12.1 INTRODUCTION

12.1.1 Basic Concepts

A material, after absorbing some energy, can become a source of light by two processes:

1. The absorbed energy is converted into low quantum energy heat that diffuses through the material, which then emits thermal radiation.
2. The absorbed energy is in part localized as high quantum energy of atoms, which then emits radiation called luminescence radiation.

We note the following:

1. The quantity and quality of thermal radiation depend primarily on the temperature rather than on the nature of the body.
2. The quality and quantity of luminescence radiation are strongly dependent on the nature of the emitting material.

Therefore, the results of investigations in the field of luminescence are relevant to the study of material bodies. The process of luminescence is started by exciting the material with UV radiation, X-rays, electrons, alpha particles, electric fields, or energy that is liberated in chemical reactions. Accordingly, luminescence is qualified as photoluminescence, Roentgen luminescence, electroluminescence, and so on. We shall limit ourselves to examining the process of photoluminescence in solids, i.e., the luminescence emission that follows the absorption of UV or optical radiation.

We have found it convenient from a pedagogical point of view to subdivide the luminescent systems into two categories, localized and delocalized. For the first category, the absorption and emission processes are associated with quantum states of optically active centers that are spatially localized to particular
sites in the solid. For the second category, these processes are associated with quantum states of the entire solid.

Regardless of the type of excitation or the nature of the system, the common character of the phenomenon of luminescence resides in the fact that, once excited, the system is left alone, without any external influence and, in this condition, it emits radiation that we may appropriately call *spontaneous*.

The purpose of this chapter is to describe the basic themes that motivate the investigations in luminescence spectroscopy, the techniques that are used to conduct these investigations and the challenges that are presented by this field of research.

In the introduction we consider the nature of luminescence research and emphasize its material-related character. We also recount briefly the history of the research in this field. In Section 12.2, we set up the theoretical bases for the treatment of the interaction of radiation with material systems. In Section 12.3, we consider the measurements that are conducted in luminescence spectroscopy and examine their simplest and fundamental aspects, apart from their more advanced technical features. We dedicate the next two Sections, 12.4 and 12.5, to the treatment of localized luminescent systems in which the radiative processes are associated with optically active centers. In the following two Sections, 12.6 and 12.7, we treat the delocalized systems in which the radiative processes are associated with quantum states of the entire solid. Finally, in Section 12.8 we consider the challenges presented by this field of research, suggesting directions of future efforts and recognizing the fact that luminescence spectroscopy is an inexhaustible source of problems for future investigations and educational applications.

### 12.1.2 History

The first reported observation of luminescent light from glowworms and fireflies is in the Chinese book *Shih-Ching* or “Book of Poems” (1200–1100 B.C.). Aristotle (384–322 B.C.) reported the observation of light from decaying fish. The first inquiry into luminescence dates circa. 1603 and was made by Vincenzo Cascariolo. Cascariolo’s interests were other than scientific: He wanted to find the so-called “philosopher’s stone” that would convert any metal into gold. He found some silvery white stones (barite) on Mount Paderno, near Bologna, which, when pulverized, heated with coal, and cooled, showed a purple-blue glow at night. This process amounted to reduction of barium sulfate to give a weakly luminescent barium sulfide:

\[
\text{BaSO}_4 + 2\text{C} \rightarrow \text{BaS} + 2\text{CO}_2
\]

News of this material, the “Bologna stone,” and some samples of it reached Galileo, who passed them to Giulio Cesare Lagalla. Lagalla called it “lapis solaris” and wrote about it in his book *De phenomenis in orbe lunae* (1612).
It is rare the case when one can insert in a scientific article a literary citation. This happens to be the case here. In *The Sorrows of Young Werther* of Goethe, the protagonist is unable to see the woman he loves because of an engagement he cannot refuse, and sends a servant to her, “only so that I might have someone near me who had been in her presence…” This is then his reaction when the servant comes back:

It is said that the *Bologna stone*, when placed in the sun, absorbs the sun’s rays and is luminous for a while in the dark. I felt the same with the boy. The consciousness that her eyes had rested on his face, his cheeks, the buttons of his jacket and the collar of his overcoat, made all these sacred and precious to me. At that moment I would not have parted with him for a thousand taler. I felt so happy in his presence.

The second important investigation on luminescence is due to Stokes and dates to the year 1852. Stokes observed that the mineral fluorspar (or fluorite) when illuminated by blue light gave out yellow light. Fluorite (CaF$_2$) is colorless in its purest form, but it absorbs and emits light when it contains such impurities as Mn, Ce, Er, etc. The term “fluorescence” was coined by Stokes and has continued to be used to indicate short-lived luminescence. A *Stokes’ law* has been formulated according to which the wavelengths of the emitted light are always longer than the wavelength of the absorbed light.

### 12.2 SPONTANEOUS EMISSION, ABSORPTION, AND INDUCED EMISSION

#### 12.2.1 Classical Bound, Radiating Electron

Let us consider first the equation of motion of a classical *bound* electron that we assume to be *nonradiating*:

\[ F = -kx = m \frac{d^2x}{dt^2} \]  \hspace{1cm} (12.1)

or

\[ \frac{d^2x}{dt^2} + \omega_0^2 x = 0 \]  \hspace{1cm} (12.2)

where

\[ \omega_0 = \sqrt{\frac{k}{m}}. \]  \hspace{1cm} (12.3)

The energy is given by
We take as solution to the equation of motion (12.1),

\[ x = x_0 \cos(\omega_0 t). \] (12.5)

This means that at time \( t = 0 \), \( x = x_0 \), and \( v = 0 \); the energy is then given by

\[ E = \frac{1}{2} k x_0^2 = \frac{1}{2} m \omega_0^2 x_0^2 \] (12.6)

A radiating electron will produce radiation due to the vibrating dipole

\[ d = \omega_0 x_0 \cos(\omega_0 t) = \Re \omega_0 e^{i\omega_0 t} \] (12.7)

The average energy radiated in the unit time is given by

\[ \bar{S} = \frac{2 \left( \ddot{d} \right)^2}{3c^3} = \frac{\omega_0^4 e^2 x_0^2}{3c^3}. \] (12.8)

The radiated energy is given out at the expense of the internal energy of the electron:

\[ \bar{S} = -\frac{\partial E}{\partial t} \left( E = \frac{1}{2} m \omega_0^2 x_0^2 \right) \] (12.9)

or

\[ \frac{\omega_0^4 e^2 x_0^2}{3c^3} = -m \omega_0^2 x_0 \frac{\partial x_0}{\partial t} \]

\[ \dot{x}_0 = -\frac{\omega_0^2 e^2}{3c^3} x_0 \] (12.10)

We can write

\[ \dot{x}_0 = -\frac{1}{2} \gamma x_0 \] (12.11)

where

\[ \gamma = \frac{2 \omega_0^2 e^2}{3mc^3} = \frac{2 \omega_0^2 e^2}{3c} \frac{1}{mc^2} = \frac{2 \omega_0^2}{3c} r_0 = \frac{2 \omega_0^2}{3} \tau \] (12.12)

and

\[ r_0 = \frac{\epsilon^2}{mc^2} = 2.8 \times 10^{-13} \text{ cm}, \]

\[ \tau = \frac{r_0}{c} = 9.38 \times 10^{-24} \text{ sec}. \]
If $\lambda = 6000$ Å, $\omega_0 = 3 \times 10^{15}$, and $\gamma = 0.6 \times 10^8$ sec$^{-1}$, the solution of (12.11) is 

$$x_0 = X_0 e^{-\frac{t}{2\gamma}}$$

Therefore, 

$$E = \frac{1}{2} m \omega_0^2 x_0^2 - \frac{1}{2} m \omega_0^2 \left( X_0 e^{-\frac{t}{2\gamma}} \right)^2$$

$$= \frac{1}{2} m \omega_0^2 X_0^2 e^{-\gamma t} = E_0 e^{-\gamma t}$$

where 

$$E_0 = \frac{1}{2} m \omega_0^2 X_0^2.$$ 

$\gamma$ is the rate of radiative decay for the classical electron.

The equation of motion, equation (12.1), needs a revision on account of the presence of radiation. We proceed as follows:

$$x = X_0 e^{-\frac{t}{2\gamma}} \cos(\omega_0 t)$$  

$$\dot{x} = -\frac{\gamma}{2} x - \omega_0 X_0 e^{-\frac{t}{2\gamma}} \sin(\omega_0 t)$$

and

$$\frac{\gamma}{2} \ddot{x} = - \left( \frac{\gamma}{2} \right)^2 x - \omega_0 \frac{\gamma}{2} X_0 e^{-\frac{t}{2\gamma}} \sin(\omega_0 t)$$

$$\ddot{x} = - \frac{\gamma}{2} \dot{x} + \omega_0 \frac{\gamma}{2} X_0 e^{-\frac{t}{2\gamma}} \sin(\omega_0 t) - \omega_0^2 x.$$ 

Summing the above two relations we obtain 

$$\ddot{x} + \gamma \dot{x} + \left[ \omega_0^2 + \left( \frac{\gamma}{2} \right)^2 \right] x = 0,$$

which represents the equation of motion of the radiating, bound electron.

### 12.2.2 Quantum Mechanical Radiative Decay

Consider a two-level quantum system, where the energy and the eigenfunction of the lower (upper) level are $E_a$ ($E_b$) and $\psi_a$ ($\psi_b$), respectively. If $\psi$ is the wavefunction of the system, then
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\[ i\hbar \frac{\partial \psi}{\partial t} = H\psi \]  \hspace{1cm} (12.21)

where

\[
\begin{cases}
H\psi_a = E_a\psi_a \\
H\psi_b = E_b\psi_b.
\end{cases}
\]  \hspace{1cm} (12.22)

In general, a quantum state of the system is given by

\[
\psi = ae^{-\frac{i}{\hbar}E_a t}\psi_a + be^{-\frac{i}{\hbar}E_b t}\psi_b.
\]  \hspace{1cm} (12.23)

For a non-radiating system, \(H\) is independent of time:

\[
\begin{cases}
\dot{a} = 0 \rightarrow a = \text{const} \\
\dot{b} = 0 \rightarrow b = \text{const}
\end{cases}
\]  \hspace{1cm} (12.24)

and

\[
\langle H \rangle = |a|^2E_a + |b|^2E_b = \text{const}.
\]  \hspace{1cm} (12.25)

Let us now allow for dipolar radiation

\[
\langle ex \rangle = \langle \psi |ex| \psi \rangle = \int \left[a e^{-\frac{i}{\hbar}E_a t}\psi_a + b e^{-\frac{i}{\hbar}E_b t}\psi_b \right] \exp \left[a e^{-\frac{i}{\hbar}E_a t}\psi_a + b e^{-\frac{i}{\hbar}E_b t}\psi_b \right] dt
\]

\[
= a^*b e^{-im\Delta}\mu_{ab} + ab^* e^{im\Delta}\mu_{ba}
\]

\[
= \text{Re} \left[ d_0 e^{-i\omega_0} \right]
\]  \hspace{1cm} (12.26)

where

\[
\omega_0 = \frac{(E_b - E_a)}{\hbar}
\]  \hspace{1cm} (12.27)

\[
\mu_{ab} = \langle \psi_a |ex| \psi_b \rangle
\]  \hspace{1cm} (12.28)

\[
\mu_{ba} = \langle \psi_b |ex| \psi_a \rangle
\]  \hspace{1cm} (12.29)

\[
d_0 = 2a^*b \mu_{ab}
\]  \hspace{1cm} (12.30)

and where we have assumed

\[
\mu_{aa} = \mu_{bb} = 0.
\]  \hspace{1cm} (12.31)

We have now from equation (12.8)

\[
S = \frac{\omega_0^4 |d_0|^2 d_0^*}{3c^3} = \frac{4\omega_0^4 |\mu_{ab}|^2 |a|^2 |b|^2}{3c^3}
\]

\[
= \frac{4\omega_0^4 |\mu_{ab}|^2 |b|^2 (1 - |b|^2)}{3c^3} = \frac{4\omega_0^4 |\mu_{ab}|^2 |b|^2}{3c^3}
\]  \hspace{1cm} (12.32)
assuming \( |b|^2 \ll 1 \). We can choose the phase of \( \Psi_b \) that makes \( b \) real:

\[
\bar{S} = \frac{4\omega_0^4 |\mu_{ab}|^2}{3c^3} b^2. \tag{12.33}
\]

The energy of the system is given by

\[
E = \langle H \rangle = b^2 E_b + a^2 E_a = b^2 E_b + (1 - b)^2 E_a \tag{12.34}
\]

If we set \( E_a = 0 \), we obtain

\[
E = b^2 \hbar \omega_0, \tag{12.35}
\]

which can be contrasted with the classical formula (equation (12.6)). For non-radiating systems, \( E \) remains constant. For radiating systems

\[
\bar{S} = -\frac{\partial E}{\partial t} = -2b \frac{\partial}{\partial t} \hbar \omega_0 = \frac{4\omega_0^4 |\mu|^2}{3c^3} b^2 \tag{12.36}
\]

where we have dropped the subscript \( \alpha \beta \) from \( \mu \). Then

\[
\frac{\partial b}{\partial t} = -\frac{1}{2} \gamma b \tag{12.37}
\]

where

\[
\gamma = \frac{4\omega_0^3 |\mu|^2}{3c^3 \hbar}. \tag{12.38}
\]

The solution of equation (12.37) is

\[
b = b_0 e^{\gamma t} \tag{12.39}
\]

and

\[
b^2 = b_0^2 e^{-\gamma t}. \tag{12.40}
\]

\( b^2 \) represents the probability of occupancy of the excited state. \( \gamma \) is the quantum mechanical rate of radiative decay or spontaneous emission. We may equate it to the Einstein coefficient \( A \):

\[
\gamma = A = \frac{4\omega_0^3 |\mu|^2}{3hc^3} = \frac{64\pi^4 v^3 |\mu|^2}{3hc^3} = \frac{64\pi^4 |\mu|^2}{3\hbar c^3} \tag{12.41}
\]

In a nonmagnetic medium of index of refraction \( n \) an oscillating dipole emits the power

\[
S = \frac{2 (\bar{d})}{3c^3} n \tag{12.42}
\]

whose time average is

\[
\bar{S} = \frac{\omega_0^4 d_0 d_0^*}{3c^3} n. \tag{12.43}
\]
Therefore, in this case,

\[ A = \frac{4\omega_0^3 |\mu|^2}{3\hbar c^3} n. \]  

(12.44)

### 12.2.3 Absorption and Emission

Consider a cavity whose walls are at temperature \( T \), and containing radiation and an ensemble of atoms, and let each atom be represented by a two-level quantum mechanical system with an energy level separation of \( \hbar \omega_0 \). In thermal equilibrium, then, energy density per unit angular frequency range at \( \omega_0 \) is given by [2]:

\[ \rho_{\omega_0} = \frac{\hbar \omega_0^3 n^3}{\pi^2 c^3 e^{\hbar \omega_0/kt} - 1} = \frac{\omega_0^2 \hbar \omega_0 n^3}{\pi^2 c^3 e^{\hbar \omega_0/kt} - 1} \]  

(12.45)

where \( n = \) index of refraction of the medium inside the cavity. We can write

\[ \rho_{\omega_0} (e^{\hbar \omega_0/kt} - 1) = \frac{\hbar \omega_0^3 n^3}{\pi^2 c^3}. \]  

(12.46)

In addition, because of detailed balance,

\[ AN_1^e + B_2 \rho_{\omega_0} N_2^e = B_1 \rho_{\omega_0} N_1^e, \]  

(12.47)

where \( N_1^e \) and \( N_2^e \) are the equilibrium populations of atoms in the lower and upper levels, respectively, and \( B_1 \rho_{\omega_0} \) and \( B_2 \rho_{\omega_0} \) are the probabilities per unit time of induced downward and upward transitions, respectively. We can write

\[ A \frac{N_1^e}{N_1^e} + B_2 \rho_{\omega_0} \frac{N_2^e}{N_2^e} = B_1 \rho_{\omega_0} \]  

