Chapter 4   Optical properties of materials

The optical properties of materials are displayed in plots of reflection, absorption, or transmission as a function of wavelength or frequency or energy, using linear or logarithmic axes. It is necessary to get used to experimental data being presented in a variety of ways!

4.1   Crystalline insulators

The transmission spectrum for sapphire (Al_2O_3) shows the typical features observed for all insulators and semiconductors, Fig. 4.1. There is high transmission in most of the wavelength range 0.2-6.0 μm. This is the transparency range of the crystal and lies within the bandgap. Hence, sapphire is colourless and transparent to the eye (colours in insulators usually come from dopants). By contrast, CdSe has a lower bandgap and is opaque for visible light.
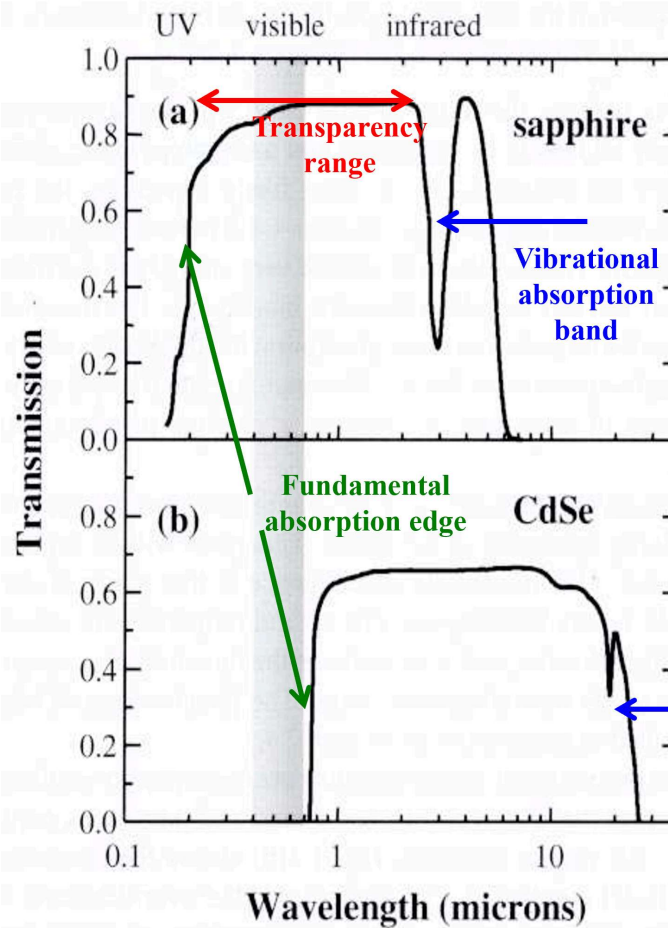
Figure 4.1: Top: transmission spectrum of a sapphire crystal 3 mm thick. Bottom: transmission of a CdSe crystal, 1.7 mm thick. Taken from Fox, Fig. 1.4. ●

The transparency drops sharply in the UV for $\lambda < 0.2$ μm due to absorption by bound electrons. The dip in the transmission at ~3 μm, and the sharp drop in transmission for $\lambda > 6$ μm, is caused by vibrational absorption; photons can resonantly drive a vibrational excitation (phonon) of the crystal lattice.

To give an idea of typical numbers, here are data for selected insulators.

Crystal	Transparency range (µm)	Index (n)
Al_2O_3 (sapphire)	0.2 -6	1.77
BaF_2	0.2 -12	1.48
Diamond	0.25 - >80	2.42
KI	0.3-40	1.67
KBr	0.21-25	1.49
MgF_2	0.12-8	1.38
NaCl	0.19-15	1.33
SiO_2 (quartz)	0.2-3	1.55
TiO_2 (rutile)	0.45-5	2.65

Figure 4.2: Transparency ranges of some crystalline insulators.

4.2 Semiconductors (bandgap < 4 eV)

 The optical properties of semiconductors (like CdSe) are similar to those of crystalline insulators, except that the electronic transitions occur at longer wavelengths.   Note that for CdSe the transparency range falls outside the visible range so we see a metallic-looking sample rather than a transparent crystal like sapphire, even though the overall properties are very similar.

In semiconductors with free carriers (electrons or holes thermally excited or introduced by doping)) free carrier absorption also reduces transmission in the infrared. The photon energy is transferred to kinetic energy of carriers within an energy band rather than exciting an electron between bands (lecture 8).

