution functions. For low photoexcitation density f_e and f_h can be approximately by Boltzmann distributions:

$$f_e \text{ or } f_h \propto \exp[-E/(kT)]$$

PL Spectrum Band-to-band Transition

$$I_{PL}(\omega) \propto \begin{Bmatrix} (\hbar\omega - E_g)^{1/2} \exp[-\hbar\omega/(kT)] \text{ for } \hbar\omega > E_g \\ 0 \end{Bmatrix}$$

where _ω is the emitted photon energy.

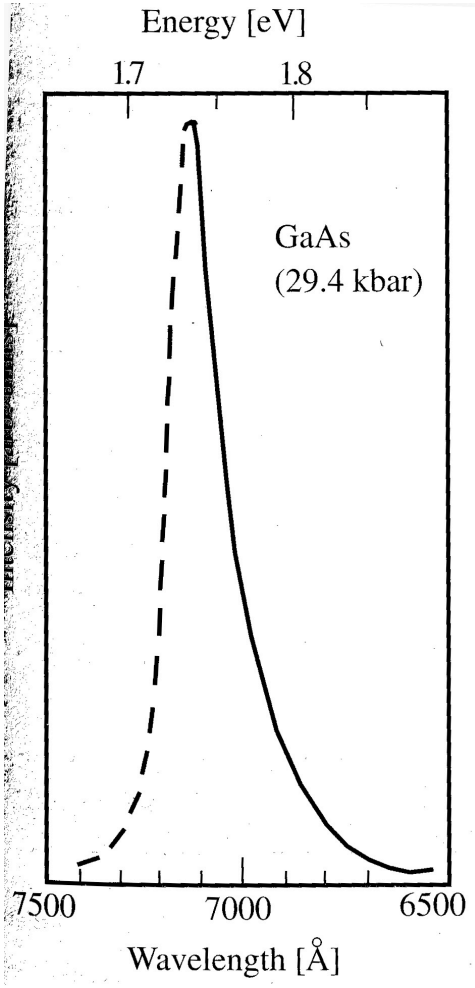


Fig. 7.3. Photoluminescence spectrum due to band-to-band transition in GaAs measured (*broken line*) at room temperature and a pressure of 29.4 kbar. The theoretical curve (*solid line*) is a plot of the expression (7.12) intensity, approximately proportional to $\exp[-\hbar\omega/(k_B T)]$, with $T = 373$ K. (From [7.16])

Free-to-bound Transitions

Band-to-band transitions tend to dominate at higher temperatures where all the shallow impurities are ionized. At sufficiently low temperatures, carriers are frozen on impurities. For example we consider a PL experiment on a p-type sample containing N_A acceptors per unit volume. At low photoexitation the density n_e of free electrons created in the conduction band is much smaller than N_A. These free electrons can recombine radiatively with the holes trapped on the acceptors. Such transitions, involving free carrier (in this case electrons) and a charge (a hole in this case) bound to an impurity, are known free-to-bound transitions. The emitted photon energy in this example is given by E_g-E_A, where E_A is the shallow acceptor binding energy. Thus, emission due to to free-to-bound transitions is a simple way of measuring impurity binding energy.