(12.48)

and

\[ Ae^{-\hbar \omega_0/kt} + B_2 \rho_{\omega_0} e^{-\hbar \omega_0/kt} = B_1 \rho_{\omega_0} \]  

(12.49)

or

\[ \rho_{\omega_0} (B_1 e^{\hbar \omega_0/kt} - B_2) = A. \]  

(12.50)

We set

\[ B_12 = B_21 = B. \]  

(12.51)

Then

\[ \rho_{\omega_0} (e^{\hbar \omega_0/kt} - 1) B = A \]  

(12.52)

\[ \frac{A}{B} = \rho_{\omega_0} (e^{\hbar \omega_0/kt} - 1) = \frac{\hbar \omega_0^3 n^3}{\pi^2 c^3} \]  

(12.53)

and
12.2 Spontaneous Emission, Absorption, and Induced Emission

\[
B = \frac{\pi^2 c^3}{\hbar\omega_0 n^3} \quad A = \frac{\pi^2 c^3}{n^3 \hbar^2 \omega_0} \frac{4n\hbar^3}{3h c} |\mu|^2 = \frac{4\pi^2}{3h^2 n^2} |\mu|^2, \quad (12.54)
\]

or

\[
\begin{align*}
A &= \frac{4n\hbar^3}{3h c} |\mu|^2 \quad \left( \text{sec}^{-1} \right) \\
B &= \frac{4\pi^2}{3h^2 n^2} |\mu|^2 \quad \left( \frac{\text{cm}^3}{\text{erg-sec}^2} \right) \\
A/B &= \frac{\hbar\omega_0 n^3}{\pi^2 c^3} \quad \left( \frac{\text{erg-sec}}{\text{cm}^3} \right). \quad (12.56)
\end{align*}
\]

Let us now consider the more realistic situation in which the energies of the two atomic levels are not sharply defined, but have a certain width \(\Delta \omega\) such that \(\Delta \omega << \omega_0\). We can set the following:

- \(N_2 A_\omega d\omega\) = number of atoms that per unit time that decay by spontaneous emission, giving out a photon with angular frequency in \((\omega, \omega + d\omega)\);
- \(N_2 B_\omega d\omega\) = number of atoms that in the unit time undergo a downward transition by induced emission, giving out a photon with angular frequency in \((\omega, \omega + d\omega)\); and
- \(N_1 B_\rho_\omega d\omega\) = number of atoms that in the unit time undergo an upward transition by the absorption of a photon with angular frequency in \((\omega, \omega + d\omega)\).

If we put a filter between the atoms and the walls that allows only the radiation in the narrow band \(d\omega\) to interact with the atoms we have

\[
N_2^e A_\omega d\omega + N_2^e B_\omega \rho_\omega d\omega = N_1^e B_\omega \rho_\omega d\omega, \quad (12.57)
\]

or

\[
A_\omega \frac{N_2^e}{N_1^e} + B_\omega \rho_\omega \frac{N_1^e}{N_1^e} = B_\omega \rho_\omega. \quad (12.58)
\]

Then

\[
A_\omega e^{-\frac{\hbar\omega_0}{kT}} + B_\omega \rho_\omega e^{-\frac{\hbar\omega_0}{kT}} = B_\omega \rho_\omega \quad (12.59)
\]

\[
\rho_\omega \left( e^{\frac{\hbar\omega_0}{kT}} - 1 \right) B_\omega = A_\omega \quad (12.60)
\]

and
\[
\frac{A_n}{B_n} = \rho_n \left(e^{\frac{\hbar \omega_n}{kT}} - 1\right) \approx \rho_n \left(e^{\frac{\hbar \omega_n}{kT}} - 1\right) = \frac{\hbar \omega_n^3}{\pi^2 c^3} = \frac{A}{B}.
\] (12.61)

If \(g(\omega)\) indicates the spectral lineshape:

\[
\int g(\omega) d\omega = 1
\] (12.62)

we can write

\[
\begin{align*}
A_n &= A g(\omega) ; \quad \int A_n d\omega = A \\
B_n &= B g(\omega) ; \quad \int B_n d\omega = B
\end{align*}
\] (12.63)

If we call \(w(\omega)d\omega\) the probability per unit time that an atom undergoes an \textit{induced} transition by absorbing or emitting a photon with angular frequency in \((\omega, \omega + d\omega)\), we find

\[
w(\omega) d\omega = B g(\omega) \rho_n c d\omega = \frac{4\pi^2}{3\hbar^2 n^2} |\mu|^2 \rho_n g(\omega) d\omega
\] (12.64)

\[
= \frac{4\pi^2}{3n\hbar^2} I(\omega) g(\omega) d\omega
\]

where

\[
I(\omega) d\omega = \rho_n \frac{c}{n} d\omega = \text{ intensity of radiation with angular frequency in } (\omega, \omega + d\omega).
\] (12.65)

We can write

\[
\int w(\omega) d\omega = \frac{4\pi^2}{3n\hbar^2} |\mu|^2 \rho_n = \frac{4\pi^2}{3n\hbar^2} |\mu|^2 I(\omega_0)
\] (12.66)

### 12.2.4 Absorption Coefficient and Absorption Cross-Section

Let us assume that a plane wave goes through a certain medium in the \(x\) direction. Let the medium consist of atoms that have two possible energy levels and let \(N_1 (N_2)\) be the concentration of atoms in the lower (higher) energy level.

The energy intensity per unit angular frequency range \(I(\omega)\), when the wave travels through the medium distance \(dx\), undergoes a change given by

\[
dI(\omega) = -w(\omega)(N_1 - N_2) \hbar \omega dx \left(\frac{\text{erg}}{\text{cm}^2}\right)
\] (12.67)

But, from equation (12.64):

\[
w(\omega) = \frac{4\pi^2}{3n\hbar^2} |\mu|^2 I(\omega) g(\omega).
\] (12.68)

Then
12.3 Measurements and Techniques

\[ dI(\omega) = -\left[ \frac{4\pi^2}{3nch} |\mu|^2 \omega g(\omega) \right] (N_1 - N_2)\hbar\omega dx \]

\[ = -\left[ \frac{4\pi^2 (N_1 - N_2)}{3nch} |\mu|^2 \omega g(\omega) \right] I(\omega) dx = -\alpha(\omega) I(\omega) dx \]

(12.69)

where the absorption coefficient \( \alpha(\omega) \) is given by

\[ \alpha(\omega) = \frac{4\pi^2 (N_1 - N_2)}{3nch} |\mu|^2 \omega g(\omega) = \frac{n\hbar\omega}{c} B(\omega)(N_1 - N_2) \quad \text{(cm}^{-1} \text{)} \]  

(12.70)

The solution of equation (12.69) is

\[ I(\omega;x) = I(\omega;x=0) e^{-\alpha x} \]  

(12.71)

We define the absorption cross-section of a radiative transition as follows

\[ \sigma(\omega) = \frac{\alpha(\omega)}{N_1 - N_2} \frac{4\pi^2}{3nch} |\mu|^2 \omega g(\omega) \quad \text{(cm}^{-1} \text{)} \]  

(12.72)

Note the following

\[ \int \alpha(\omega) d\omega = \frac{4\pi^2 (N_1 - N_2)}{3nch} |\mu|^2 \omega = \frac{n\hbar\omega}{c} B(\omega)(N_1 - N_2) \quad \text{(cm}^{-1} \text{sec}^{-1}) \]  

(12.73)

In Table 12.1, we have summarized the results obtained in the previous sections.

12.3 MEASUREMENTS AND TECHNIQUES

Luminescence spectroscopy relies on four fundamental measurements: (1) absorption spectra, (2) luminescence spectra, (3) excitation spectra, and (4) response to pulsed excitation. Technical improvements or breakthroughs have not and probably will not produce any conceptually new additions to these four basic measurements. The data that they make available can be considered “scarce” when one contrasts them with the complexity of the processes. However, an attentive and appropriate usage of the different techniques generally yields a satisfactory model for the system under investigation.

12.3.1 Absorption Spectra

The main purpose of absorption measurements is to set the energy level scheme and to identify particular levels that may be convenient to “pump” the system for the purpose of obtaining luminescence or laser emission. If the concentration of the optically active centers is known, the ratio of the absorption coefficient and of the concentration gives the absorption cross-section.
**Table 12.1** Summary of Section 12.2 formulas.

\[
 w(\omega) = \frac{4\pi^2}{3n^2\hbar^2} |\mu|^2 \rho_{\omega} g(\omega) = \frac{4\pi^2}{3n\hbar^2} |\mu|^2 I(\omega) g(\omega) = \frac{\sigma(\omega) I(\omega)}{\hbar\omega}
\]

\[
w = \int w(\omega) d\omega = \frac{4\pi^2}{3n^2\hbar^2} |\mu|^2 \rho_{\omega_0} = \frac{4\pi^2}{3n\hbar^2} |\mu|^2 I(\omega_0) = B\rho_{\omega_0} \quad \text{(sec}^{-1})
\]

\[
\alpha(\omega) = \frac{4\pi^2}{3nch} |\mu|^2 \log_2(\omega) = \frac{nh\omega}{c} B_\alpha (N_1 - N_2) \quad \text{(cm}^{-1})
\]

\[
\sigma(\omega) = \frac{\alpha(\omega)}{N_1 - N_2} = \frac{4\pi^2}{3nch} |\mu|^2 \log_2(\omega) \quad \text{(cm}^2)
\]

\[
\int \alpha(\omega) d\omega = \frac{4\pi^2}{3nch} |\mu|^2 \omega_0 = \frac{nh\omega_0}{c} B(N_1 - N_2) \quad \text{(cm}^{-1} \text{sec}^{-1})
\]

\[
\int \sigma(\omega) d\omega = \frac{4\pi^2}{3nch} |\mu|^2 \omega_0 = \frac{nh\omega_0}{c} B = \frac{2\pi^2 e^2}{mc} f \quad \text{(cm}^2\text{sec}^{-1})
\]

where the f-number is

\[
f = \frac{2m\omega_0}{3\hbar e^2} |\mu|^2 \quad \text{(pure number)}
\]

\[
A = \frac{1}{\tau_p} = \frac{4n\omega_0^3}{3hc^3} |\mu|^2 = \frac{2e^2\omega_0^2 n}{mc^2} f \quad \text{(sec}^{-1})
\]

\[
A_\alpha = Ag(\omega) \quad \text{(pure number)}
\]

\[
B_\alpha = Bg(\omega) \quad \text{\left(\frac{\text{cm}^2}{\text{erg-sec}}\right)}
\]

\[
\frac{A}{B} = \frac{\hbar\omega_0^3 n^3}{\pi^2 e^3} \quad \left(\frac{\text{erg-sec}}{\text{cm}^3}\right)
\]

\[
\frac{A_\alpha}{B_\alpha} = \frac{A}{B}
\]

\[
\text{ft}_{\omega_0} = 1.5\frac{\lambda^2}{n}
\]

The conventional absorption measurements are related to transitions originating in the ground state of the material. Transitions originating in an excited state and ending up in still higher states may be observed if one is able to populate the initial state. This procedure is called excited state absorption (ESA).
and has been found useful towards elucidating the process by which certain systems are excited prior to the emission of luminescence. It is worth noticing that the ESA signal is dependent on the strength of the excitation of the initial level.

The absorption spectra are generally obtained by using an instrument called an absorption spectrophotometer, which compares the intensity of a beam of light impinging on a sample with the intensity of the same beam after traversing the sample:

$$I_0(\lambda) = I_i(\lambda)e^{-\alpha(\lambda)L} \tag{12.74}$$

Here

- $I_i(\lambda)$ = intensity of the input beam at wavelength $\lambda$
- $I_0(\lambda)$ = intensity of the output beam at wavelength $\lambda$
- $\alpha(\lambda)$ = absorption coefficient of the material at wavelength $\lambda$
- $L$ = thickness of the sample.

Information about the absorption coefficient is often given as optical density (OD):

$$OD = \log \frac{I_i(\lambda)}{I_0(\lambda)} \tag{12.75}$$

An $OD = 1$ corresponds to an absorption of 90%, an $OD = 2$ to an absorption of 99%. Given $OD$, the coefficient of absorption can be obtained as follows

$$\alpha(\lambda) = \frac{1}{L} OD \ln 10. \tag{12.76}$$

We note that $\alpha(\lambda)$ is independent of the intensity of the incoming beam $I_i$. The absorption measurement can then be considered an absolute measurement.

A common feature of the absorption spectrophotometer is the presence of two chambers, one for the sample and one for the reference material. This arrangement allows the apparatus to sort out all the features of the material that may reduce the intensity of the output beam, $I_0$, such as reflection from the walls of the material, not due to the absorption.

### 12.3.2 Luminescence Spectra

We measure the luminescence spectra to identify the luminescent states. They may also help to establish energy levels, especially the position of the ground state multiplets. The changes of spectra with temperature provide information regarding such temperature time-dependent processes as thermal line broadening and thermal change of line positions. The dependence of the spectral intensity on the concentration of luminescent centers may provide information on the threshold of quenching and on up-conversion.

The step preceding the emission of the luminescence is an excitation process that has the purpose of populating the luminescent level(s). This excitation may be achieved by lamps or lasers. Accordingly, we may use wide band or selective excitation. Wide band excitation is useful for pumping systems with wide
absorption bands, such as those generally presented by transition metal ions in solids.

Selective excitation may be achieved by filtering the light of a lamp or by using a laser. Lasers have become common in spectroscopy laboratories; they provide high light intensity in a very narrow spectral band. The exciting light sources can be continuous or pulsed.

For continuous sources generally the beam of light is chopped and the signal from the photomultiplier is sent to a lock-in amplifier before being recorded. The lock-in amplifier is tuned at the chopping frequency and selects out signals only at this frequency coming from the photomultiplier, reducing considerably the presence of noise.

For pulsed sources the signal from the photomultiplier is sent to a boxcar integrator that integrates the signal over time. The boxcar is triggered at the same rate as the pulsed source. It is provided with a “time window” whose length and position with respect to the trigger pulse can be varied, making this device very useful for obtaining time-resolved spectra. The time window of the boxcar can also be moved continuously making the boxcar adapt to perform lifetime measurements.

### 12.3.3 Excitation Spectra

The excitation spectra tell us in what spectral region we have to pump the system in order to obtain the emission that is being monitored. Excitation spectra are essential for recognizing the presence of energy transfer among different centers; say those of type $A$ and those of type $B$. Energy transfer from $A$ to $B$ is present if the excitation spectrum of $B$ contains bands typical of $A$. Excitation spectra can also help in the assignment of luminescence transitions. A study of the temperature dependence of the monitored luminescence of $A$ when pumped via the absorption bands of $A$ and when pumped via the absorption bands of $B$ gives information about the role played by phonons in the energy transfer process.

In order to acquire an excitation spectrum we monitor the intensity of a specific luminescence line while continuously changing the wavelength of the exciting light. This is generally achieved by putting a monochromator between a wide-spectrum source and the sample and a filter between the sample and the detector. The detection system may use a combination chopper/lock-in if the source is continuous or a boxcar if the source is pulsed.

### 12.3.4 Responses to Pulsed Excitation

The decay constant $\tau$ of an exponentially decaying luminescence signal is the lifetime of the level from which the transition originates. It includes a radiative part and a non-radiative part as follows:
where
\[
\frac{1}{\tau} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{non-rad}}(T)}
\]

The probability of non-radiative decay is affected by the temperature of the sample. If \( \tau \) is found to be independent of temperature, then
\[
(\tau_{\text{non-rad}})^{-1} = 0.
\]

The decay pattern of a luminescence signal may not be exponential when the excitation energy reaches the luminescence level after undergoing a number of downward steps. If the number of this step is \( n \), then the decay signal will contain \((n + 1)\) exponentials. It may be difficult to disentangle all the exponentials because the components faster than the response time of the detecting apparatus leave no trace.