To give an idea of typical numbers, here are data for selected technologically important semiconductors

Crystal	Transparency range (µm)	Index (n)
Ge	1.8 - 23	4.00
Si	1.2 – 15	3.42
GaAs	1.0 – 20	3.16
CdTe	0.9 – 14	2.67
CdSe	0.75 - 24	2.50
ZnSe	0.45 – 20	2.41
GaN	0.4 – 13	2.3

Figure 4.3: Transparency ranges of some crystalline semiconductors.

4.3 Glasses

Many, very diverse materials can form glasses, but the glass we know best is made by fusing sand (silica: SiO_2) with other elements (the choice determines the refractive index and dispersion). Glasses exhibit optical properties of typical insulators but are not crystalline.

As an amorphous solid, the atomic structure of glass lacks any long range translational periodicity, as shown in Fig. 4.4. However, the local chemical bonding constrains the possible atomic positions so that glasses do possess a high degree of short-range order. For example, in

silica there is a tetrahedral arrangement of oxygen atoms around the silicon atoms, whereas in selenium, the atoms form chains.
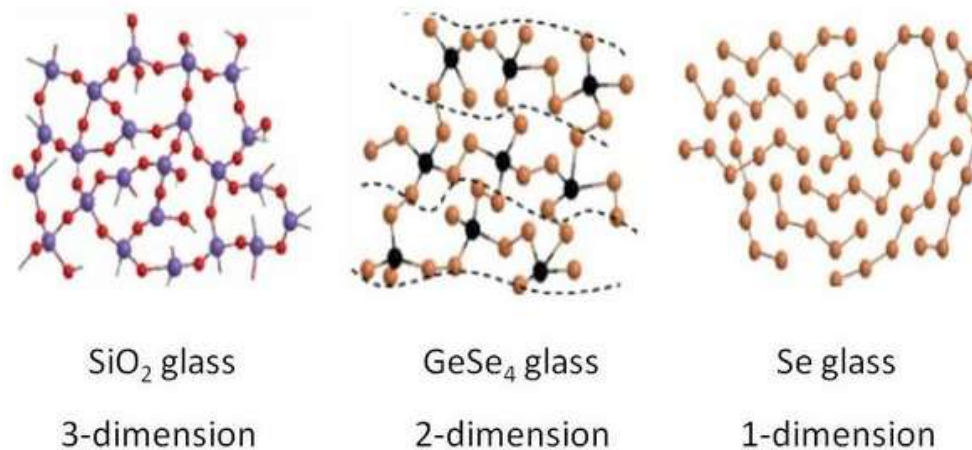

Figure 4.4: Schematic structure of SiO_2 glass (also known as fused silica), amorphous $GeSe_4$ and amorphous Se. ●

4.4   Doped glasses and doped crystalline insulators

Coloured glass filters and stained glass are made by the addition of semiconductors and other dopants. Colour may be controlled by:

- Varying the composition of the dopant e.g. an alloy semiconductor like $Cd_xZn_{1-x}Se$ where the bandgap is tuned by varying x.

- Changing the size of semiconductor crystallites (quantum dots) within the glass. "Quantum size effects" occur when crystallite size is comparable to electron wavelength and change the bandgap.

- Transition metal and rare earth ions are used extensively to dope glasses and insulating crystals to make solid state laser materials. Some gemstones owe their colour to transition metal impurities. Here, discrete optical transitions of isolated impurity atoms are broadened to give absorption bands, Fig.4.5..
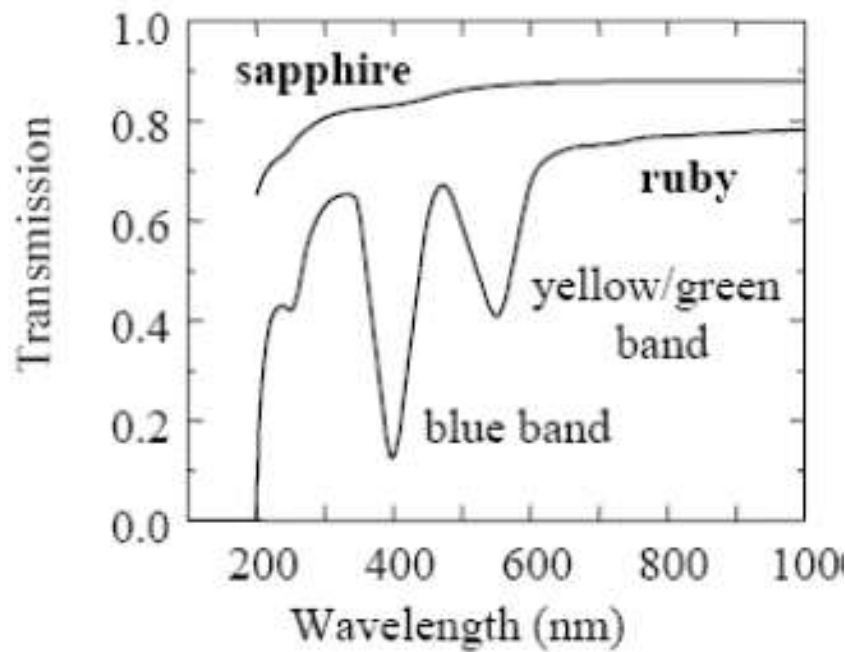
Figure 4.5: Ruby: Al2O3 (sapphire) with 0.05% Cr3+ appears red because it absorbs in the blue and yellow/green regions. ●