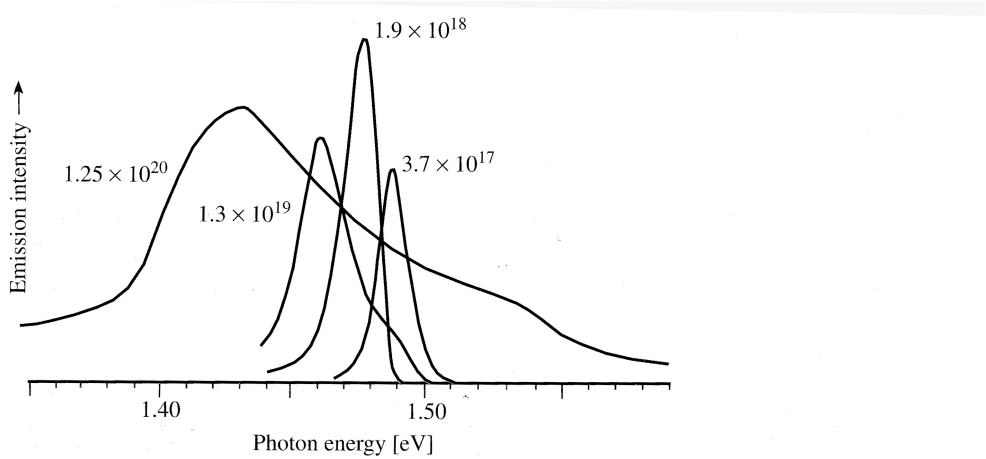


Fig. 7.4. Electroluminescence of p-type (Zn-doped) GaAs at 4.2K for increasing dopant concentrations in units of cm^{-3}. (From [Ref. 7.15, p. 136])

Donor-Acceptor Pair Transitions

Quite often a semiconductor may contain both donors and acceptors. Such semiconductors are said compensated because, under equilibrium conditions, some of the electrons from donors will be captured (or compensated) by the acceptors. As a result, a compensated sample contains both ionized donors (D^+) and acceptors (A^-).

By optical excitation, electrons and and holes can be created in the conduction and valence bands, respectively. These carriers can then be trapped at the D^+ and A^- sites to produce neutral D^0 and A^0 centers. In returning to equilibrium some of the electrons on the neutral donors will recombine radiatively with holes on the neutral acceptors. This process is known as a donor-acceptor pair transition (or DAP transition).
It can be represented by the reaction

$$D^0 + A^0 \rightarrow \hbar\omega + D^+ + A^- .$$

At first sight one may expect tha photon emitted in a DAP transition to have the energy

$$\hbar\omega = E_g - E_A - E_D .$$

In the above expression we have neglected the Coulomb interaction between the ionized donors and acceptors.

Donor-Acceptor Pair Transitions

$$\hbar\omega = E_g - E_A - E_D + e^2/(\varepsilon R)$$

The emitted photon energy is increased by the amount $e^2/(\varepsilon R)$ because the energy of the final state is lower by the Coulomb attraction.
Since the values of R are discrete, the DAP transitions produce a series of sharp peaks - converging towards the photon energy E_g-E_a-E_d (corresponding to R=∞).