An additional mechanism that may contribute to the decay of a luminescent level is due to the emission of vibronic lines, corresponding to transitions that involve the emission of one photon and the emission or absorption of a photon. These transitions have been found to contribute to the probability of decay of such systems as \( \text{Al}_2\text{O}_3:Cr \) (ruby) and \( \text{YAG:Cr} \) [3].

Pulsed excitation is generally achieved by sending a pulse of light at a selected wavelength in order to excite a particular level of the emitting center. The response of a particular emission line is monitored by filtering the luminescence emission. The detection of the response signal can be done by looking, on a scope, directly at the signal following the exciting pulse or by using a boxcar integrator and moving the time window.

### 12.4 LOCALIZED SYSTEMS

#### 12.4.1 Introduction

The most important classes of localized luminescent centers are transition metal ions (TMI) and rare earth ions (REI) that have been intentionally doped into ionic insulating host materials. The luminescence properties of these systems depend on both the dopant ion and the host. Another class of localized centers is defects in solids. One such center is an electron trapped at a vacant lattice site. These defects often absorb in the optical region giving the crystal color, and so are called *color centers.*
The host materials for localized, optically active centers are large band gap (usually > 6 eV) ionic solids. The large gap renders the host transparent to visible radiation, and also prevents any electrons from bridging the gap thermally, so that an undoped host is optically and electrically inert. Common host materials include alkaline halides, oxides, fluorides, chlorides, tungstates, phosphates, and garnets, to name but a few.

### 12.4.2 The Hamiltonian of an Ion in a Solid

For an optically active ion in a solid, the Hamiltonian can be written as

\[ H = H_{FI} + H_{L} + H_{CF}, \]

where \( H_{FI} \), \( H_{L} \) and \( H_{CF} \) are the Hamiltonians for the free ion, lattice, and crystal field interaction, respectively.

The free ion Hamiltonian, \( H_{FI} \), includes all electric and magnetic interactions in the ion, and for many-electron atoms is quite cumbersome. Extensive treatments on the various interactions contained in \( H_{FI} \) are given in \([4–6]\). Considering only the most important interactions, \( H_{FI} \) can be written in the following form:

\[ H_{FI} = H_{0} + H_{C} + H_{SO}. \]

\( H_{0} \) includes the kinetic energy of the electrons, and the electrostatic interaction of each electron with an average (spherically symmetric) potential due to the nucleus and the other electrons. Since all valence electrons are subject to the same potential, the eigenstates of \( H_{0} \) corresponding to a particular configuration are degenerate.

\( H_{C} \) accounts for the electrostatic interaction among the electrons in the unfilled shell. This interaction splits the ground configuration into different spectral terms, that is, energy levels with common values of \( S \) and \( L \). Such terms are identified using the \( ^{2S+1}L \) notation. \( L^2, S^2, L_z, \) and \( S_z \) all commute with the \( H_{C} \) and so the corresponding quantum numbers (\( L, S, M_L, \) and \( M_S, \) respectively) are valid. The energies of the states are independent of \( M_L \) and \( M_S \), and so have a degeneracy of \((2L + 1)(2S + 1)\).

For rare earth ions, the spin-orbit term \( H_{SO} \) is the next most important interaction, followed by the crystal field interaction, \( H_{CF} \). This is the so-called weak crystal field scheme. For transition metal ions \( H_{CF} \) is larger than \( H_{SO} \), so that either the medium or strong field scheme is relevant. We first consider the rare earth ions.

### 12.4.3 Rare Earth Ions in Solids

#### 12.4.3.1 Energy Levels of Rare Earth Ions in Solids

The rare earth elements include the lanthanides and the actinides. By far the most important of these as luminescent centers are the lanthanides, particularly when
localized systems running from 1 (Ce$^{3+}$) to 13 (Yb$^{3+}$). The 4f-electrons are responsible for the optical activity of the center. The 5s- and 5p-shells are located farther from the nucleus than the 4f-shell, and partially shield the 4f-electrons from the nearby ligands. This shielding renders the crystal field interaction ($H_{CF}$) much smaller than the spin orbit interaction, $H_{SO}$.

For REI, then, the next most important term in the Hamiltonian is $H_{SO}$, which is given by

$$H_{SO} = \sum_i \xi_i \mathbf{I}_i \cdot \mathbf{s}_i.$$  \hspace{1cm} (12.81)

This interaction splits each spectral term into different levels, called $J$-multiplets (or $J$-manifolds). The operators $\mathbf{J}^2 = (\mathbf{L} + \mathbf{S})^2$ and $J_z = (\mathbf{L}_z + \mathbf{S}_z)$ commute with the $H_{SO}$, so that $J$ and $M_J$ are good quantum numbers. Each $J$-multiplet has a degeneracy of $2J + 1$. For rare earth ions, these splittings are large enough to cause some mixing of states of different $L$ and $S$ and of equal $J$-values. Nevertheless, the $J$-multiplets are commonly labeled using $S$, $L$, and $J$ quantum numbers according to the usual spectral designation $^{2S+1}L_J$, where $J$ runs from $L + S$ to $L - S$.

The remaining interaction is that of the crystal field with the rare earth ion. $H_{CF}$ consists of a static term ($H_{CF$-static}) and a dynamic term ($H_{CF$-dynamic}). We consider only the static term here since it makes a more important contribution to the energy.

Due to the shielding of the 4f-electrons, there is little or no overlap of their wavefunctions with those of the ligands. Thus, we consider the ion to be under the influence of an external field—this is the crystalline field approximation. In this approximation, $H_{CF$-static} is the interaction of the electrons with the potential due the ligands, $V(\mathbf{r})$.

$$H_{CF$-static} = \sum_i e V(\mathbf{r}_i).$$  \hspace{1cm} (12.82)

The sum is over all 4f electrons, and $V(\mathbf{r}_i)$ reflects the symmetry at the site of the REI. This interaction splits each $J$-multiplet into no more than $(2J + 1)$ levels for ions with an even number of $f$-electrons and no more than $(J + 1/2)$ levels for ions with an odd number of $f$-electrons. The number of levels into which each multiplet splits depends on the symmetry of the crystal field—for higher ion site symmetries there are fewer levels. The splittings due to $H_{CF}$ typically range from ten to a few hundred cm$^{-1}$.

The observed energy levels of the rare earth ions in LaCl$_3$ are shown in Figure 12.1. Because $H_{CF}$ is small, the energy levels are similar in other ionic solids [5, 6]. Most of the energy levels of the REI are known up to about 40,000 cm$^{-1}$. Research continues to locate and identify the higher lying 4f-levels [7, 8].
12.4.3.2 Spectral Features of REI in Solids

The small crystal field interaction implies that the energy levels of REI are not very sensitive to the motion of the lattice. Thus, f→f transitions are characterized
by sharp lines, with linewidths on the order of 1 cm$^{-1}$ at low temperatures. A sample REI emission spectrum is shown in Figure 12.2. Typical radiative lifetimes range from 10 μsec to a few msec.

Although radiative transitions do occur between f-levels, luminescence spectra show certain lines very weak or missing entirely. This is due to one or more of the following factors:

1. Certain transitions may be only weakly allowed. This depends, in part, on the symmetry of the crystal field.
2. An excited REI can decay via the emission of phonons instead of a photon. Such transitions are called multiphonon transitions, and are discussed in Section 12.5.3.
3. The REIs are in thermal equilibrium; each ion reaches thermal equilibrium with the lattice, and so they are in equilibrium with one another. Thus, the levels of the ground multiplet (or of an excited metastable multiplet) are populated according to the Boltzmann distribution. (The idea of the lattice as a heat reservoir is found to be widely true, but may not hold on very short timescales during which local nonequilibrium phonon populations can be created [9, 10].)

REI spectra also exhibit sidebands to the zero-phonon line. These sidebands represent vibronic transitions (Section 12.5.4), which involve the emission of a photon and the simultaneous emission or absorption of one or more phonons. For

---

**Figure 12.2** Luminescence spectrum of YALO : Pr (0.05%) at 22 K. Excitation was into the $^3P_0$ level at 460 nm.
REI, such sidebands usually involve a single phonon, and are much weaker than the zero-phonon line. The structure of the sidebands reflects somewhat the phonon spectrum of the host lattice.

In many systems, the REIs are situated at two or more types of lattice sites. Due to differences in the local crystal field, the same transition at the different sites will generally appear at different energies, complicating the spectra considerably. In glasses, the random positioning of the ions leads to a continuum of crystal field interactions and to bands on the order of 100 cm\(^{-1}\) wide.

We conclude this section with the observation that the spectral features of REI can be traced back to their peculiar charge distribution, namely, that the optically active 4f electrons are shielded from the crystalline field by the outer 5s- and 5p-shells. The next group of ions to be considered, the transition metal ions, has valence electrons that are exposed to the crystalline field, and exhibit a vastly different behavior.

### 12.4.4 Transition Metal Ions in Solids

#### 12.4.4.1 Introduction

The class of transition metals consists of those elements with unfilled d-shells. In pure form they are metals, with electrical and thermal properties usually associated with metals. When doped into insulators, however, such similarities are less evident. Their spectroscopic properties vary significantly ion to ion and host to host. We restrict our discussion to those elements most commonly used as dopants in optical materials, the 3d elements.

When doped into a solid, these elements form positive ions, the valency of which is host-dependent. The outer 4s-electrons are stripped from the ion and reside closer to the anions of the solid. Common valencies and shell configurations of each ion are shown in Table 12.2.

<table>
<thead>
<tr>
<th>Transition Metal Ion</th>
<th>Electronic Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(^{3+}), V(^{4+})</td>
<td>1s(^2) 2s(^2) 2p(^6) 3s(^2) 3p(^6) 3d(^1)</td>
</tr>
<tr>
<td>V(^{3+}), Cr(^{4+})</td>
<td>1s(^2) 2s(^2) 2p(^6) 3s(^2) 3p(^6) 3d(^2)</td>
</tr>
<tr>
<td>V(^{2+}), Cr(^{3+}), Mn(^{4+})</td>
<td>1s(^2) 2s(^2) 2p(^6) 3s(^2) 3p(^6) 3d(^3)</td>
</tr>
<tr>
<td>Cr(^{4+}), Mn(^{3+})</td>
<td>1s(^2) 2s(^2) 2p(^6) 3s(^2) 3p(^6) 3d(^4)</td>
</tr>
<tr>
<td>Mn(^{2+}), Fe(^{3+})</td>
<td>1s(^2) 2s(^2) 2p(^6) 3s(^2) 3p(^6) 3d(^5)</td>
</tr>
<tr>
<td>Fe(^{2+}), Co(^{3+})</td>
<td>1s(^2) 2s(^2) 2p(^6) 3s(^2) 3p(^6) 3d(^6)</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>1s(^2) 2s(^2) 2p(^6) 3s(^2) 3p(^6) 3d(^7)</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>1s(^2) 2s(^2) 2p(^6) 3s(^2) 3p(^6) 3d(^8)</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>1s(^2) 2s(^2) 2p(^6) 3s(^2) 3p(^6) 3d(^9)</td>
</tr>
</tbody>
</table>
12.4.4.2 Energy Levels of Transition Metal Ions in Solids

Optical transitions in these centers involve the 3d-electrons, which are in the outermost shell and so are exposed to the crystal field. Consequently, $H_{CF}$ is larger than $H_{SO}$, and is often on that same order of magnitude as the interaction $H_C$ among the 3d-electrons.

The simplest transition metal ion (TMI) has only one 3d-electron, so that $H_C$ is zero. Following the interaction with the central field, the next strongest term in the Hamiltonian is the $H_{CF}$. Though several crystal field symmetries are possible, in many oxide hosts the TMI is situated at a site with octahedral (or near octahedral) symmetry (Figure 12.3). At an octahedral site the angular parts of the wavefunctions are linear combinations of spherical harmonics [11], the plots of which are shown in the Figure 12.4. The following observations can be made regarding these wavefunctions.

![Figure 12.3 Transition metal ion in an oxide at a site of octahedral symmetry.](image)

1. The wavefunctions are even. In fact, each wavefunction is invariant under all symmetry operations of the octahedral field.
2. The wavefunctions $d_{xy}$, $d_{xz}$, and $d_{yz}$ are identical both in shape and in their relative orientation with respect to the surrounding ions, and so have the same energy. These states are labeled as $t_{2g}$.
3. The wavefunctions $d_{z^2}$ and $d_{x^2-y^2}$ are directed toward the $O^{2-}$ ions and so have higher interaction energies than the $t_{2g}$ states. The energy of these two states is identical. These states are labeled $e_{2g}$.

Given observations 2. and 3. above, this system exhibits two energy levels as shown in Figure 12.5. The difference in energy between the two levels is commonly designated as $10D_q$, where $D_q$ is a measure of the strength of the crystal field. We note that for a TMI in a site having cubic symmetry, the system
also splits into two energy levels. For example, in Ti$^{3+}$-doped Al$_2$O$_3$, the crystal field is mainly cubic, with a slight trigonal distortion. The splitting between the ground state ($^2T_2$) and the excited state ($^2E$) is around 19,000 cm$^{-1}$ [12]. The absorption band occurs in the blue-green region, accounting for the crystal’s pink color.

Figure 12.4 The wavefunctions of a 3d$^1$ system in an octahedral environment. The ground state wavefunctions are labeled (a) $d_{x^2}$, (b) $d_{y^2}$, and (c) $d_{z^2}$, and the excited states are (d) $d_{x^2-y^2}$ and (e) $d_{3z^2-r^2}$.

Figure 12.5 Splitting of the ground configuration due to an octahedral field for a 3d$^1$ system.

When there is more than one 3d electron, the configuration interaction $H_C$ must be included. Taking into account the crystal field, but before including the $H_C$, each 3d-electron will be in either the $t_{2g}$ or $e_{2g}$ state. The state of the system, then, is a product of one-electron states. For the case of a 3d$^2$ system (Cr$^{3+}$ or V$^{3+}$) the states are $(t_{2g})^2$, $t_{2g}e_{2g}$, and $(e_{2g})^2$.

When $H_C$ is included, the one-electron product states are split. For a 3d$^2$ system, the new states are assigned the group theoretical labels: A$_1$, A$_2$, E, T$_1$, and T$_2$. Since the spins of this system are parallel or antiparallel, the total spin quantum number, S, is either 1 or 0, and $2S + 1$ is 3 either or 1, respectively.
Including spin, the following labels describe the states: $^1\text{A}_1$, $^3\text{A}_2$, $^1\text{E}$, $^3\text{T}_1$, $^1\text{T}_1$, $^3\text{T}_2$, and $^1\text{T}_2$.

The energy of each state depends on the strength of the crystal field. This dependence is usually depicted in a Tanabe-Sugano diagram [13] of the type shown in Figure 12.6, which shows the 3d$^2$ splittings in an octahedral field. At zero crystal field, the levels are designated according to the free ion spectral terms, shown to the left of the diagram. In the strong field limit, the slopes of the lines approach one of three possible values, which are associated with the $(t_{2g})^2$, $t_{2g}e_{2g}$, and $(e_{2g})^2$ orbitals.

Figure 12.6 Tanabe-Sugano diagram for a 3d$^2$ ion in an octahedral field.

12.4.4.3 Spectral Features of TMI in Solids

Absorption and emission spectra of TMI in solids generally show broad bands, though sharp lines are occasionally observed. The absorption and emission spectra of Ti$^{3+}$:Al$_2$O$_3$ are shown in Figure 12.7. The broad bands result from the 3d-electrons’ exposure to the neighboring ions, making the wavefunctions sensitive to the position of the nearby ions.
Note the large Stokes shift between the peaks of the absorption and emission bands. This can be understood in the following way. Absorption of a photon results in a redistribution of the charge of the 3d-electrons. The neighboring ions then “see” the new potential and relax to a new equilibrium position. During relaxation, the center gives up energy to the lattice, usually by emitting phonons. A similar relaxation process occurs following the emission of a photon. Since part of the absorbed energy is given up to the lattice, less is available for the emitted photon.