There are two major broadening mechanisms:

- Coupling of the dopant electronic energy levels to lattice vibrations
- Crystal field effects i.e, the electric fields produced by neighbouring atoms shift the dopant electronic energies (Stark effect).

Common dopants in laser gain media are

- rare earth ions e.g. Nd^{3+}, atomic configuration $[Xe]4f^3$ (common host - yttrium aluminium garnate)
- Transition metal ions e.g. Ti^{3+}, atomic configuration $[Ar]3d^1$ (common host: sapphire)

$3d$ orbitals are more extended and less shielded by other electrons than $4f$ so that crystal field broadening is much greater in transition metal ions than in rare earth ions.

4.5 Metals

Metals typically have a high reflectivity in the visible range below a characteristic frequency called the plasma frequency, due to the interaction of light with *free* electrons.

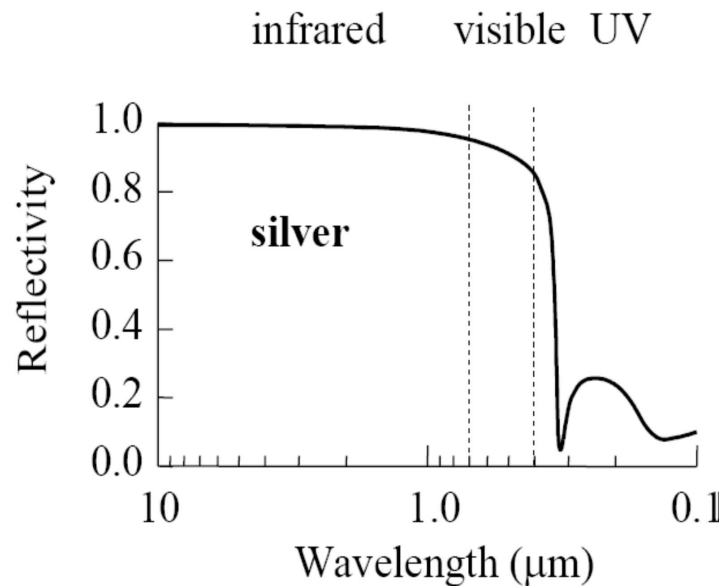For silver, the reflectivity is close to 100% in the infrared, Fig. 4.6.

Figure 4.6: Reflectivity of silver from the infrared to the ultraviolet. From Fox, Fig. 1.5. ● The reflectivity starts to fall in the visible spectrum where interband transitions (responsible for metal colour) occur and drops sharply in the ultraviolet, where metals are transparent.

4.6   Molecular (organic) materials

Organic compounds (those based on carbon-carbon bonds) can be crystalline or amorphous. Covalent bonds within molecules are strong but molecules are bonded to each other by weak van der Waal's forces so that optical properties of molecular solids are similar to those of constituent molecules.