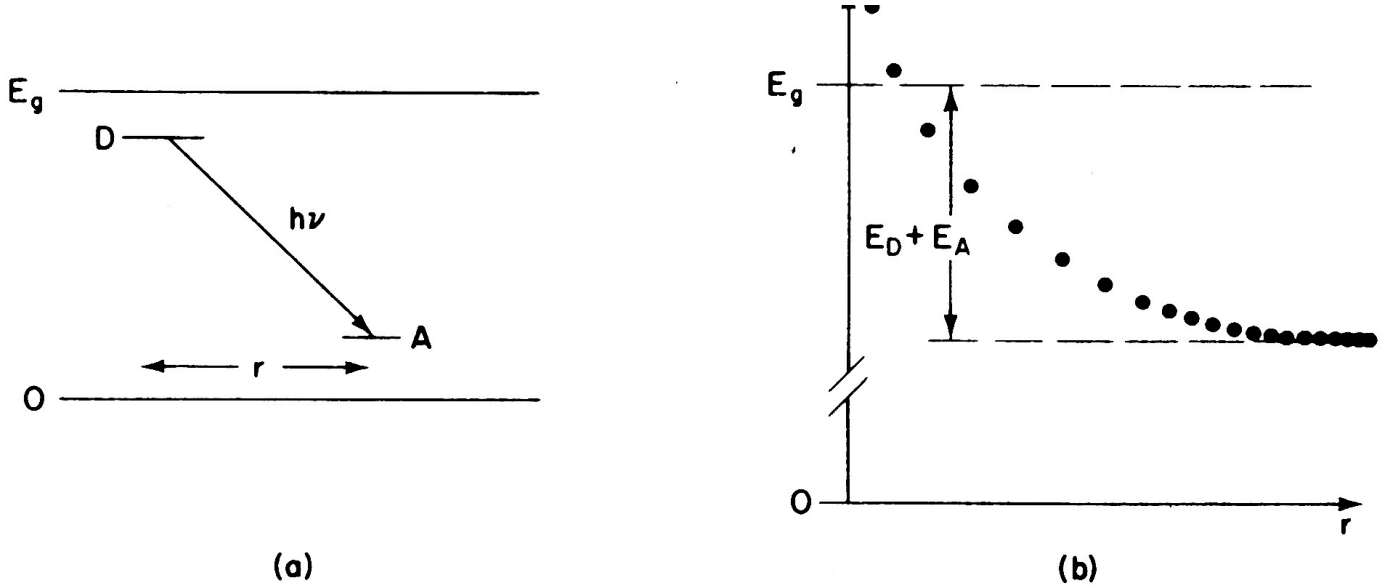


Fig. 6-38 (a) Donor-to-acceptor transition; (b) effect of coulomb interaction on emission energy (*r* is the donor–acceptor separation).

Donor-Acceptor Pair Transitions

At large values of R (>40Å) the emission lines overlap, forming a broad spectrum, while the discrete line structure can be resolved only for pair separations in the range of 10-40Å

