

of transmission or transmissivity  $T$  is defined likewise as the ratio of the transmitted power to the incident power. If there is no absorption or scattering, then by conservation of energy we must have that:

$$R + T = 1. \quad (1.1)$$

The propagation of the beam through a transparent medium is described by the refractive index  $n$ . This is defined as the ratio of the velocity of light in free space  $c$  to the velocity of light in the medium  $v$  according to:

$$n = \frac{c}{v}. \quad (1.2)$$

The refractive index depends on the frequency of the light beam. This effect is called **dispersion**, and will be discussed in detail in Section 2.3. In colourless transparent materials such as glass, the dispersion is small in the visible spectral region, and it therefore makes sense to speak of ‘the’ refractive index of the substance in question.

The absorption of light by an optical medium is quantified by its **absorption coefficient**  $\alpha$ . This is defined as the fraction of the power absorbed in a unit length of the medium. If the beam is propagating in the  $z$  direction, and the intensity (optical power per unit area) at position  $z$  is  $I(z)$ , then the decrease of the intensity in an incremental slice of thickness  $dz$  is given by:

$$dI = -\alpha dz \times I(z). \quad (1.3)$$

This can be integrated to obtain **Beer’s law**:

$$I(z) = I_0 e^{-\alpha z}, \quad (1.4)$$

where  $I_0$  is the optical intensity at  $z = 0$ . The absorption coefficient is a strong function of frequency, so that optical materials may absorb one colour but not another.

In the next section we will explain how both the absorption and the refraction can be incorporated into a single quantity called the complex refractive index. Knowledge of this quantity enables us to calculate the reflectivity  $R$ , and hence the transmissivity  $T$ . This last point follows because the transmissivity of an absorbing medium of thickness  $l$  is given by:

$$T = (1 - R_1) e^{-\alpha l} (1 - R_2), \quad (1.5)$$

where  $R_1$  and  $R_2$  are the reflectivities of the front and back surfaces respectively. This formula applies to the transmission of light through an optical medium such as the one shown in Fig. 1.1. The first and third terms on the right hand side of eqn 1.5 account for the transmission of the front and back surfaces respectively, while the middle term gives the exponential decrease in intensity due to the absorption according to Beer’s law. If the front and back surfaces have equal reflectivities  $R$ , as will usually be the case, then eqn 1.5 simplifies to:

$$T = (1 - R)^2 e^{-\alpha l}. \quad (1.6)$$

Equation (1.5) ignores the possibility of multiple reflections between the front and back surfaces. These will have to be included if the surfaces are parallel and the reflection coefficients are sufficiently large. We will come across some examples where these effects are important when we consider semiconductor laser diodes in Section 5.4.3 and optical bistability in Section 11.4.3. In many cases, however, the effects are small enough to be neglected, as shown in Exercises 1.8 and 1.9.

The optical density, and hence the absorption coefficient, is usually worked out from the measured transmissivity of the sample. This requires accurate normalization of the reflection losses at the surfaces. (See Exercise 1.10.)

The absorption of an optical medium can also be sometimes quantified in terms of the **optical density** (O.D.). This is sometimes called the **absorbance**, and is defined as:

$$\text{O.D.} = -\log_{10} \left( \frac{I(l)}{I_0} \right), \quad (1.7)$$

where  $l$  is the length of the absorbing medium. It is apparent from eqn 1.4 that the optical density is directly related to the absorption coefficient  $\alpha$  through:

$$\text{O.D.} = \frac{\alpha l}{\log_e(10)} = 0.434 \alpha l. \quad (1.8)$$

In this book we will quantify the absorption by  $\alpha$  instead of the optical density because it is independent of the sample length.

The phenomenon of luminescence was studied extensively by George Stokes in the nineteenth century before the advent of quantum theory. Stokes discovered that the luminescence is down-shifted in frequency relative to the absorption, an effect now known as the **Stokes shift**. Luminescence cannot be described easily by macroscopic classical parameters because spontaneous emission is fundamentally a quantum process (see Appendix B).

The simplest sequence of events that takes place in luminescence is illustrated in Fig. 1.3. The atom jumps to an excited state by absorbing a photon, then relaxes to an intermediate state, and finally re-emits a photon as it drops back to the ground state. The Stokes shift is explained by applying the law of conservation of energy to the process. It is easy to see that the energy of the photon emitted must be less than that of the photon absorbed, and hence that the frequency of the emitted light is less than that of the absorbed light. The magnitude of the Stokes shift is therefore determined by the energy levels of the atoms in the medium.