Organic materials can be classified as *saturated* : valence electrons form strong localised bonds between atoms; *conjugated*: bonding is based on delocalised orbitals spread over the whole molecule and is weaker. Conjugated polymers are the basis of organic electronics, Fig. 4.7.
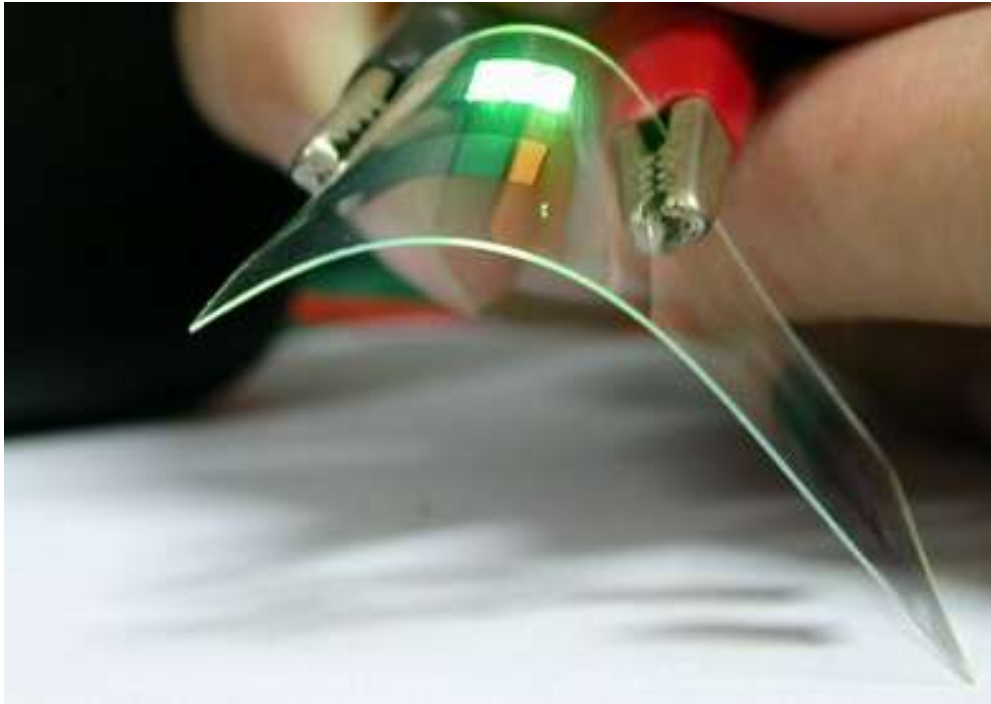
Figure 4.7: Organic light emitting diode: flexible electronics. ●

4.6.1 The HOMO-LUMO gap

In organic materials, the energy levels are those of a vibrationally broadened single molecule. Optical transitions generally involve changes in both electronic and vibrational states, and there is no conventional band gap because electrons are localised on molecules, rather than occupying band states delocalised through the whole material.

There is however an energy gap between the highest occupied (HO) and lowest unoccupied (LU) molecular orbitals (MO). Strong binding means that *saturated* molecular solids have this HOMO-LUMO gap in the ultraviolet, e.g. common plastics such as polythene. *Conjugated* molecules can have gaps in the visible spectrum because of weaker binding – they are used in fluorescent dyes and OLED TVs.

4.7 Luminescence

In a semiconductor picture, luminescence involves the recombination of conduction band (CB) electron with valence band (VB) hole. So, one might expect the emitted photon energy to be that of the (direct) band gap E_G (as measured by absorption measurements).

However, the emitted photon energy is usually lower than the incident photon energy and one reason for this is the formation of an exciton by the electron-hole pair before it recombines.

4.7.1 Excitonic PL and point defects

Photoexcited electrons and holes bind (via their Coulomb attraction) to form *excitons* (H atom-like). Excitons are roughly analogous to a hydrogen atom but the exciton binding energy E_x is typically ~ 10^{-3} Rydberg and the exciton Bohr radius is much larger than that of H. If R_H is the Rydberg constant for the hydrogen atoms, we can write the binding energy and Rydberg for the exciton as follows:

$$E_x = -\frac{R_x}{n^2}$$
$$R_x = R_H \frac{\mu}{m_0 \varepsilon_r^2}. \qquad (4.1)$$