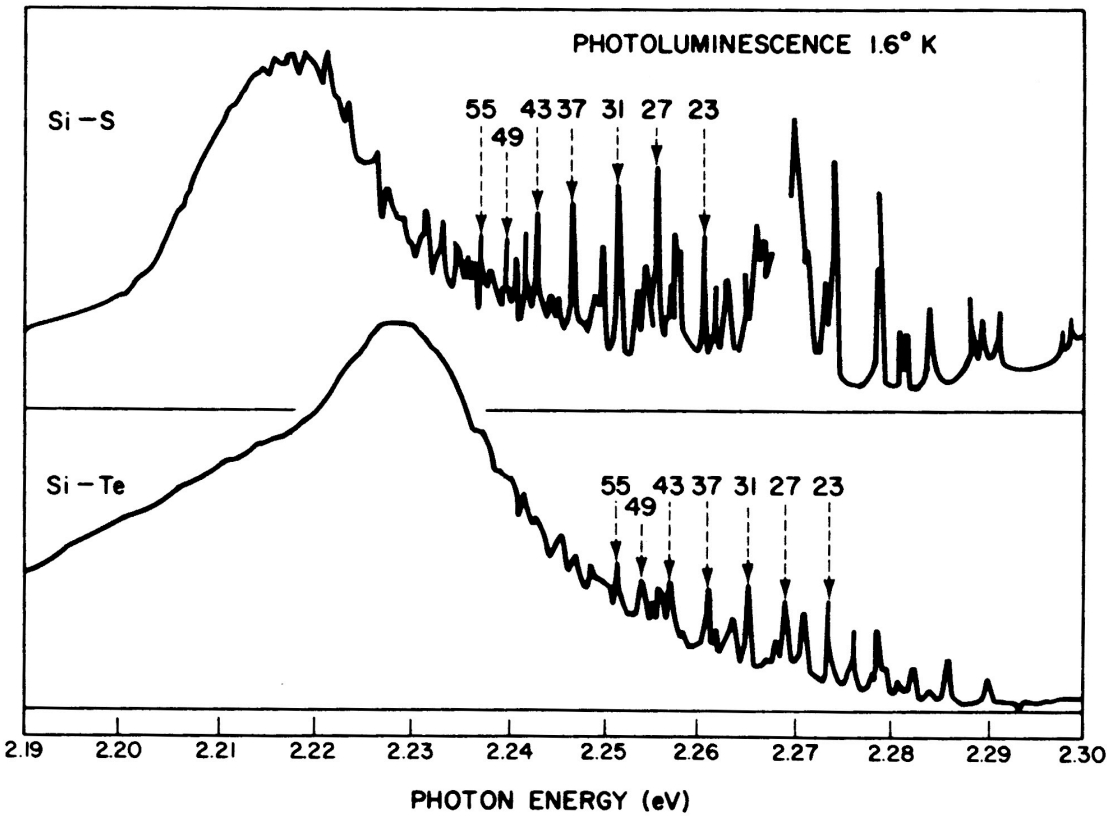


Fig. 6-39 Photoluminescence spectra of GaP crystals at 1.6°K, showing the isolated pair lines and the broad pair edge emission band corresponding to Si–S and Si–Te acceptor–donor combinations. Some of the shell numbers are given.[45]