**Figure 12.7** Polarized (a) absorption spectra and (b) emission spectra of Ti$^{3+}$ in Al$_2$O$_3$ [12].

### 12.4.4.4 The Configurational Coordinate Model

The broad bands and large Stokes shift are related to one another, and can be understood using a *configurational coordinate* (CC) model [14, 15]. In this model, each electronic energy level is represented by a parabola on an energy vs. position diagram (Figure 12.8). The position coordinate can be considered one of the normal coordinates of the crystal, though it is often associated with the “breathing mode” of the ligands about the central TMI. The equilibrium position depends on the electronic state of the system. Horizontal lines within each parabola represent vibrational levels.
The assumptions included in the model are the following:

1. The adiabatic approximation: The electrons and nuclei are separated into fast and slow subsystems, respectively. The electronic wavefunctions depend parametrically on the position of the nearby nuclei. The motion of the nuclei is determined by a potential defined by an average position of the electrons. Physically, this is justified by the fact the mass of the electron is much less than the nuclear mass.

2. The harmonic approximation: The electronic states that result from the adiabatic approximation have potential curves that are parabolic. Physically, this assumes that the amplitude of the TMI vibrations is small.

3. The Franck-Condon principle: This asserts that during a radiative transition the electronic charge is redistributed before the nuclei can react. Thus, transitions are represented by vertical arrows in the CC diagram. This is justified on the same basis as the adiabatic approximation.

Further discussions of these assumptions can be found in [14] and [16].

In Figure 12.8 the ground and excited electronic levels are labeled \( u \) and \( v \), respectively, and their parabolas are offset from one another by a distance \( a \). We assume identical force constants for each parabola. The vibrational levels of \( u \) and \( v \) are labeled as \( n \) and \( m \), respectively, and the associated vibrational wavefunctions are \( \phi_n \) and \( \phi_m \). Transitions in absorption and emission are represented by upward and downward arrows, respectively. In absorption, the electron moves from the state \( |u_n\rangle \) to \( |v_m\rangle \), creating \((m - n)\) phonons in the process. After a transition (absorption or emission), the ion relaxes to a new equilibrium position by releasing phonons to the surrounding lattice.

The Stokes shift between absorption and emission and the shape of the spectral bands are determined by both the force constant of the vibration, \( k \), and the offset, \( a \). The most important parameter in the model is the Huang-Rhys parameter \( S_0 \) which is defined in
where $\omega$ is the angular vibrational frequency of the system. $S_0$ is also the average number of phonons created or destroyed in the transition [17]. The physical meaning of $S_0$ can be understood in the following manner. The lattice motion induces a local strain, which depends on the electronic state of the ion. If the strain is similarly affected for two electronic states, the value of $S_0$ between those two states is small. If two states affect the strain very differently, then $S_0$ will be large. The constant $S_0$, then, describes the relative coupling of the electronic wavefunctions to the vibrationally induced strains in the lattice.

Enforcement of the Franck-Condon principle leads to the result that the strength of a transition from $|v_m\rangle$ to $|u_n\rangle$ is proportional to the square of the overlap between the vibrational wavefunctions of the two states:

$$W_{m,n} \propto |\langle \phi_{v_m} | \phi_{u_n} \rangle|^2.$$  \hspace{1cm} (12.84)

These overlap integrals are called the Franck-Condon factors. In thermal equilibrium, the vibrational levels of the initial electronic state are populated according to the Boltzmann distribution, so that $W_{m,n}$ has an inherent temperature dependence.

A CC model for ruby (Cr$^{3+}$:Al$_2$O$_3$) is shown in Figure 12.9, along with the absorption and emission spectra. Note that the transitions from the ground $^4A_2$ state to the upper $^4T_1$ and $^4T_2$ states, are spin-allowed. The $^4T_1$ and $^4T_2$ states are offset from the $^4A_2$ state, and so exhibit broad absorption bands. In emission, the situation is different. Following absorption into the $^4T_2$ state, the ion relaxes to the base of the $^4T_2$ parabola, emitting phonons in the process. From that point, there is a feeding into the $^2E$ state, which is accompanied by the further emission of phonons. Because there is a small offset between the $^4A$ and $^2E$ states, the $^2E \rightarrow ^4A$ emission is a sharp line. (This is the 694-nm ruby laser emission line.) This transition is between states of different spin, and so it is weak. The lifetime of the $^2E$ state is correspondingly long at 3 ms.

**Figure 12.9** The configurational coordinate diagram and absorption and emission spectra of Cr$^{3+}$: Al$_2$O$_3$ [18].
12.4.5 Color Centers in Solids

12.4.5.1 Introduction

Even the purest crystals are found to have defects in the crystalline structure. The defect centers of concern in this section are color centers, some of which are given in Table 12.2. These are most widely found in alkaline halides, though they also occur in oxides, fluorides, and other miscellaneous hosts. Unless otherwise stated, our discussion assumes alkaline halide host materials.

Table 12.2 Color centers in alkaline halides.

<table>
<thead>
<tr>
<th>Color Center</th>
<th>Description in Alkaline Halides</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>One electron trapped at an anion site</td>
</tr>
<tr>
<td>F+</td>
<td>Two electrons trapped at an anion site</td>
</tr>
<tr>
<td>F3 (M)</td>
<td>Two neighboring F-centers along the 110 axis</td>
</tr>
<tr>
<td>F2+</td>
<td>Two neighboring vacant anion sites (along 110 axis) containing a single electron</td>
</tr>
<tr>
<td>F3 (R)</td>
<td>Three neighboring F-centers forming an equilateral triangle</td>
</tr>
<tr>
<td>FA</td>
<td>F-center adjacent to a smaller alkali impurity ion</td>
</tr>
<tr>
<td>VK</td>
<td>Singly ionized halogen-ion molecule formed from two adjacent halides</td>
</tr>
</tbody>
</table>

12.4.5.2 Energy Levels of F Centers

A single crystal often contains more than one type of color center. Consequently, the spectra often show several broad bands in absorption. The simplest of these centers is the F center, which consists of a single electron trapped at an anion vacancy (Figure 12.10). F centers can be formed either chemically or by bombardment with particles (e−, p+, neutrons) or high-energy radiation (ultraviolet, X-ray, γ-ray). A more complete discussion of F centers can be found in [19].
In cubic lattices, such as alkaline halides, the obvious physical model for the F center is that of a particle in a three-dimensional box of length \(2l\), where \(l\) is the distance from the center of the vacancy to the nearest alkaline cation. The energy difference between the two lowest levels of such a particle is
\[
\Delta E = \frac{3\pi^2 h^2}{8ml^2},
\]
where we note the \(l^{-2}\) dependence. Data on the low energy absorption band of F centers in several alkaline halides are found to obey the following (Mollwo-Ivey) law: \(\Delta E = 17.7(l)^{-1.84}\). The nearly \(l^{-2}\) dependence lends some credibility to the particle-in-a-box model. Generally, absorption spectra show only one excited level associated with an isolated F center before the onset of the conduction band.

The F center has also been described as a hydrogen-like atom, where the electron is held at a central location by the surrounding charge rather than pulled in by the nucleus. In the so-called “point-ion” approximation, the electron moves in a spherically symmetric potential. The energy level structure is similar in some ways to that of a hydrogen atom; the first energy level is well separated from the ground state, and then numerous closely spaced levels entering the conduction band of the solid.

The states of the color center are labeled according to the irreducible representations of the site symmetry. For alkaline halides the ground and first excited states are \(\Gamma_1^+\) and \(\Gamma_4^-\), respectively. It is found that the lowest electronic states exhibit character consistent with 1s and 2p states of the hydrogen atom. The s- and p-type states emerge naturally from the point-ion model. Even the particle-in-a-box ground and first excited state wavefunctions show s and p character, respectively (Figure 12.11).
12.4.5.3 Spectral Features of F Centers

The potential in which the electron is situated is determined completely by the charge distribution of the nearby ions. As a result, the coupling between the F center and the lattice is strong, and absorption and emission spectra exhibit broad bands and large Stokes shifts, on the order of 1 eV. Figure 12.12 shows the absorption and emission of an F center in KBr. No zero phonon line is observed, and absorption and emission bands show no structure, even at low temperature. A configurational coordinate diagram of an F center has a large offset between the ground and excited state parabolas, and a Huang-Rhys parameter $S_0$ on the order of 30.

Absorption from the $1s$ state to the $2p$ state is an allowed transition with an f-number on the order of unity. Because of the relaxation of the nearby ions following excitation, the matrix element driving the emission process can be very different from that responsible for absorption. If the transition is from a $p$-state to an $s$-state, the f-number will again be close to 1.

The quantum efficiency of emission from the $2p$ state is close to unity at low temperatures. As the temperature is raised, the quantum efficiency decreases due to the presence of one or more quenching processes. One such process is nonradiative decay from the $2p$ to the $1s$ state. Another process is thermal activation from the occupied $2p$ state into the conduction band. Following absorption, the $2p$ state moves to within a few tenths of an eV of the conduction band. Photoconductivity experiments show thermal activation into the conduction band at temperatures around 100 K, depending on the host. Other quenching processes, including the interaction with other centers, have also been proposed [21]. At room temperature, the luminescence from F centers in alkaline halides is often severely quenched. Most color center lasers operate at liquid nitrogen temperature for this reason.
12.4.5.4 Other Color Centers

We briefly describe the optical properties of two other color centers, the $F_A$ center in alkaline halides and the $F^+$ center in oxides. The $F_A$ center (Figure 12.13) is an $F$ center in which a neighboring halide ion is replaced by a smaller halide ion, e.g., $Na^+$ replaces $K^+$ in KCl. This reduces the symmetry of the $F$ center from cubic to tetragonal, and splits the excited 2p triplet into two levels. The splitting is on the order of 0.2 eV. An energy level diagram is shown in Figure 12.13b. Optical absorption measurements show one transition polarized along the vacancy-impurity ion axis and a twofold degenerate transition polarized perpendicular to that axis. The emission spectrum shows a single band.

Finally, we consider an $F^+$ center in oxides (Figure 12.14). By definition, an $F^+$ center is one in which the net charge of the center is +1 with respect to the ion that would normally occupy that site. Since the oxygen has a charge of $-2$ in solids, the $F^+$ center has one electron at an oxygen vacancy, analogous to the $F$ center in alkaline halides. Because of the net positive charge at the vacancy site, the electron is bound more tightly to the vacancy than in alkaline halides. Both the ground (1s) and excited state (2p) wavefunctions are more localized, and so the coupling to the lattice is less than for an $F$ center in alkaline halides. Consequently the absorption and emission bands show vibronic structure and a relatively small Stokes shift, a few tenths of an eV (e.g., Figure 12.14b).
12.5 Processes in Localized Systems

12.5.1 Introduction

The processes affecting the spectral characteristics of optically active centers include both radiative and non-radiative types. In this section we discuss the origin of these processes and their effects on the luminescence properties of the system.

Of the non-radiative processes, many of them include the emission and/or absorption of phonons. In fact, phonon-related processes are important to the luminescence properties of virtually all optically active centers, even those where the ion is only weakly coupled to the lattice. To understand why this is so, recall that the density of phonons for a monatomic solid in the frequency range between \( \omega \) and \( \omega + d\omega \) is:

\[
n(\omega)d\omega = \frac{1}{\exp(h\omega/kT) - 1} \frac{3\omega^2}{2\pi^2 c_s^2} d\omega.
\]  

(12.86)
With the velocity of sound in a solid \( c_s \) on the order of \( 5 \times 10^5 \text{ cm/sec} \), assuming \( T = 300 \text{ K} \) and a Debye temperature of 1000 K, the total number of phonons is on the order of \( 10^{23} \text{ /cm}^3 \). This high phonon density makes phonon-related processes ubiquitous, affecting all the spectral characteristics (e.g., intensity, lineshape, linewidth, and lifetime) of optical centers in solids.

### 12.5.2 Radiative Decay

#### 12.5.2.1 Radiative Transitions Between f-Levels of REI in Solids

The probability of absorption or emission of radiation is determined by matrix elements of the form \( \langle \psi_b | D | \psi_b \rangle \), where \( D \) is the operator responsible for the transition. For rare earth ions in gaseous form, the 4f-states are of odd parity. If \( D \) is the electric dipole operator, which is odd, then the matrix element vanishes. Thus, electric dipole transitions between f-states are forbidden. In a crystal, however, such transitions are frequently observed. In this section, we show that this is because the crystal field interaction mixes some of the character of the upper nearby configurations of opposite parity (e.g., 5d and 6s) into the 4f states.

Because \( H_{\text{CF-static}} \) is small, we treat it as a perturbation. We define \(|u_i\rangle\) to be the free ion states of the 4f and 5d configurations, respectively. To the first order in the perturbation, the 4f state of the ion in a solid, \(|\psi_j\rangle\), is

\[
|\psi_j\rangle = |u_{i'}\rangle + \sum_j \frac{\langle u_{i'} | V_{\text{odd}} | u_{i}\rangle}{E_{j} - E_{i'}} |u_{i}\rangle.
\]

(12.87)

The sum is over all free ion states belonging to the 5d configuration, \( V_{\text{odd}} \) represents the odd components of \( H_{\text{CF-static}} \), and \( E_{j} \) and \( E_{i'} \) are the energies of \(|u_{i'}\rangle\) and \(|u_{i}\rangle\), respectively. When there is inversion symmetry at the rare earth ion site, \( V_{\text{odd}} = 0 \) and no mixing occurs. If the ion site lacks inversion symmetry, mixing is always present.

The matrix element of the electric dipole operator between two states of the type given by equation (12.87) is:

\[
\langle \psi_j | e \mathbf{r} | \psi_k \rangle = \sum_m \frac{\langle u_{i'} | V_{\text{odd}} | u_{m}\rangle}{E_{j} - E_{m}} \langle u_{m} | e \mathbf{r} | u_{i}\rangle + \sum_j \frac{\langle u_{i'} | V_{\text{odd}} | u_{i}\rangle}{E_{k} - E_{i'}} \langle u_{i} | e \mathbf{r} | u_{i'}\rangle.
\]

(12.88)

Transitions are driven by the square of equation (12.88). Since the terms of the form \( |\langle u_{i} | e \mathbf{r} | u_{i'}\rangle|^2 \) are nonzero, electric dipole transitions between 4f states can occur whenever \( V_{\text{odd}} \neq 0 \). Transitions of this type have f-numbers on the order of \( 10^{-6} \).

We note that magnetic dipole and electric quadrupole transitions are allowed even among pure f-states, and obey the selection rules, \( \Delta L, \Delta J \leq 1 \) and \( \Delta L, \Delta J \leq 2 \), respectively. Transitions are frequently observed, however, with \( \Delta L \) and \( \Delta J \) as
large as 6. Based on both theoretical and experimental evidence, it is generally agreed that the vast majority of f→f transitions are electric dipole in nature.

12.5.2.2 Judd-Ofelt Theory of Radiative Transitions for REI in Solids

While the strength of a radiative transition from the ground state to an excited state is readily measured in absorption, the strength of a radiative transition between excited levels is not easily determined experimentally. In this section, we summarize a method (called the Judd-Ofelt method) of predicting the strength of such transitions for REI in solids [23, 24].

The task is to simplify equation (12.88) into an expression whereby radiative transition rates can be estimated. We make the first simplification by invoking the property of closure over the terms of the form \( |u_j\rangle \langle u_j'| \). To do this, however, the term \( E^c_j \) must be held constant for all values of \( j \). Thus, the first assumption in the Judd-Ofelt theory is to set \( E^c_j = E^c \), making all states of the \( 4f^{n-1}5d \) configuration degenerate. We are left with

\[
\langle \psi_j | e^r | \psi_i \rangle = \frac{\langle u_j | V_{\text{odd}} e^r | u_k \rangle}{E_i - E^c} + \frac{\langle u_k | V_{\text{odd}} e^r | u_j \rangle}{E_k - E^c} \quad (12.89)
\]

This assumption greatly simplifies the calculations. The crystal field operator and electric dipole operator have been combined, and only the knowledge of the free-ion 4f wavefunctions is required.