This can generate optical transitions (absorption or PL) at an energy below the band gap, $E_{PL} = E_G - R_x/n^2$. Often this effect is only clear at low temperature, but can modify the optical absorption even at room temperature, Fig. 4.8.
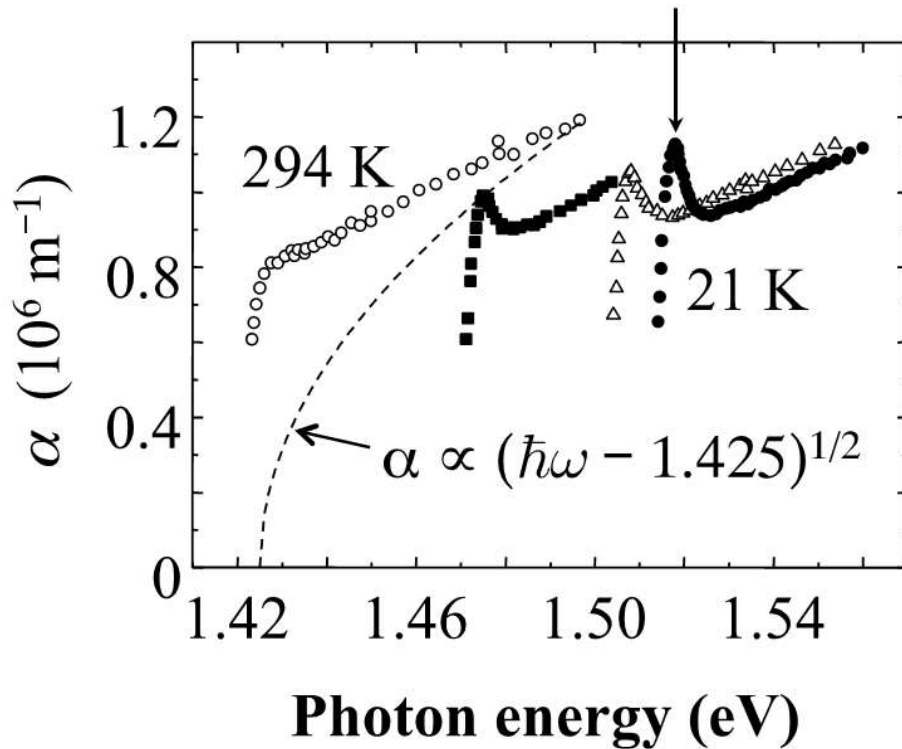

Figure 4.8: Experimental absoprtion spectra of GaAs as a function of temperature, showing the $n = 1$ exciton developing at low temperature. ●

Excitons are classified into two types:

- **weakly bound** (Wannier) with high screening of the Coulomb interaction (large ε_r) and low reduced mass μ (typical of compound inorganic semiconductors)
- **tightly bound** (Frenkel), with high reduced effective mass (typical of molecular systems).

Small μ
Large ε$_r$ Semiconductors

Large μ   Insulators(e.g. alkali halides)
Small ε$_r$ Molecular crystals

a

Free (Wannier)
radius >> a
small binding energy
moves freely through crystal

Tightly-bound (Frenkel)
radius ~ a
large binding energy
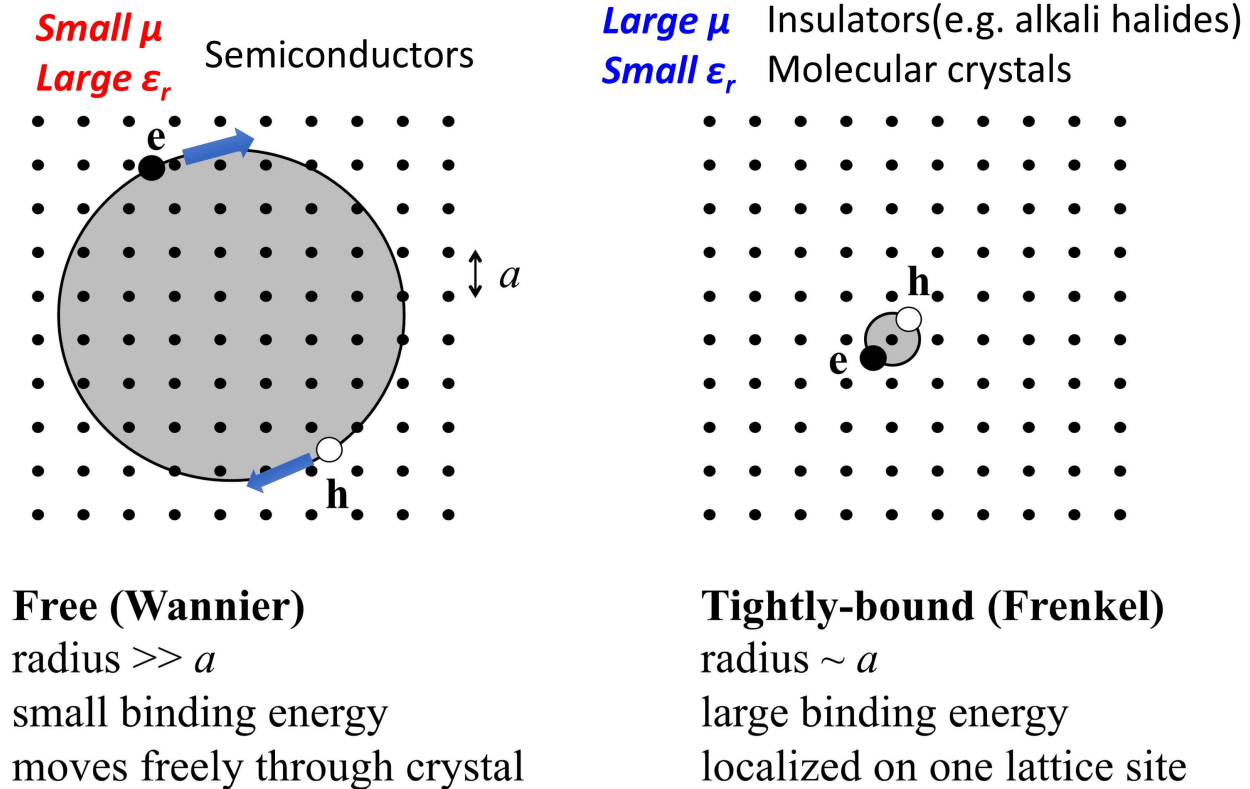localized on one lattice site