Radiative Recombinations

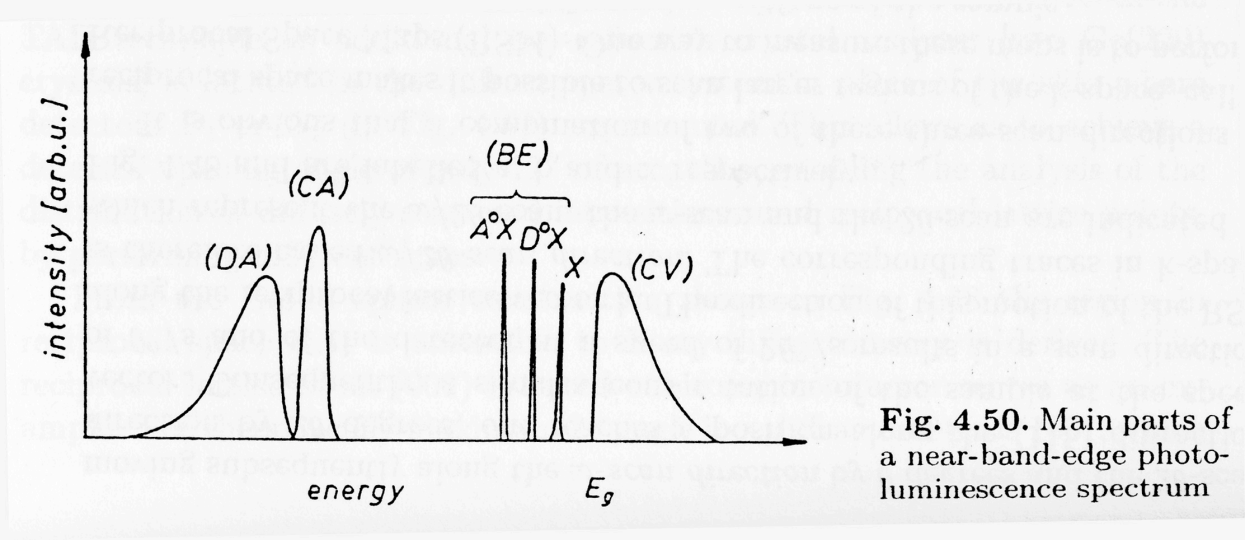


Fig. 4.50. Main parts of a near-band-edge photoluminescence spectrum

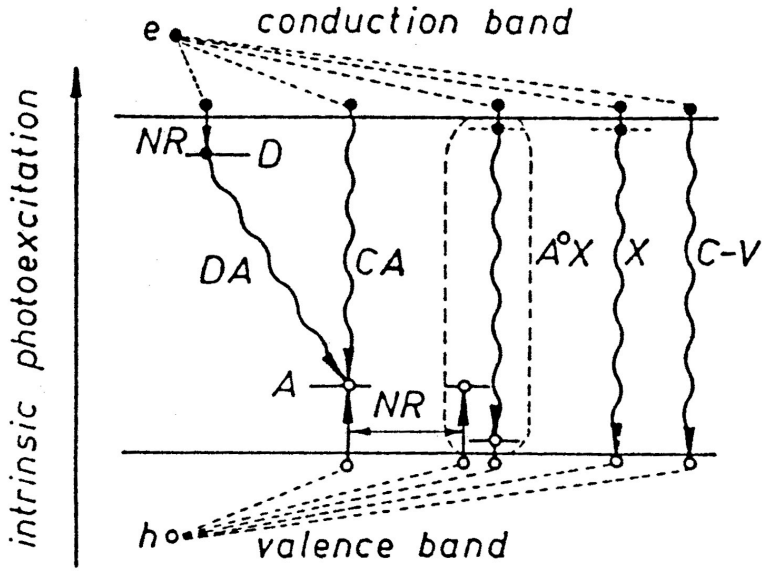


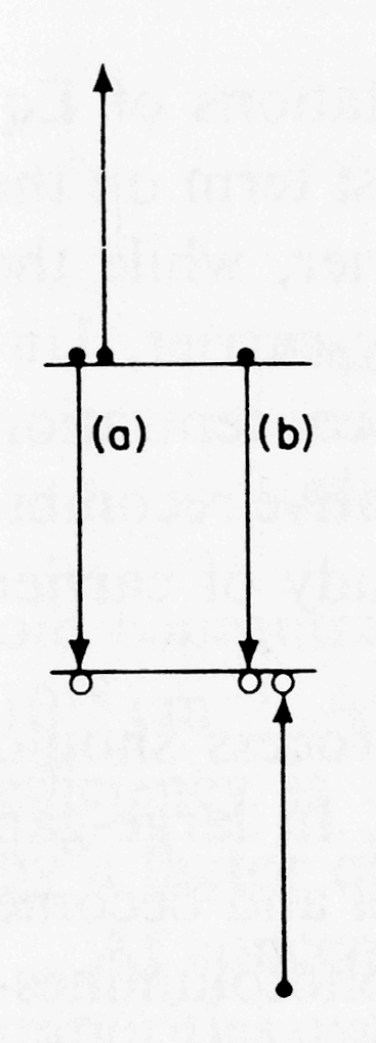
Fig. 4.51. Schematic representation of donor- or acceptor-related and direct radiative recombinations [4.215]

Nonradiative Recombination

An electron-hole pair can recombine nonradiatively (non emitting photons).

There are several recombination processes which do not result in external photon emission: Auger effect, surface recombination, and phonon emission.

Auger effect: the energy released by a recombining electron is immediately absorbed by another electron (three-body collision, involving two electrons and one hole, with no net photon emission).



Nonradiative Recombinations

Surface recombination

A surface is a strong perturbation of a lattice. High concentration of deep and shallow levels can occur and these may act as recombination centers.

Recombination through defects or inclusions (precipitates).

A macroscopic defect or inclusion could induce a deformation of the band structure producing a barrier (of height E*). Only hot carriers with sufficient energy to overcome this barrier (KT>E*) can recombine.

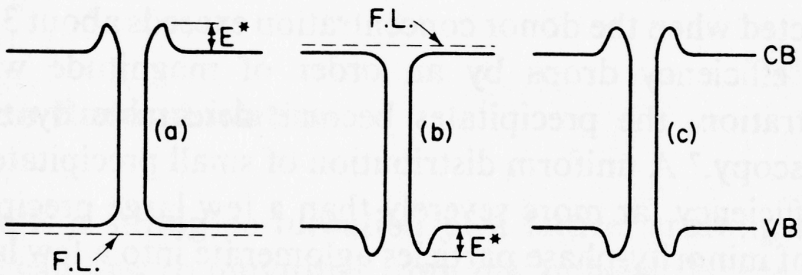


Fig. 7-5 Nonradiative recombination center surrounded by a barrier.