The next assumption is to set \( E_i = E_k \), which essentially assumes that the energy difference between the 4f-levels is much smaller than the interconfigurational energy. This allows the terms in equation (12.89) to be combined.

By squaring the resulting matrix element, separating the radial and angular parts of the integral, and carrying out the necessary tensor algebra, the equation for the radiative transition probability becomes

\[
P = \sum_{\lambda=2,4,6} \Omega_\lambda \left( \langle \psi_k | U^{(\lambda)} | \psi_i \rangle \right)^2 \quad (12.90)
\]

The \( \langle \psi_k | U^{(\lambda)} | \psi_i \rangle \) are reduced matrix elements and have been tabulated [25]. They do not vary significantly from host to host. The \( \Omega_2, \Omega_4, \) and \( \Omega_6 \), are known as the Judd-Ofelt parameters, and are experimentally determined using a best fit to absorption data. In spite of the assumptions, the Judd-Ofelt method has been generally successful in predicting the radiative rates between REI 4f-levels [26].

12.5.2.3 Radiative Transitions Between d-Levels of TMI in Solids

In Section 12.4.4.2 it was noted that for a TMI at a location of inversion symmetry (e.g., octahedral), the 3d-orbitals are even. Thus, electric dipole matrix elements between states belonging to the 3d configuration are zero. For electric
dipole transitions to occur, there must be a distortion to the inversion symmetry. This distortion introduces odd components into $H_{CF}$ and mixes the character of crystal field states of higher configurations (e.g., $3d^{n-1}4p$) into those of the $3d^n$ configuration. This can occur through vibrational motion of the nearby ligands, but here we assume that the crystal contains a static distortion, and that it can be treated using perturbation techniques.

Considering the $^3T_2$ state of $V^{3+}$ in an octahedral field, for example, the corrected wavefunction, $\psi(3T_2)$, to the first order, is

$$\psi(3T_2) = \left| u(3T_2) \right| + \sum \frac{u_j'}{E(3T_2) - E_j'} \left| u(3T_2) \right|$$

where $\left| u(3T_2) \right|$ is the state of the system in the octahedral field, $\left| u_j' \right|$ represents a state of an upper (odd) configuration in the same field, and $E(3T_2)$ and $E_j'$ are their respective energies. The odd components of $H_{CF}$-static are labeled $V_{\text{odd}}$. A similar expression can be obtained for $\psi(3T_1)$. The matrix element of the electric dipole operator between the corrected $3T_2$ and $3T_1$ states is

$$\langle \psi(3T_1) | er | \psi(3T_2) \rangle = \sum \frac{u_j'}{E(3T_2) - E_j'} \left| \psi(3T_2) \right| \langle u(3T_1) | er | u_j' \rangle$$

Typically, the energy denominators in equation (12.92) are large (several eV) and $V_{\text{odd}}$ is small, so that the transitions are weak: $f$-numbers are on the order of $10^{-4}$.

We note that since the spin-orbit interaction is small in TMI, to a large degree $S$ remains a good quantum number. Thus, transitions between states of different $S$ values are very weak.

Magnetic dipole transitions are allowed between $3d$ states, even in a perfect octahedral field. In spite of this, they are not as important as electric dipole transitions unless the TMI is at a site having perfect octahedral symmetry, such as in the host MgO, where electric dipole transitions are strictly forbidden. Magnetic dipole transitions in TMI have $f$-numbers on the order of $10^{-6}$.

### 12.5.3 Multiphonon Decay

The process considered here is the decay of an excited ion by the emission of phonons, commonly called multiphonon decay (Figure 12.15). In this section, we
find an expression for the multiphonon decay rate of ions in solids, considering first the case of rare earth ions.

The first step is to express the crystal field as a Taylor expansion about the equilibrium position of the ion:

\[ H_{\text{CF}} = H_{\text{CF-static}} + \sum_i \frac{\partial V}{\partial Q_i} Q_i + \text{higher order terms} \quad (12.93) \]

In equation (12.93) \( V \) is the potential seen by the electrons and the \( Q_i \) are the normal modes of vibration of the lattice. At a lattice site with no inversion symmetry, the zeroth order term, \( H_{\text{CF-static}} \), is responsible for breaking the \( f \rightarrow f \) parity selection rule, allowing radiative electric dipole transitions within the 4f configuration. The first order and higher order terms describe modulations of the crystal field due to vibrations of the ligands, and is what we have termed \( H_{\text{CF-dynamic}} \). It is also called the ion-lattice or electron-phonon interaction. This couples the motion of the electron to that of the lattice, allowing for phonon transitions between electronic states.

To obtain an expression for the multiphonon decay rate, one may take the first order term in equation (12.93) to the \( n \)th order of the perturbation. Alternatively, one can use the higher ordered term in equation (12.93) to a lower order of perturbation. No matter the approach, the result takes the following form:

\[ W_{\text{MP}} (n) = W_{\text{MP}} (n-1) C, \quad (12.94) \]

where \( W_{\text{MP}}(n) \) and \( W_{\text{MP}}(n-1) \) are the multiphonon decay rates of an \( n \) and \( n-1 \) phonon process, respectively, and \( C \) is a constant much less than unity. This leads to the so-called energy gap law [27]:

\[ W_{\text{MP}} (n) = W_0 e^{-n\Delta E}. \quad (12.95) \]

Figure 12.15 Two-level system showing the radiative \((W_R)\) and multiphonon \((W_{\text{MP}})\) decay processes.
$W_0$ is a constant, and $\Delta E$ is the energy gap to the next lowest level. If $\hbar \omega$ is the energy of the phonons involved, then $\Delta E = n \hbar \omega$. The high energy phonons play the dominant role since fewer phonons are required, thereby lowering the order of the process. The constant $\alpha$ in equation (12.95) describes the ion-lattice coupling strength, and is determined experimentally. The energy gap law has been found to be valid for REI in solids [28].

An alternative starting point for describing the multiphonon decay rate is to express a non-adiabatic interaction Hamiltonian in the adiabatic approximation. This leads to a similar energy gap law for the case of REI [29].

The temperature dependence of this process is related to the number of available phonons in the host, particularly the high energy phonons. The average occupation number of phonons in the $i$th mode is $N(\omega_i) = \left[ \exp(\hbar \omega_i/kT) - 1 \right]^{-1}$, and the emission of a phonon is proportional to $(N(\omega_i) + 1)$. The $n$th order multiphonon decay rate goes as $(N(\omega_i) + 1)^n$. This temperature dependence has been verified [30].

Observations have lead to the following rule of thumb for REI: If the energy difference to the next lowest level requires seven phonons or more, the dominant decay mechanism is radiative; otherwise it prefers to emit non-radiatively.

For TMI, a perturbation approach to multiphonon decay is not feasible. The multiphonon decay process and its temperature dependence are well described, however, using the configurational coordinate model. In this model, the ion first undergoes a non-radiative transition from state $|v_m\rangle$ to state $|u_n\rangle$, as shown in Figure 12.16. This transition is driven by the ion-lattice interaction, and the rate at which it occurs can be accurately calculated by summing by the Franck-Condon factors, equation (12.84), weighted of course by the population of the initial state $|v_m\rangle$. The transition is favored at the point where two parabolas cross, since that is where the Franck-Condon factors are greatest. Once in the electronic state $|u\rangle$, the system decays rapidly by giving up phonons to the lattice, resulting in the thermalization of $|u\rangle$. The work of Struck and Fonger [31] provides an in-depth discussion of this method.

![Figure 12.16 Configurational coordinate diagram showing a non-radiative transition from $|v_m\rangle$ to $|u_n\rangle$.](image-url)
12.5.4 Vibronic Transitions

A vibronic transition in emission involves the creation of a photon and a simultaneous creation or absorption of one or more phonons. Schematic diagrams of the vibronic transitions are shown in Figure 12.17. At low temperatures, the vibronic sidebands appear on the high (low) energy side of the zero-phonon line in absorption (emission). At high temperatures, vibronic lines appear on both the high and low energy sides of the zero-phonon line. The vibronic spectrum of Pr-doped YAG is shown in Figure 12.18.

As with multiphonon decay, vibronic transitions are driven by the ion-lattice interaction. These transitions occur via two different types of processes, commonly labeled the M and the Δ processes [32]. Whereas both processes apply to the rare earth ions, the Δ process is most relevant to transition metal ions and color centers.

![Figure 12.17 Vibronic transitions in (a), (b) emission and (c), (d) absorption. (b) and (d) are anti-Stokes processes and occur only at high temperatures. (a) and (c) occur at all temperatures.](image1)

![Figure 12.18 Vibronic emission spectrum of the $^1D_2$ level of Pr:YAG at 25 K.](image2)
In equation (12.87) we saw that the odd components of $H_{\text{CF-static}}$ causes the mixing of opposite parity states into the 4f-states of REI, allowing radiative transitions to occur. The $M$ process occurs when the vibrations of the nearby ligands introduce odd components into $H_{\text{CF-dynamic}}$, thus leading to radiative transitions. Because they are vibrationally induced, these transitions are accompanied by a phonon. The $M$ process is especially important in systems where the ion is at a site of inversion symmetry.

The $\Delta$ process occurs in systems where the equilibrium position of the optical center with respect to the ligands changes following an electronic transition. In the configurational coordinate model, this means that $S_0$ is greater than zero. For $\Delta$ processes, the intensity $I$ of the vibronic transitions is given by

$$I = I_0 e^{-S_0 S_0^N / N!}$$

(12.96)

where $I_0$ is the intensity of the zero-phonon line and $N$ is the number of phonons involved in the process. This function is called a Pekarian distribution, and is plotted in Figure 12.19 for different values of $S_0$. For REI, $S_0 \approx 0.1$, so that most of the energy is in the zero-phonon line.

![Figure 12.19](image)

**Figure 12.19** Plots of vibronic emission intensity versus number of phonons for various values of $S_0$ according to the Pekarian distribution in equation (12.96).

Vibronic transitions of REI can exhibit a strong host-dependence, with the ratio of the area under the zero-phonon line to the area under the vibronic sidebands changing by as much as two orders of magnitude depending on the host [33]. Equation (12.96) is also applicable to transition metal ions and color centers. For TMI $S_0$ is between 2 and 10, so they often exhibit a zero-phonon line and strong vibronic sidebands. In color centers $S_0$ is often on the order of 30, and the transitions are almost always purely vibronic.
12.5.5 Energy Transfer

When more than one optically active center is present, an excited center may impart all or part of its energy to a nearby center, a process called energy transfer. This can happen radiatively or non-radiatively.

In the radiative process (Figure 12.20a), the excited ion emits a photon and another ion absorbs that photon before it leaves the crystal. This process obeys a \(1/R^2\) law and has little effect on the lifetime of the radiating level.

Some non-radiative energy transfer processes are shown in Figures 12.20b–d. The ion from which the energy is being transferred is called the sensitizer \(S\). The ion to which the energy is transferred is called the activator \(A\). We first consider the case of resonant energy transfer, shown is Fig. 12.20b.

![Figure 12.20](image)

Figure 12.20 Energy transfer processes: (a) radiative, (b) resonant, non-radiative, (c) phonon-assisted, non-radiative and (d) non-radiative cross-relaxation.

The initial state of the system is an excited sensitizer and an activator in the ground state; the final state of the system is a sensitizer in ground state and an activator in excited state. The relevant Hamiltonian is the coulombic interaction between the electrons of the sensitizer and those of the activator. Forster [34] and Dexter [35] developed the following equation for the resonant energy transfer rate \(W_{SA}\) between \(S\) and \(A\):

\[
W_{SA} = K \frac{Q_A}{R^n \tau_S} \int \frac{g_S(E)g_A(E)}{E^4} dE .
\]

(12.97)

In equation (12.97), \(K\) is a constant, \(Q_A\) is the area under the absorption band of the activator, \(\tau_S\) is the lifetime of the sensitizer, and \(R\) is the distance between the sensitizer and the activator. \(g_S\) and \(g_A\) are the normalized shape functions of the emission bands of the sensitizer and the absorption bands of the activator, respectively. The integral includes the overlap of these two functions, and is essentially a conservation of energy statement.

The \(R^n\) term is determined by the multipolar interaction between \(S\) and \(A\). In most cases, the dipole-dipole (\(n = 6\)) mechanism is dominant. In cases where the dipole-dipole term vanishes due to symmetry, then the dipole-quadrupole (\(n = 8\)) or quadrupole-quadrupole (\(n = 10\)) terms may dominate. The exchange interaction may also drive the transfer, but is important only when \(S\) and \(A\) are in close proximity to one another [36].
Experimentally, one can gain insight into the nature of the interaction by examining the response of the system to pulsed excitation. Based on the work of Förster [37], assuming an even distribution of sensitizers and activators, the evolution in time of the population density \( n_S \) of excited sensitizers goes as

\[
\frac{d}{dt} n_S(t) = n(0) \exp \left( -\frac{t}{\tau_S} - \Gamma \left( 1 - \frac{3}{q} \frac{C_A}{C_0} \frac{t^{\frac{3}{q}}}{\tau_S^q} \right) \right). \tag{12.98}
\]

In equation (12.98), \( C_A \) is the acceptor concentration, \( C_0 \) is the sensitizer concentration at which energy transfer is equally likely as spontaneous deactivation, \( \tau_S \) is the lifetime of the sensitizer in the absence of the acceptor, and \( q = 6, 8, \) or 10 depending on whether the multipolar interaction is dipole-dipole, dipole-quadrupole, or quadrupole-quadrupole, respectively. A best fit of the decay curve to this equation can be used to determine the type of interaction.

In phonon-assisted energy transfer (Figure 12.21c) the overlap integral in equation (12.97) is close to zero, and energy difference between the emission of the sensitizer and absorption of the activator must be made up for by the absorption or creation of one or more phonons. The following observations can be made regarding phonon-assisted transfer.

1. The transfer rate obeys an exponential energy gap law if the gap is much larger than the phonon energy [38], that is, if more than one phonon is required. This situation is frequently encountered in REI.
2. If \( W_{SA} \) is much faster than the decay rate of the upper levels of both \( S \) and \( A \), the two levels become thermalized according to the Boltzmann distribution.
3. For TMI, the phonon-assisted energy transfer rate generally increases with temperature. For REI, the rate can increase or decrease with temperature depending on the energy levels involved [39].

### 12.5.6 Upconversion

The term “upconversion” applies to processes whereby a system excited with photons of energy \( h\nu_1 \) emits photons at a frequency \( h\nu_2 \), where \( h\nu_2 \gg h\nu_1 \). The importance of this phenomenon is due, in part, to the fact that it can generate short wavelength emission without having to rely on UV excitation, which can have deleterious secondary effects (such as creation of color centers and excitation of deep traps).

The scheme in Figure 12.21a is called excited state absorption (ESA) and involves a single ion. In this process two photons are absorbed sequentially, and the intermediate state is real. Non-radiative relaxation to a lower level may or may not occur following the absorption of the first photon.

Figure 12.21b shows a process called two-photon absorption (TPA). In this process, the two photons are absorbed simultaneously, and the intermediate state is a virtual one.
Another type of upconversion is a two-ion energy transfer process in which the activator is initially in an excited state (Figure 12.21c). This is referred to as upconversion by energy transfer (ETU). Three-ion up-conversion, an example of which is shown in Figure 12.21d, has been observed, but such processes are very weak. All upconversion processes are nonlinear, since they require the absorption of at least two photons. ESA and ETU are the most common. Experimentally, the two mechanisms can be distinguished from one another by examining the system’s response to pulsed (laser) excitation. Both systems show a rise followed by a decay. For ESA-type upconversion, the rise time is within the lifetime of the pump (laser) pulse. For ETU, the luminescence peak occurs after the laser pulse is over, with the rise time depending on the decay time of the luminescent state and the ETU rate. The reader is referred to a recent review of upconversion processes by Auzel [40].