Figure 4.9: Schematic view of Wannier and Frenkel excitons. ●

Excitons can themselves bind to impurities (donors, acceptors) or vacancies, especially at low temperatures; these can be analogous to H_2 and PL from bound excitons is an extremely sensitive and useful diagnostic of those impurities. A striking example is provided by GaP, Fig. 4.10.
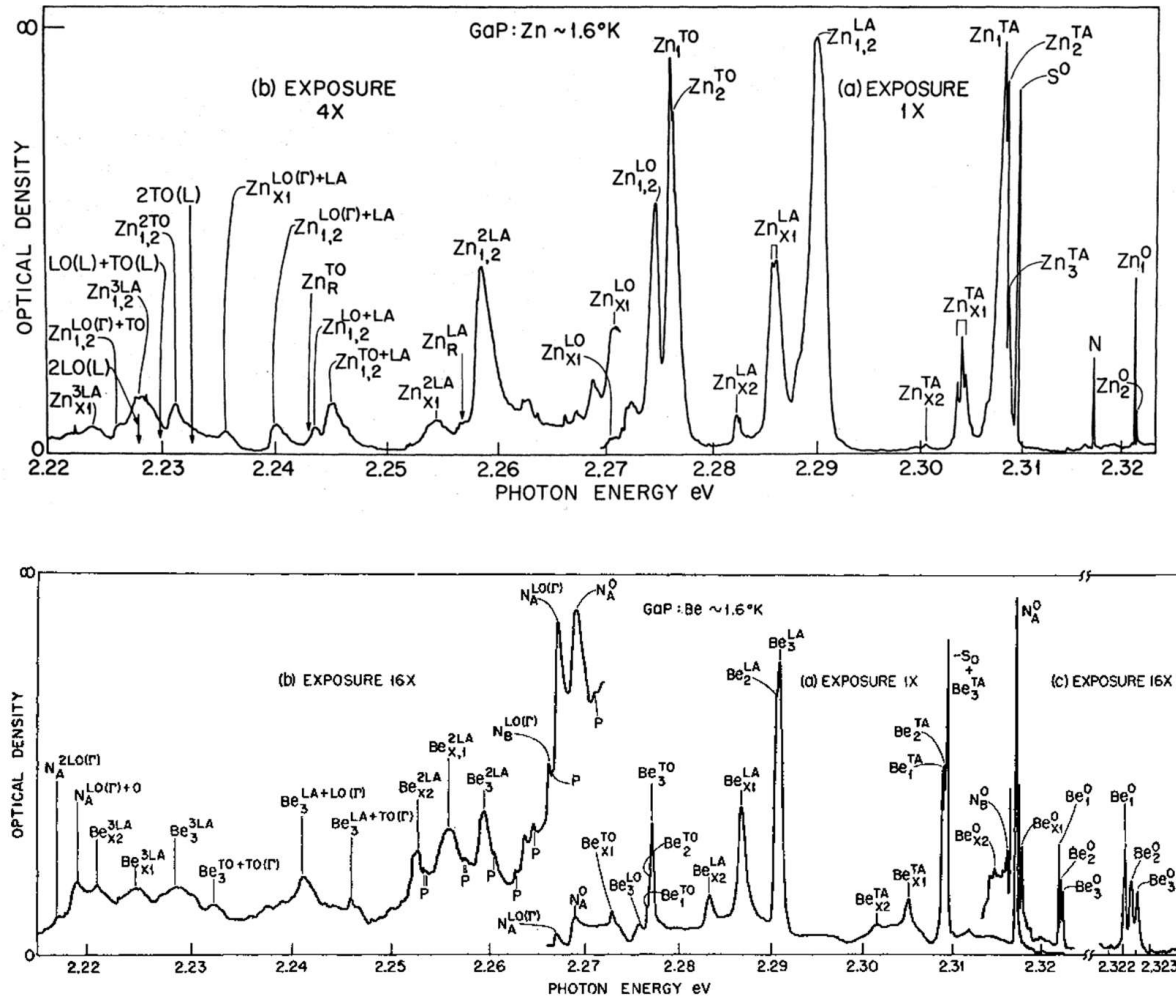
Figure 4.10: Photoluminescence of excitons bound to neutral acceptors in gallium phosphides (GaP) doped with zinc, measured at 1.6 K. Source: https://journals.aps.org/prb/abstract/10.1103/PhysRevB.4.1926 ●

4.7.2 Models of PL dynamics

A simple model of the PL process shows how it can be used to provide both *energetic* and *dynamical* information about photoexcited carriers. If carriers are generated at rate g and recombine with rate $1/\tau$, then a differential equation for the number of photoexcited carriers n can be written as follows:
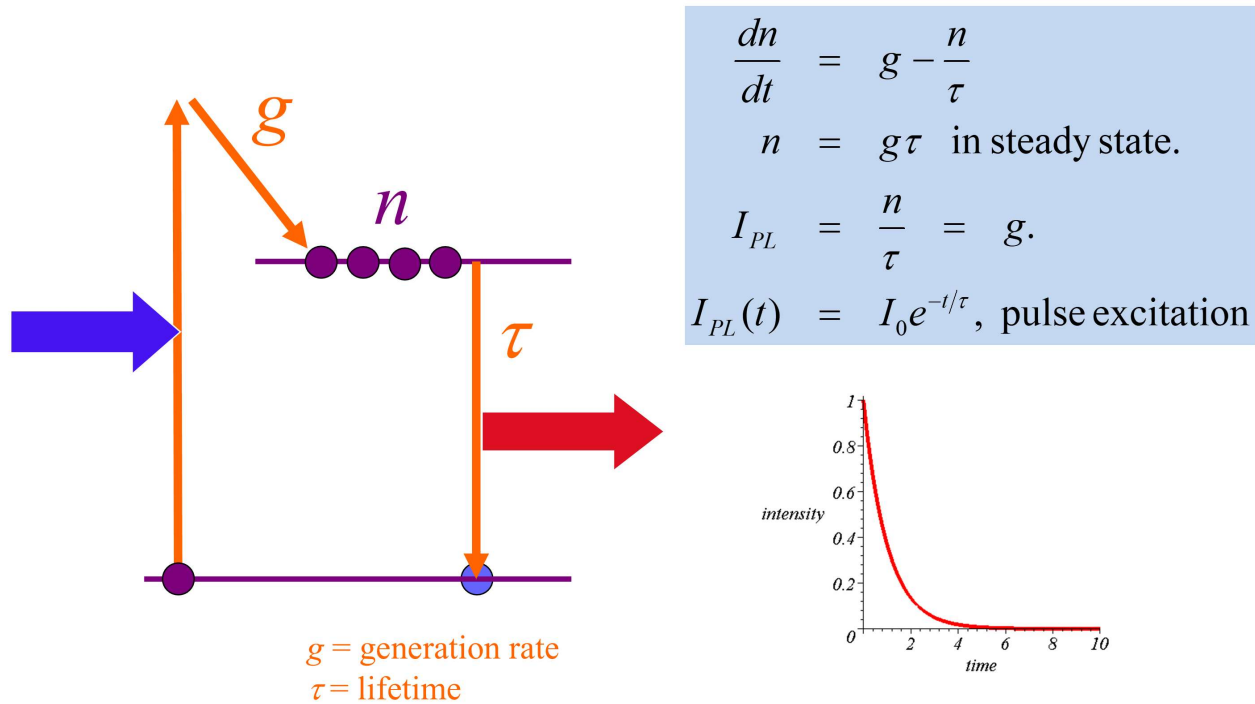
$$\frac{dn}{dt} = g - \frac{n}{\tau}$$