![Figure 12.21](image-url)  
Figure 12.21 Upconversion processes: (a) excited state absorption (ESA), (b) two-photon absorption (TPA), (c) upconversion by energy transfer (ETU), and (d) three-ion cooperative energy transfer.

### 12.5.7 Line Broadening and Shifting with Temperature

In this section we discuss the affect of temperature on the width and position of the zero-phonon lines, particularly in REI-doped solids.

#### 12.5.7.1 Spectral Line Broadening with Temperature

The width of a spectral line is affected by several mechanisms, including inhomogeneous broadening, direct one-phonon processes, multiphonon decay,
radiative decay, and Raman scattering. Inhomogeneous broadening is caused by variations in the crystal field local to the REI. This effect is not temperature-dependent, and so will not be discussed here. Direct one-phonon processes, multiphonon decay, and radiative decay all affect width of the level by reducing its lifetime. With lifetimes of luminescent REI levels generally longer than a $10^{-7}$ sec, the sum of the contributions of these processes as given by the uncertainty principle is less than 0.01 cm$^{-1}$. Raman scattering involves the simultaneous absorption and emission of phonons, usually of two different frequencies. The electronic state of the ion is unchanged in the process, so that the lifetime is not affected. Experience has shown that the main contribution to the linewidth is from Raman processes and is on the order of a few cm$^{-1}$.

Raman scattering is a second order process. Using a perturbation approach, the probability of the ion absorbing an ion at frequency $\omega_i$ and emitting a phonon of $\omega_j$ is

$$ P_{ij} = A \omega_i \omega_j N(\omega_i)(N(\omega_j) + 1). \quad (12.99) $$

$N(\omega_i)$ and $(N(\omega_j) + 1)$ refer to the absorption and emission of a phonon, respectively, where $N(\omega_i) = [\exp(h\omega_i/kT) - 1]^{-1}$ is the number of phonons in the $i$th mode. $A$ is a constant describing the ion-lattice interaction strength.

Assuming a phonon density of states given by the Debye distribution and integrating over all allowed phonon frequencies, the contribution to the linewidth becomes

$$ \Delta E = A' \left( \frac{T}{T_D} \right)^2 \int_0^{\infty} \frac{x^6 e^x}{(e^x - 1)^2} \, dx. \quad (12.100) $$

$T_D$ is the Debye temperature of the solid. Experimental data of linewidth versus temperature are usually fitted to equation (12.100) treating $A'$ and $T_D$ as adjustable parameters [42].

### 12.5.7.2 Shift of Spectral Lines with Temperature

In Section 12.4 we discussed the effect of $H_{\text{CF-static}}$ on the energy of the system. The contribution of $H_{\text{CF-dynamic}}$ to the energy of an ion in a solid is revealed in the shift of the spectral lines with temperature. As in the case of line broadening, Raman scattering is found to be the dominant process.

The contribution of Raman processes to the energy of the $i$th level is

$$ \delta E_i = \sum_{j,k} \frac{\langle i,k | H_{\text{CF-dyn}} | j,k \pm 1 \rangle \langle j,k \pm 1 | H_{\text{CF-dyn}} | i,k \rangle}{E_i - E_j + \hbar \omega_k} + \langle i,k | H_{\text{CF-dyn}} | i,k \rangle. \quad (12.101) $$

The sum over $j$ includes all the electronic states of the system except the $i$th state. The sum over $k$ includes all phonon modes.
Assuming a Debye phonon distribution, and also that the energy difference between electronic levels is greater than the phonon energies, equation (12.101) reduces to

$$\delta E_i = A'' \left( \frac{T}{T_D} \right)^4 \int_0^{T/T_D} \frac{x^3}{e^x - 1} \, dx,$$

(12.102)

where $A''$ is a constant. A fit of this equation to lineshift data allows one to determine the Debye temperature of the solid. We note the following:

1. Raman scattering involves the participation of real intermediate states. For REI, these states include all unoccupied 4f-levels as well as those of the upper configurations.
2. The experimentally observed shift is the difference in the energy shifts of the two levels involved in the transition.

Experimental data show that lines shift generally toward the red, though blue shifts are sometimes observed. Typically, the observed shift is on the order of 10 cm$^{-1}$ as the temperature is varied from 4 K to 500 K [42].

### 12.6 DELOCALIZED SYSTEMS

#### 12.6.1 Density of One-Electron States and Fermi Probability Distribution

Given a volume $V = L^3$ the number of one-particle states in the range $dp_x dp_y dp_z$ is

$$\frac{V}{8\pi^3} d k_x d k_y d k_z = \frac{V}{\hbar^3} dp_x dp_y dp_z. \quad (12.103)$$

The number of one-particle states in the range $(p, p + dp)$ is

$$g(p) dp = \frac{V}{\hbar^3} \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} p^2 \sin \theta \, d \theta \, d \phi \, dp = \frac{4\pi V}{\hbar^3} p^2 \, dp \quad (12.104)$$

and, if the particles are electrons, taking the spin into account,

$$2 g(E) dE = 2 g(p) \frac{dp}{dE} dE = \frac{4\pi V}{\hbar^3} p^2 \left( \frac{2m}{E} \right)^{1/2} E^{1/2} dE \quad (12.105)$$

Given a system of Fermions at temperature $T$, the probability distribution that specifies the occupancy probability is

$$F(E) = \frac{1}{e^{(E - E_F)/kT} + 1}. \quad (12.106)$$

In metals $E_F$, the Fermi energy, is the energy of the most energetic quantum state occupied at $T = 0$. At $T \neq 0$, $E_F$ is the energy of a quantum state that has the
probability 0.5 of being occupied. The number of available states in \((E, E + dE)\) for a system of electrons is

\[
2g(E)dE = \frac{4\pi V}{h^3} (2m)^{3/2} E^{1/2} dE = \frac{8\sqrt{2}\pi m^{3/2}}{h^3} V E^{1/2} dE
\]

(12.107)

The Fermi energy at \(T = 0\) is determined by

\[
N = \int_0^E 2g(E)dE = \frac{8\sqrt{2}\pi m^{3/2}}{h^3} V \int_0^{E_F} E^{1/2} dE
\]

\[
= \frac{16\sqrt{2}\pi m^{3/2}}{3h^3} V E_F^{3/2}.
\]

(12.108)

Then

\[
E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V}\right)^{2/3} = \frac{0.12\hbar^2}{m} n^{2/3}
\]

(12.109)

where \(n = N/V\).

### 12.6.2 Classification of Crystalline Solids

Crystalline solids are arranged in a repetitive 3D structure called a lattice. The basic repetitive unit is the unit cell. Prototypes of crystalline solids are: (i) copper—metal, (ii) diamond—insulator, and (iii) silicon—semiconductor. We can classify the solid according to three basic properties:

1. Resistivity \(\rho\) at room temperature:
   \[
   \rho = \frac{E}{J} \quad (\Omega m)
   \]
   where \(E = \) electric field, \(J = \) current density.

2. Temperature coefficient of resistivity
   \[
   \alpha = \frac{1}{\rho} \frac{d\rho}{dt} \quad (K^{-1})
   \]

3. Number density of charge carriers, \(n\) (m\(^{-3}\)).

The resistivity of diamond is greater than \(10^{24}\) times the resistivity of copper. Some typical parameters for metals and undoped semiconductors are reported in Table 12.3.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Copper (metal)</th>
<th>Silicon (semiconductor)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n)</td>
<td>m(^{-3})</td>
<td>(9 \times 10^{28})</td>
<td>(1 \times 10^{15})</td>
</tr>
<tr>
<td>(\rho)</td>
<td>(\Omega m)</td>
<td>(2 \times 10^{-8})</td>
<td>(3 \times 10^{3})</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>K(^{-1})</td>
<td>(4 \times 10^{-3})</td>
<td>(-70 \times 10^{-3})</td>
</tr>
</tbody>
</table>

Table 12.3 A comparison of the properties of metals and semiconductors.
If we assemble \( N \) atoms, each level of an isolated atom splits into \( N \) levels in the solid. Individual energy levels of the solid form bands, with adjacent bands being separated by gaps. A typical band is only a few eV wide. Since the number of levels in one band may be on the order \( \sim 10^{24} \), the energy levels within a band are very close.

### 12.6.2.1 Insulators

The electrons in the filled upper band have no place to go: The vacant levels of the band can be reached only by giving an electron enough energy to bridge the gap. For diamond the gap is 5.5 eV. For a state at the bottom of the conduction band, the energy difference \( E - E_F \) is 0.5\( E_g \), since, as we shall see later, the Fermi energy for undoped semiconductors is approximately at the middle of the gap. Therefore we have \( (E - E_F) \gg kT \), and we can write for the probability that one electron occupies a quantum level at the bottom of the conduction band as

\[
P(E) = \frac{1}{e^{(E-E_F)/kT} + 1} \approx e^{(E-E_F)/kT} = e^{-\frac{E_g}{2kT}}.
\]

At room temperature such a probability has the value

\[
P(E) = e^{-5.5/2(0.026)} \approx 1.2 \times 10^{-46}
\]

and is negligible.

### 12.6.2.2 Metals

The feature that defines a metal is that the highest occupied energy level falls near the middle of an energy band. Electrons have empty levels to which they can go!

A classical free electron model can be used to deal with the physical properties of metals. This model predicts the functional form of Ohm’s law and the connection between the electrical and thermal conductivity of metals, but does not give correct values for the electrical and thermal conductivities. This deficiency can be remedied by taking into account the wave nature of the electron.

### 12.6.2.3 Semiconductors

In this section we shall treat semiconductors that do not contain any impurity, generally called intrinsic semiconductors. We shall see later how the presence of impurities affects greatly the properties of semiconductors. The band structure
of a semiconductor is similar to that of an insulator: The main difference is that a semiconductor has a much smaller energy gap $E_g$ between the top of the highest filled band (valence band) and the bottom of the lowest empty band (conduction band) above it. For diamond, $E_g = 5.5\text{eV}$ whereas for Si, $E_g = 1.1\text{eV}$.

The charge carriers in Si arise only because, at thermal equilibrium, thermal agitation causes a certain (small) number of valence band electrons to jump over the gap into the conduction band. They leave an equal number of vacant energy states called holes. Both electrons in the conduction band and holes in the valence band serve as charge carriers and contribute to the conduction. The resistivity of a material is given by:

$$\rho = \frac{m}{e^2 n \tau}$$  \hspace{1cm} (12.111)

where $m$ is the mass of the charge carrier, $n$ is the number of charge carriers/\text{V}, and $\tau$ is the mean time between collisions of charge carriers. Now, $\rho_C = 2 \times 10^{-8} \Omega$, $\rho_S = 3 \times 10^3 \Omega\text{m}$, and $n_C = 9 \times 10^{28} \text{m}^{-3}$, $n_S = 1 \times 10^{16} \text{m}^{-3}$, so that

$$\frac{\rho_S}{\rho_C} = 10^{11} \quad \text{and} \quad \frac{n_C}{n_S} = 10^{13}.$$  

The vast difference in the density of charge carriers is the main reason for the great difference in $\rho$.

We note than the temperature coefficient of resistivity is positive for Cu and negative for Si. The atom Si has the following electronic configuration

$$\underbrace{2s^2\text{core}}_{\text{Si}} 3s^2 \text{3p}^2.$$  

Each Si atom has a core containing 10 electrons and contributes its $3s^23p^2$ electrons to form a rigid two-electron covalent bond with its neighbors. The electrons that form the Si-Si bonds constitute the valence band of the Si sample. If an electron is torn from one of the four bonds so that it becomes free to wander through the lattice, we say that the electron has been raised from the valence to the conduction band.

### 12.6.3 Intrinsic Semiconductors

We shall now present a model for an intrinsic semiconductor. In general the number of electrons per unit volume in the conduction band is given by

$$n_c = \int_{E_c}^{\infty} N(E) F(E) dE$$  \hspace{1cm} (12.112)

where $N(E) = \text{density of states}$ and $E_c = \text{energy at the bottom of the conduction band}$.

We expect $E_F$ to lie roughly halfway between $E_c$ and $E_c$: The Fermi function decreases strongly as $E$ moves up in the conduction band. To evaluate the integral in equation (12.112), it is sufficient to know $N(E)$ near the bottom of
the conduction band and integrate from $E = E_c$ to $E = \infty$. Near the bottom of the conduction band, according to equation (12.105), the density of states is given by:

$$N(E) = \frac{4\pi}{h^3} \left(2m_e^*\right)^{3/2} (E - E_c)^{1/2}$$

(12.113)

where $m_e^*$ = effective mass of the electron near $E_c$. Then

$$n_e = \frac{4\pi}{h^3} \left(2m_e^*\right)^{3/2} \left[ \int_{E_c}^{\infty} \frac{(E - E_c)^{1/2}}{e^{(E-E_c)/kT} + 1} dE \right]$$

(12.114)

$$\frac{4\pi}{h^3} \left(2m_e^*\right)^{3/2} \int_{E_c}^{\infty} \frac{(E - E_c)^{1/2}}{e^{(E-E_c)/kT} - 1} dE.$$  

The integral may then be reduced to one of type

$$\int_0^{\infty} x^{1/2} e^{-x^2} dx = \frac{\pi^{1/2}}{2}$$

(12.115)

and we obtain the number of electrons per unit volume in the conduction band:

$$n_e = 2 \left(\frac{2\pi m_e^* kT}{h^3}\right)^{3/2} e^{(E_f-E_c)/kT}. \quad (12.116)$$

Let us now consider the number of holes per unit volume in the valence band:

$$n_h = \int_{E_v}^{E_v} N(E) \left[1 - F(E)\right] dE$$

(12.117)

where $E_v = $ energy at the top of the valence band. $1 - F(E)$ decreases rapidly as we go down below the top of the valence band (i.e., holes reside near the top of the valence band). Therefore, in order to evaluate $n_h$, we are interested in $N(E)$ near $E_v$:

$$N(E) = \frac{4\pi}{h^3} \left(2m_h^*\right)^{3/2} (E_v - E)^{1/2}$$

(12.118)

where $m_h^*$ = effective mass of a hole near the top of the valence band. For $E_F - E_v >> kT$,

$$1 - F(E) = 1 - \frac{1}{e^{(E-E_v)/kT} + 1} \approx e^{(E-E_f)/kT} \quad (12.119)$$

Substituting (12.118) and (12.119) into (12.117), we obtain

$$n_h = \int_{E_v}^{E_v} N(E) \left[1 - F(E)\right] dE$$

$$= \frac{4\pi}{h^3} \left(2m_h^*\right)^{3/2} \left[ \int_{E_v}^{\infty} (E_v - E)^{1/2} e^{(E-E_v)/kT} dE \right]$$

(12.120)

$$= 2 \left(\frac{2\pi m_h^* kT}{h^2}\right)^{3/2} e^{(E_f-E_v)/kT}. \quad (12.120)$$

We now use the fact that
and equate the two expressions for \( n_c \) and \( n_h \) given by equations (12.116) and (12.120), respectively. We find

\[
E_F = \frac{E_c + E_v}{2} + \frac{3}{4} kT \ln \frac{m_h^*}{m_e^*},
\]

(12.122)

If \( m_e^* = m_h^* \), \( E_F \) lies exactly halfway between \( E_c \) and \( E_v \). Replacing equation 12.122 in the expression for \( n_c = n_h \) we find

\[
n_c = n_h = 2 \left( \frac{2\pi kT}{\hbar^2} \right)^{3/2} \left( \frac{m_e^* m_h^*}{m_e m_h} \right)^{3/4} e^{-\frac{E_v}{2kT}}
\]

(12.123)

At room temperature,

\[
2 \left( \frac{2\pi kT}{\hbar^2} \right)^{3/2} m^{3/2} \approx 10^{19} \text{ cm}^{-3},
\]

where \( m \) = mass of the electron.

### 12.6.4 Doped Semiconductors

#### 12.6.4.1 \( n \)-Type Semiconductors

Consider the phosphorus atom's electronic configuration:

\[
P : \text{1s}^2 \text{2s}^2 \text{2p}^6 \text{3s}^2 \text{3p}^3 \quad (Z = 15).
\]

If a P atom replaces a Si atom it becomes a donor. The fifth extra electron is only loosely bound to the P ion core: It occupies a localized level with energy \( E_d \ll E_g \) below the conduction band. By adding donor atoms, it is possible to increase greatly the number of electrons in the conduction band. Electrons in the conduction band are majority carriers. Holes in the valence band are minority carriers.

**Example:** In a sample of pure Si the number of conduction electrons is \( \approx 10^{16} \text{ m}^{-3} \). We want to increase this number by a factor \( 10^6 \). We shall dope the system with P atoms creating an \( n \)-type semiconductor. At room temperature the thermal agitation is so effective that practically every P atom donates its extra electron to the conduction band.

The number of P atoms that we want to introduce in the system is given by

\[
10^6 n_0 = n_0 + n_p,
\]

or

\[
n_p = 10^6 n_0 - n_0 \approx 10^6 n_0 = 10^6 \times 10^{16} = 10^{22} \text{ m}^{-3}.
\]

The number density of Si atoms in a pure Si lattice is
because \( N_a = \) Avogadro number, \( \rho = \) density of Si = 2,330 kg/m\(^3\) and \( A = \) molar mass = 28.1 g/mol = 0.028 kg/mol. The fraction of P atoms we seek is approximately

\[
\frac{n_p}{n_{Si}} = \frac{10^{22}}{5 \times 10^{28}} = \frac{1}{5 \times 10^6}.
\]

Therefore, if we replace only one Si atom in five million with a phosphorous atom, the number of electrons in the conduction band will be increased by a factor of \(10^6\).

### 12.6.4.2 p-Type Semiconductors

Consider the electronic configuration of an aluminum atom:

\[
\text{Al : } 1s^2 2s^2 2p^6 3s^2 3p^1 \quad (Z = 13).
\]

If an Al atom replaces a Si atom it becomes an acceptor. The Al atom can bond covalently with only three Si atoms; there is now a missing electron (a hole) in one Al-Si bond. With a little energy an electron can be torn from a neighboring Si-Si bond to fill this hole, thereby creating a hole in that bond. Similarly, an electron from some other bond can be moved to fill the second hole; in this way the hole can migrate through the lattice. It has to be understood that this simple picture should not be taken as indicative of a hopping process, since a hole represents a state of the whole system. Holes in the valence band are now majority carriers. Electrons in the conduction band are minority carriers. We compare the properties of an \(n\)-type semiconductor and of a \(p\)-type semiconductor in Table 12.4.

### 12.6.5 Model for a Doped Semiconductor

Most semiconductors owe their conductivity to impurities, i.e., either to foreign atoms put in the lattice or to a stoichiometric excess of one of its constituents. Energy level scheme for an \(n\)-type semiconductor and a \(p\)-type semiconductor is shown schematically in Figure 12.22.
12.6.5.1 *n*-Type Semiconductors

At $T = 0$ all the donor levels are filled. At low temperatures only a few donors are ionized; the Fermi level is halfway between donor levels and the bottom of the conduction band. If we assume that $E_F$ is below the bottom of the conduction band by more than a few $kT$, then we can use in this case a formula similar to equation (12.116) and find

$$n_c = 2 \left( \frac{2\pi m^* kT}{h^2} \right)^{3/2} e^{(E_i - E_c)/kT} \quad (12.124)$$

Figure 12.22 Energy level scheme for (a) an *n*-type semiconductor, and (b) a *p*-type semiconductor. $E_i$ is the energy of the donor level (a) or the acceptor level (b).

If $E_F$ lies more than a few $kT$ above the donor level at $E_d$, the density of empty donors is equal to

$$n_d \left[ 1 - F(E_d) \right] \approx n_d e^{(E_d - E_F)/kT} \quad (12.125)$$
Equating (12.124) and (12.125) we obtain

\[ E_F = \frac{1}{2}(E_d + E_c) + \frac{kT}{2} \ln \left( \frac{n_d}{2} \left( \frac{2\pi m^* k T}{h^2} \right)^{-3/2} \right). \]  \hspace{1cm} (12.126)

At \( T = 0 \), \( E_F \) lies halfway between the donor level and the bottom of the conduction band. As \( T \) increases, \( E_F \) drops (see Figure 12.23). Putting the expression for \( E_F \) from equation (12.126) in \( n_c \) given by equation (12.124), we find

\[ n_c = \left( \frac{2\pi m^* k T}{h^2} \right)^{3/4} \frac{E_c - E_F}{e^{2kT}}. \]  \hspace{1cm} (12.127)

**Figure 12.23** The variation of the position of the Fermi level with temperature with a donor level 0.2 eV below the bottom of the conduction band for three different values of \( n_d \) [43]

### 12.6.5.2 p-Type Semiconductors

The case of \( p \)-type semiconductors can be treated in a similar way. \( n_h \) has an expression similar to that for \( n_c \). The Fermi level lies halfway between the acceptor level and the top of the valence band at \( T = 0 \). As \( T \) increases, \( E_F \) rises.

Figure 12.24 represents schematically the behavior of the Fermi level for an \( n \)-type and for a \( p \)-type semiconductor. The figure illustrates the fact that as the temperature increases the Fermi level for an \( n \)-type semiconductor does not drop indefinitely as indicated by (12.127). As the temperature increases the intrinsic excitations of the semiconductor become more important and the Fermi level tends to set in the middle of the gap. Similar effects take place for the \( p \)-type semiconductor. For additional considerations, the reader is referred to the book by Dekker (see bibliography at the end of this chapter).
12.7 PROCESSES IN DELOCALIZED SYSTEMS

12.7.1 Direct Gap and Indirect Gap Semiconductors

The energy of the band gap of a semiconductor determines the spectral region in which the electronic transitions, both in absorption and emissions, take place. For visible or near infrared transitions we need materials with gaps ~1-1.7eV. A list of such materials is provided in Table 12.5.

Table 12.5 A list of typical semiconductors.

<table>
<thead>
<tr>
<th>Material</th>
<th>Type</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Indirect</td>
<td>1.16</td>
</tr>
<tr>
<td>InP</td>
<td>Direct</td>
<td>1.42</td>
</tr>
<tr>
<td>GaAs</td>
<td>Direct</td>
<td>1.52</td>
</tr>
<tr>
<td>GaP</td>
<td>Indirect</td>
<td>2.3</td>
</tr>
<tr>
<td>AlP</td>
<td>Indirect</td>
<td>2.5</td>
</tr>
<tr>
<td>SiC</td>
<td>Indirect</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Direct gap transitions take place when the maximum energy of the valence band and the minimum energy of the conduction band both occur in correspondence to a value of the linear momentum equal to zero or at the same \( \vec{k} = 0 \). Such semiconductors are called direct gap semiconductors.

In other materials, the maximum of the valence band and the minimum of the conduction band occur at different values of \( \vec{k} \). Such materials are called indirect gap semiconductors.

It is interesting to consider the case of the semiconductor GaAs. By changing the chemical composition of this material according to the formula \( \text{GaAs}_{1-x}\text{P}_x \), it is possible to change the band gap from 1.52 eV with \( x = 0 \) to 2.3 eV with \( x = 1 \). In addition, for \( x > 0.4 \) the material changes its character from that of a direct

![Diagram](image-url)
gap to an indirect gap semiconductor. Mixtures of InP and AlP can also yield gaps from 1.42 to 2.5 eV.

12.7.2 Excitations in Insulators and Large Band Gap Semiconductors

If a beam of light with photons exceeding in energy the energy gap goes through an insulator or a semiconductor, it raises an electron from the valence band into the conduction band for each photon absorbed, leaving behind a hole. The electron and the hole may move away from each other contributing to the photoconductivity of the material. On the other hand, they may combine producing an exciton, a hydrogen-like or a positron-electron pair-like structure. Excitons are free to move through the material. Since the electron and the hole have opposite charge, excitons are neutral and, as such, are difficult to detect. When an electron and a hole recombine, the exciton disappears and its energy may be converted into light or it may be transferred to an electron in a close-by atom, removing an electron from this atom and producing a new exciton.

Excitons are generally more important in insulators and in semiconductors with large gaps, even if some excitonic effects in small gap materials have been observed. Excitons do not obey the Fermi-Dirac statistics and therefore it is not possible to obtain a filled band of excitons. Excitons may also be created in doped semiconductors. In these, however, the free charges provided by the impurities tend to screen the attraction between electrons and holes, and excitonic levels are difficult to detect.

Two models are generally used to deal with excitons in solids. These models are more than two different ways of looking at the same problem; rather, they reflect two extreme physical situations:

a) a model in which the electron, after its excitation, continues to be bound to its parent atom; and

b) a model where the electron loses the memory of its parent atom and binds together with a hole.

The first case corresponds to the so-called Frenkel exciton and the second case to the Wannier exciton. Experimentally, the Frenkel exciton is in principle recognizable because the optical transitions responsible for the production of the exciton occur in the same spectral region of the atomic transitions. Experimentally, the transitions responsible for the production of a Wannier exciton fit a hydrogen-like type of behavior.
12.7.3 Radiative Transitions in Pure Semiconductors

12.7.3.1 Absorption

The absorption optical spectra of pure semiconductors generally present the following features (see Figure 12.25):

a) A region of strong absorption is present in the ultraviolet with a possible extension to the visible and infrared, due to electronic transitions from the valence to the conduction band. These interband transitions produce mobile electrons and holes that contribute to the photoconductivity. The value of the absorption coefficient is typically $10^5$–$10^6$ cm$^{-1}$. On the high energy side, the absorption band (~20 eV) decreases in value smoothly in a range of several eV. On the low energy side, the absorption decreases abruptly and may decrease by several orders over a range of a few tenths of an eV. In semiconductors, this region of the absorption spectrum is referred to as the absorption edge.

b) The low energy limit of the absorption edge corresponds to the photon energy necessary to move an electron across the minimum energy gap $E_g$. The exciton structure appears in the absorption edge region. It is more evident in insulators such as ionic crystals than in semiconductors.

c) At longer wavelengths the absorption rises again due to free-carrier absorption, i.e., electronic transitions within the conduction or valence bands. This absorption extends to the infrared and microwave regions of the spectrum.

d) A set of peaks appear at energies 0.02 to 0.05 eV ($\lambda = 50$–20 $\mu$m), due to the interaction between the photons and the vibrational modes of the lattice. In ionic crystals, the absorption coefficient may reach $10^3$ cm$^{-1}$; in homopolar crystals the absorption coefficient is generally much lower, such as $10^2$–$10^3$ cm$^{-1}$.

e) Impurities, if present in the semiconductor, may be responsible for absorption in the region of, say, 10$^{-2}$ eV or so. This absorption is observable for $kT$ lower than the ionization energy.

f) If the semiconductor contains paramagnetic impurities the absorption spectrum will present absorption lines in the presence of a magnetic field that splits the Zeeman levels.

g) An absorption peak in the long wavelength region may be present in the presence of a magnetic field, due to cyclotron resonance of the mobile carriers.
We want to make some additional considerations regarding the features a) and b) of the absorption spectrum. Interband transitions can take place subject to the two conditions of energy and conservation of wavevector:

\[
\begin{aligned}
E_f - E_i &= \hbar \omega (\vec{k}') \\
\vec{k}_f - \vec{k}_i &= \vec{k}'
\end{aligned}
\] (12.128)

where the subscripts f and i refer to the final and initial one electron states and \(\vec{k}'\) is the wave vector of the absorbed photon of energy \(\hbar \omega (\vec{k}')\). Since the wavelength of the radiation is much longer than the lattice constant, \(\vec{k}'\) is much smaller than the size of the reciprocal lattice constant and \(\vec{k}'\) can then be neglected in the second equation (12.128). This means that in an \((E, \vec{k})\) diagram we should rely on vertical transitions.

The interband absorption is restricted by the conditions (12.128) and shows a structure that depends on the density of final states. The peaks can be presumably associated with values of \(\vec{k}\) about which the empty and the filled bands run parallel:

\[
\vec{v} \cdot \vec{k} E_v (\vec{k}) = \vec{v} \cdot \vec{k} E_c (\vec{k}).
\] (12.129)

In such a case there is a large density of initial and final states available for the transitions in a small range of energies.

In Section 12.7.1 we have made a distinction between direct gap and indirect gap semiconductors. For the former, the maximum of the valence band energy and the minimum of the conduction band energy occur frequently at \(\vec{k} = 0\), (but not always, e.g., this is not true for Ta-doped halides of lead salts), whereas for the latter they occur at different values of \(\vec{k}\). In indirect gap semiconductors, the absorption transitions at the band edge are phonon-assisted and have probability
smaller than that of the direct gap absorption transitions. The absorption edge of
the indirect gap absorption may show features related to the available phonon
energies.

We now turn our attention to the excitonic structure of the absorption band.
We have two models at our disposal: the Frenkel model and the Wannier model.
In the Frenkel model, an excited electron describes an orbit of atomic size
around an atom with a vacant valence state; this model is more appropriate for
ionic insulators. The Wannier model represents an exciton as an electron and a
hole bound by the Coulomb attraction, but separated by several lattice sites. This
model is more appropriate for semiconductors.

An example of the Frenkel exciton is given by the crystal MnF₂ [45] in which
the excited state may be considered to consist of an electron and a hole residing
in the same ion. The excitation can travel throughout the system via the energy
transfer mechanism. A good example of the Wannier exciton is given by Cu₂O,
which presents absorption lines up to \( n = 11 \). [46]

12.7.3.2 Emission

Following the absorption process, an excited electron can decay radiatively by
emitting a photon (possibly accompanied by a phonon) or non-radiatively by
transforming its excitation energy entirely into heat (phonons). The following
reasons make the emission data relevant:

1) Emission is not simply the reversal of absorption. In fact, the two
phenomena are thermodynamically irreversible and therefore, emission
spectroscopy furnishes data not available in absorption.

2) Emission is easier to measure than absorption, since its intensity depends
on the intensity of excitation.

3) The applications of emission from solids, such as those of fluorescent
lights and television, far outnumber the application of absorption.

In Section 12.7.5, we discuss the photon emission processes in solids.

12.7.4 Doped Semiconductors

Two types of impurities are particularly important when considering the optical
behavior of semiconductors.

\textit{Donors:} As we have seen in Section 12.6.4, when a material made of group IV
atoms, like Si or Ge, is doped with a small amount of group V atoms like As, the
extra electrons of these atoms continue to reside in the parent atoms, loosely
bound to them. The binding energy, called \( E_D \), is typically around 0.01 eV. It is
in fact 0.014 eV for As, 0.0098 eV for Sb and 0.0128 eV for P. \( E_D \) is also called
the ionization energy of the donor atom. The electrons that a donor puts in the
conduction band, because of thermal excitation, cannot produce luminescence, because this process needs, besides an excited electron, a hole where the electron can go, and the valence band, being filled with electrons, has no holes.

Acceptors: If a material made of group IV atoms, such as Si or Ge, is doped with group III atoms, such as Ga or Al, a hole for each of these atoms forms and remains loosely bound to the parent atom. The amount of energy necessary to move an electron from the top of the valence band to one of these holes is labeled $E_A$ and is typically around 0.03 eV. $E_A$ may also be called the ionization energy of the acceptor.

Both types of impurities can be doped into the same crystal, deliberately, or they may be due to the fact that it is practically impossible to fabricate semiconductor crystals of perfect purity.

12.7.5 Radiative Transitions Across the Band Gap

We shall now examine, following Elliott and Gibson [47], the radiative processes that can take place across the band gap of a semiconductor (see Figure 12.26).