$$n = g\tau \quad \text{in steady state.}$$

$$I_{PL} = \frac{n}{\tau} = g.$$

$$I_{PL}(t) = I_0 e^{-t/\tau}, \quad \text{pulse excitation}$$

g = generation rate
τ = lifetime

Figure 4.11: PL model without non-radiative recombination. ●

Fig. 4.11 shows how expressions for the PL intensity (i) in steady state and (ii) after an excitation pulse can be modelled. In the second case, measurement of $I(t)$ gives the recombination rate rate $1/\tau$; the parameter τ is referred to as the *radiative lifetime*. These expressions are obviously rather trivial if radiative recombination is the only possible outcome.
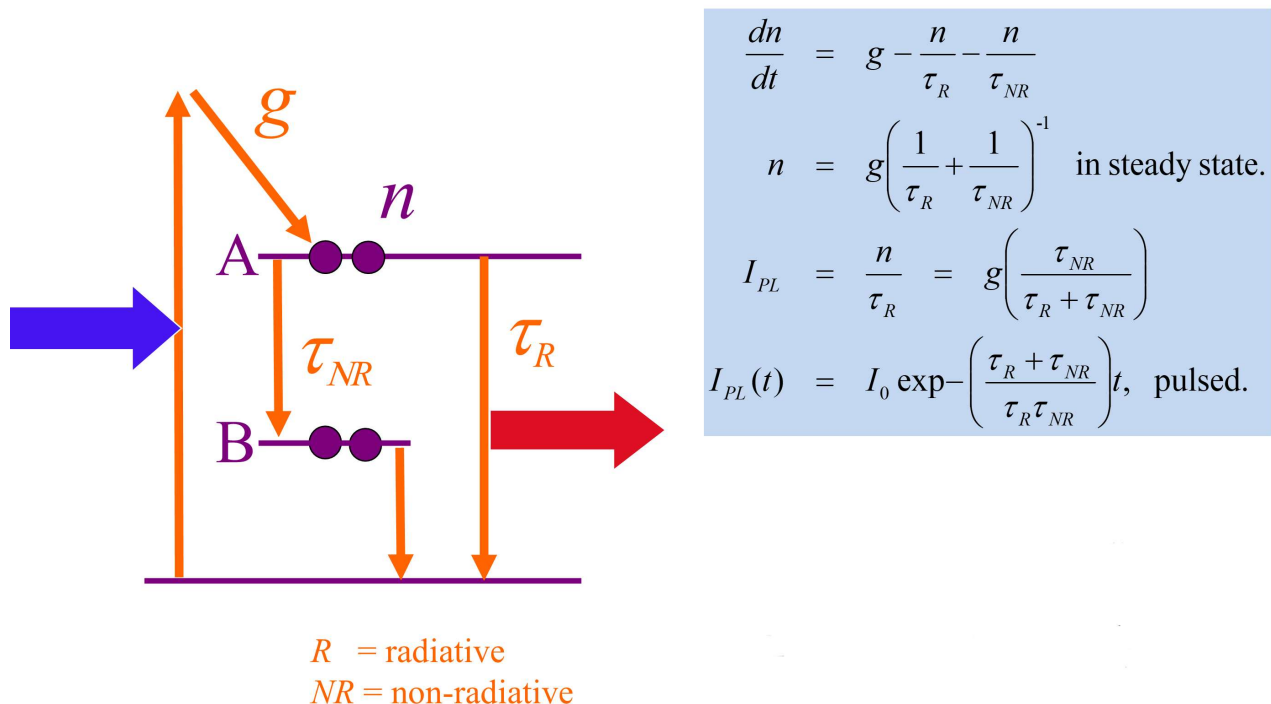

$$\frac{dn}{dt} = g - \frac{n}{\tau_R} - \frac{n}{\tau_{NR}}$$

$$n = g\left(\frac{1}{\tau_R} + \frac{1}{\tau_{NR}}\right)^{-1} \quad \text{in steady state.}$$

$$I_{PL} = \frac{n}{\tau_R} = g\left(\frac{\tau_{NR}}{\tau_R + \tau_{NR}}\right)$$

$$I_{PL}(t) = I_0 \exp-\left(\frac{\tau_R + \tau_{NR}}{\tau_R \tau_{NR}}\right)t, \quad \text{pulsed.}$$

R = radiative
NR = non-radiative

Figure 4.12: PL model including non-radiative recombination. ●

Fig. 4.12 shows how we can include non-radiative recombination; we allow for two competing recombination pathways, with lifetimes τ_R and τ_{NR}, of which only one results in PL being emitted. These lifetimes are often strongly dependent on temperature, and the temperature also affects the probability of re-excitation from level B back to level A. This is a key reason why the results of Fig. 4.10 had to be obtained at $T = 1.6$K.

We can define a *quantum efficiency* η for the PL process as the probability of a photon being emitted after one is absorbed; in this second case, $\eta = \tau_{NR}/(\tau_R + \tau_{NR})$.