Processes $A$ and $B$: An electron excited to a level in the conduction band will thermalize quickly with the lattice and reside in a region $\sim 1 \ kT$ wide at the bottom of the conduction band. Thermalization is generally achieved by phonon emission, but also, less frequently, by phonon-assisted radiative transitions. If such photons have energy exceeding $E_B$, they can be reabsorbed and promote another electron to the conduction band.

Process $C$: The recombination of electrons and holes with photon emission, the reverse process to absorption, is possible, but not very likely, because of competing processes. It may be present only in high purity single crystals. The widths of the related emission bands are expected to be $\sim 1 \ kT$ because the thermalized electrons and holes reside at the band edges in this range of energy.

Figure 12.26 Transitions producing emission of photons in solids.
Process D: The radiative decay of the exciton can be observed at low temperature in very pure crystals. There are two types of decay: 1) the decay of the free exciton, and 2) the decay of an exciton bound to an impurity. Transitions of the first type are observed at low temperatures. Since the exciton levels are well-defined, a sharply structured emission can be expected.

As for the transitions of the second type, they may be observed in materials of high purity into which impurities are purposely doped. An exciton may bind itself to one such impurity; the energy of the bound exciton is lower than the $n=1$ energy by an amount equal to the binding energy of the exciton to the impurity. It may be noted that emission from bound excitons in indirect gap materials can take place without the assistance of phonons because the localization of a bound exciton negates the requirement of wavevector conservation. Bound electron emission is observed at low temperature and is generally much sharper than free electron emission.

Processes F and G: The transitions related to these processes are between the band edges and donors and acceptors and are commonly observed in solids. In particular, we may have conduction band to neutral acceptor ($F$) and neutral donor to valence band ($G$) transitions. They may be phonon-assisted.

Process H: In the transitions related to these processes, an electron leaves a neutral donor and moves to a neutral acceptor. After such a transition both donor and acceptor are ionized and have a binding energy equal to

$$E_b = -\frac{e^2}{4\pi\varepsilon_0 kr}$$

(12.130)

where $r$ is the donor-acceptor distance. The energy of the transition is then

$$\hbar\omega(r) = E_g - E_A - E_D + \frac{e^2}{4\pi\varepsilon_0 kr}$$

(12.131)

An example of such a transition is given by GaP-containing sulfur donors and silicon acceptors, both set in phosphor sites.

12.7.6 Non-Radiative Processes

In the great majority of cases, recombination of electrons and holes takes place by emission of phonons. Since the probability of such processes decreases with the number of phonons emitted, these processes are favored by the presence of intermediate levels between the valence and the conduction bands produced by impurities or defects.

An additional mechanism, known as the Auger process could be responsible for the non-radiative recombination of electrons and holes. In an Auger process, an electron undergoes an interband transition and gives the corresponding energy to another conduction band electron, which is then brought to a higher level in the same band. The latter electron decays then to the bottom of the band with the phonon emission facilitated by the near continuum of states. In most cases,
however, the mechanism of non-radiative decay has not been identified with certainty.

12.7.7 p-n Junctions

12.7.7.1 Basic Properties

A p-n junction consists of a semiconductor crystal doped in one region with donors and in an adjacent region with acceptors. Assume, for simplicity’s sake, that the junction has been formed mechanically by pushing towards each other a bar of n-type semiconductor and a bar of p-type semiconductor, so that a junction plane divides the two regions (see Figure 12.27).

Let us now examine the motion of the electrons (majority carriers of the n-type bar) and of holes (majority carriers of the p-type bar). Electrons on the n-side of the junction plane tend to diffuse (from right to left in the figure) across this plane and go to the p-side, where there are only very few electrons. On the other hand, holes on the p-side tend to diffuse (from left to right in the figure) and go to the n-side, where there are only very few holes.

![Diagram of a p-n junction](image)

**Figure 12.27** a) An n-type material and a p-type material joined to form a p-n junction. b) Space charge associated with uncompensated donor ions at the right of the junction plane and acceptor ions at the left of the plane. c) Contact potential difference associated with the space charge. d) Diffusion current $I_{\text{diff}}$ made up by majority carriers, both electrons and holes, compensated in an isolated p-n junction by a current $I_{\text{drift}}$ made up by minority carriers.
The \( n \)-side region is full with positively charged donor ions. If this region is isolated, the positive charge of each donor ion is compensated by the negative charge of an electron in the conduction band. But, when an \( n \)-side electron diffuses towards the \( p \)-side, a donor ion, having lost its compensating electron, remains positively charged, thus introducing a fixed positive charge near the junction plane. An electron arriving to the \( p \)-side quickly combines with an acceptor ion and introduces a fixed negative charge near the junction plane on the \( p \)-side. Holes also diffuse, moving from the \( p \)-side to the \( n \)-side, and have the same effect as the electrons.

Both electrons and holes, with their motion, contribute to a diffusion current \( I_{\text{diff}} \), that is conventionally directed from the \( p \)-side to the \( n \)-side. An effect of the motion of electrons and holes across the junction plane is the formation of two space charge regions, one negative and one positive. These two regions together form a depletion zone of width \( d_o \) in Figure 12.27, so called because it is relatively free of mobile charge carriers. The space charge has associated with it a contact potential difference \( V_0 \) across the depletion zone, which limits the further diffusion of electrons and holes.

Let us now examine the motion of the minority carriers: electrons on the \( p \)-side and holes in the \( n \)-side. The potential \( V_0 \) set by the space charges represents a barrier for the majority carriers, but favors the diffusion of minority carriers across the junction plane. Together both types of minority carriers produce with their motion a drift current \( I_{\text{drift}} \) across the junction plane in the sense contrary to that of \( I_{\text{diff}} \). An isolated \( p-n \) junction in equilibrium presents a contact potential difference \( V_0 \) between its two ends. The average diffusion current \( I_{\text{diff}} \) that moves from the \( p \)-side to the \( n \)-side is balanced by the average drift current \( I_{\text{drift}} \) that moves in the opposite direction.

Note the following:

a) The net current due to holes, both majority and minority carriers, is zero.

b) The net current due to electrons, both majority and minority carriers, is zero.

c) The net current due to both holes and electrons, both majority and minority carriers included, is zero.

12.7.7.2 The Junction Rectifier

When a potential difference is applied across a \( p-n \) junction with such a polarity that the higher potential is on the \( p \)-side and the lower potential is on the \( n \)-side—an arrangement called forward-bias connection (Figure 12.28a)—a current flows through the junction. The reason for this phenomenon is that the \( p \)-side becomes more positive than it was before and the \( n \)-side more negative,
with the result that the potential barrier $V_o$ decreases, making it easier for the majority carriers to move through the junction plane and increasing considerably the diffusion current $I_{\text{diff}}$. The minority carriers sense no barrier and are not affected, and the current $I_{\text{drift}}$ does not change.

Another effect that accompanies the setting of a forward bias connection is the narrowing of the depletion zone, due to the fact that the lowering of the potential barrier must be associated with a smaller space charge. The space charge is due to ions fixed in their lattice sites, and a reduction of their number produces a reduction of the width of the depletion zone. If the polarity is reversed in a backward-bias connection (Figure 12.28b) with the lower potential on the $p$-side and the higher potential on the $n$-side of the $p$-$n$ junction, the applied voltage increases the contact potential difference and, consequently, $I_{\text{diff}}$ decreases while $I_{\text{drift}}$ remains unchanged. The result is a very small back current $I_B$.

![Figure 12.28](image)

**Figure 12.28** a) Forward-bias connection of a $p$-$n$ junction, showing the narrowed depletion zone and the large forward current $I_F$. b) Backward-bias connection of a $p$-$n$ junction, showing the widened depletion zone and the small back current.
12.7.7.3 Radiative Processes in \textit{p-n} Junctions and Applications

In a simple semiconductor, one electron-hole pair may combine with the effect of releasing an energy $E_g$ corresponding to the band gap. This energy in silicon, germanium, and other simple semiconductors is transformed into thermal energy, i.e., vibrational energy of the lattice. In certain semi-conductors, such as GaAs, the energy of a recombined electron-hole pair can be released as a photon of energy $E_g$. However, due to the limited number of electron-hole possible recombinations at room temperature, pure semi-conductors are not apt to be good emitters.

Doped semiconductors also do not provide an adequate large number of electron-hole pairs, with the $n$-type not having enough holes and the $p$-type not enough electrons.

A semiconductor system with a large number of electrons in the conduction band and a large number of holes in the valence band can be provided by a heavily doped $p$-$n$ junction. In such systems, a current can be used in a forward-bias connection to inject electrons in the $n$-type part of the junction and holes in the $p$-part. With large dopings and intense currents the depletion zone becomes very narrow, perhaps a few microns wide, and a great number of electrons are in the $n$-type material and a large number of holes in the $p$-type material. The radiative recombination of electrons and holes produces a light emission called \textit{electroluminescence}, or, more aptly, \textit{injection electroluminescence}.

The materials used for \textit{light emitting diodes} (LEDs) comprise such alloys as GaAs$_{1-x}$P$_x$, in which the band gap can be varied by changing the concentration $x$ of the P atoms. For $x = 0.4$ the material is a direct-gap semiconductor and emits red light. Almost pure GaP produces green light, but, since it is an indirect-gap semiconductor, it has a low transition probability.

The passage of current through a properly arranged $p$-$n$ junction can generate light. The reverse process is also possible, where a beam of light impinging on a suitable $p$-$n$ junction can generate a current. This principle is at the basis of the \textit{photo-diode}.

A remote TV control consists of an LED that sends a coded sequence of infrared light pulses. These pulses are detected by a photo-diode that produces the electrical signals that perform such various tasks as change of volume or channel.

In a forward biased $p$-$n$ junction, a situation may be created in which there are more electrons in the conduction band of the $n$-type material than holes in the valence band of the $p$-type material. Such a situation of population inversion is essential for the production of \textit{laser action}. Of course, in addition to this condition the appropriate geometry for the $p$-$n$ junction is necessary in order to allow the light to be reflected back and forth and produce the chain reaction of stimulated emission. In this way, a $p$-$n$ junction can act as a \textit{$p$-$n$ junction laser}, with a coherent and monochromatic light emission.
12.8 DIRECTION OF FUTURE EFFORTS

12.8.1 Why Luminescence?

Before projecting into the future, it seems worthwhile to ask Why has luminescence spectroscopy been such a fruitful field? Some possible responses to this question are:

1. The basic study of luminescent systems has been a precursor to the development of the laser (laser diodes and doped insulator-based lasers) and several other devices/materials that enjoy widespread application.
2. The study is good in itself, in that it acts as a probe to the understanding of very complex systems, lending insight into their static and dynamic properties.

Static: Luminescence allows us to (1) study the energy levels that cannot be identified solely by absorption measurements, (2) help probe the symmetry of the host material, and (3) reveal the existence of excitonic levels and to provide the means to study them.

Dynamic: Through luminescence, we (1) probe collective excitations of solids, such as phonons, magnons, etc. and (2) track the energy as the system decays from an excited level to the ground level, revealing the existence of processes such as energy transfer, upconversion, and non-radiative decay.

From the essentially inexhaustible source of luminescent systems, there emerges a continuous stream of new data and with it a deeper understanding of the processes relevant to those systems.

Luminescence spectroscopy remains a vibrant field of research, even 400 years since the investigation into the Bologna stone, over 150 years since Stokes’s observations on luminescence from fluorspar, and after more than a half century of modern, scientific inquiry. The body of past work has revealed only some of the dynamics, complexity, and possibilities of luminescent systems. As testament to the validity of past investigations, we have been educated in the workings of these systems, and presented with more questions and challenges as we move forward.

12.8.2 Challenges and Future Work

Though luminescence spectroscopy has much to offer, the complexity of these systems renders the task of establishing general criteria for luminescent systems very difficult, posing continual challenges to workers in the field. The ultimate goal, of course, is to improve the predictive value of our knowledge so that we can accurately predict the response of a system to an impulse of excitation.

The realization of this goal is an extremely difficult task. The luminescence properties depend not just on the general features of the solid, but also on its
more nuanced features—breaks in symmetry, impurities, clustering of ions, local charge distributions, phonon properties of the solid, etc. Indeed, an accurate prediction of even the most fundamental process of luminescence, the radiative transition probability, requires precise knowledge of the wavefunctions of the system, something that has heretofore proven elusive.

This complexity, which provides the challenges of the field, is also the source of the usefulness of luminescent materials. These systems are so varied and complex that they can be designed for a wide variety of applications. Even after several decades of successes, developments of optical materials and their applications continues to proceed rapidly.

Advances in the field of luminescence spectroscopy will continue to be aided by the following:

1. The emergence of new materials: These include the historically important single crystals, glasses, and thin films, as well as novel materials such as ceramics, nanoparticles, nano-layered systems, quantum wires, and quantum dots.

2. Advances in technology: This includes femtosecond lasers, high intensity lasers, and more sophisticated electronics. Advances in computing have allowed for easier manipulation of data and made theoretical calculations accessible to those with even modest computing facilities by modern standards.

3. The demands of the market: For numerous applications, there is a desire for light sources—lasers, in particular—that are more efficient, of higher intensity, more compact, cheaper, faster, and that operate over a wide bandwidth. Recently, for example, the areas of reading, storing, and transmitting data have been particularly instrumental in providing impetus for the development of new materials and devices.

The following list presents a few areas of research that should be particularly fruitful to the field of luminescence, both in the development of luminescence-related technologies and in the understanding of basic physical phenomena.

1. The understanding and control of non-radiative losses: Following excitation, a luminescent system often releases at least part of its energy as heat. By controlling these losses one can, in principle increase or otherwise tailor the radiative emission.

One system in which the control over non-radiative processes can be exercised is nanomaterials. Because of the small particle size involved, the phonon spectrum is no longer a continuum, but is discrete. The lower frequency modes, in particular, are not present [48]. Thus, phonon-related processes may be suppressed in these systems, making radiative processes more probable.

Another possibility for controlling non-radiative decay is through the use of femtosecond laser pulse-shaping techniques. For example, a method called coherent wavepacket excitation can create a superposition state of vibrational modes in an upper electronic state. The ensuing motion directs the excitation energy to the opposite side of the parabola (in a configurational coordinate model), instead of simply decaying via phonon emission to the base of the parabola, offering the possibility of altering the normal decay process [49].
Also, Auzel et al. [10] have shown that under condition of high excitation density, the multiphonon decay rate in rare earth-doped glasses is inhibited. Such an effect could have important consequences in the development of certain lasers where high excitation densities can be achieved.

2. Extension to higher energy regions: To date, work on rare earth ion-doped systems has concentrated mainly on energy levels roughly below 40,000 cm\(^{-1}\). Though these represent only a small fraction of the 4f-levels, they have been utilized for many applications. A continuation into the higher 4f-and 5d energy levels seems promising for both scientific and technological reasons.

3. Shorter time scales: The use of femtosecond lasers has yet to be exploited in luminescent materials, particularly in the investigation of the decay of an excited system by phonon emission. With the period of lattice vibrations on the order of 50 femtoseconds, and phonon emission occurring over several vibrational periods, femtosecond laser pulses could be used to study phonon emission processes while they are in progress. The pump-probe technique seems especially suitable for such investigations.

4. Nonlinear processes: The importance of nonlinear processes, such as upconversion and two-photon excitation, will continue to expand, particularly as high power lasers become more accessible. UV lasers pumped by visible lasers and relying on upconversion could provide an application for nonlinear effects. Using upconversion or two-photon absorption, one can even access the vacuum ultraviolet region without the need for special optics or an evacuated excitation system.

From the current vantage point, we see two major societal factors that will drive research in the field. First, the scarcity of nonrenewable energy resources, the growing demand for these resources, and concerns about the environment will provide an impetus for the development of more energy efficient lighting. Second, the rapid a growth in communications will require improved optical systems, one important component of which will be solid state lasers.

The response to these and other forces will be the continued research into the fundamental processes of luminescence, resulting in more answers and, equally likely, more challenges. Using the past as an example, our scientific curiosity and imagination will lead us to reconfirm, time and again, the observation attributed to van Vleck: “Every crystal, a surprise.”

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