Scattering is caused by variations of the refractive index of the medium on a length scale smaller than the wavelength of the light. This could be caused by the presence of impurities, defects, or inhomogeneities. Scattering causes attenuation of a light beam in an analogous way to absorption. The intensity decreases exponentially as it propagates into the medium according to:

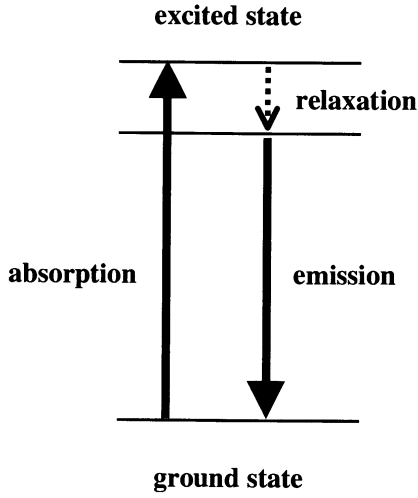
$$I(z) = I_0 \exp(-N\sigma_s z), \quad (1.9)$$

where  $N$  is the number of scattering centres per unit volume, and  $\sigma_s$  is the **scattering cross-section** of the scattering centre. This is identical in form to Beer's law given in eqn 1.4, with  $\alpha \equiv N\sigma_s$ .

The scattering is described as **Rayleigh scattering** if the size of the scattering centre is very much smaller than the wavelength of the light. In this case, the scattering cross-section will vary with the wavelength  $\lambda$  according to:

$$\sigma_s(\lambda) \propto \frac{1}{\lambda^4}. \quad (1.10)$$

The Rayleigh scattering law implies that inhomogeneous materials tend to scatter short wavelengths more strongly than longer wavelengths.



**Fig. 1.3** Luminescence process in an atom. The atom jumps to an excited state by absorption of a photon, then relaxes to an intermediate state, before re-emitting a photon by spontaneous emission as it falls back to the ground state. The photon emitted has a smaller energy than the absorbed photon. This reduction in the photon energy is called the Stokes shift.

**Example 1.1**

The reflectivity of silicon at 633 nm is 35% and the absorption coefficient is  $3.8 \times 10^5 \text{ m}^{-1}$ . Calculate the transmission and optical density of a sample with a thickness of  $10 \mu\text{m}$ .

*Solution*

The transmission is given by eqn 1.6 with  $R = 0.35$  and  $\alpha l = (3.8 \times 10^5) \times (10 \times 10^{-6}) = 3.8$ . This gives:

$$T = (1 - 0.35)^2 \cdot \exp(-3.8) = 0.0095 .$$

The optical density is given by eqn 1.8:

$$\text{O.D.} = 0.434 \times 3.8 = 1.65 .$$

## 1.3 The complex refractive index and dielectric constant

In the previous section we mentioned that the absorption and refraction of a medium can be described by a single quantity called the **complex refractive index**. This is usually given the symbol  $\tilde{n}$  and is defined through the equation:

$$\tilde{n} = n + i\kappa . \quad (1.11)$$

The real part of  $\tilde{n}$ , namely  $n$ , is the same as the normal refractive index defined in eqn. 1.2. The imaginary part of  $\tilde{n}$ , namely  $\kappa$ , is called the **extinction coefficient**. As we will see below,  $\kappa$  is directly related to the absorption coefficient  $\alpha$  of the medium.

The relationship between  $\alpha$  and  $\kappa$  can be derived by considering the propagation of plane electromagnetic waves through a medium with a complex refractive index. If the wave is propagating in the  $z$  direction, the spatial and time dependence of the electric field is given by (see eqn A.32 in Appendix A):

$$\mathcal{E}(z, t) = \mathcal{E}_0 e^{i(kz - \omega t)} , \quad (1.12)$$

where  $k$  is the wave vector of the light and  $\omega$  is the angular frequency.  $|\mathcal{E}_0|$  is the amplitude at  $z = 0$ . In a non-absorbing medium of refractive index  $n$ , the wavelength of the light is reduced by a factor  $n$  compared to the free space wavelength  $\lambda$ .  $k$  and  $\omega$  are therefore related to each other through:

$$k = \frac{2\pi}{(\lambda/n)} = \frac{n\omega}{c} . \quad (1.13)$$

This can be generalized to the case of an absorbing medium by allowing the refractive index to be complex:

$$k = \tilde{n} \frac{\omega}{c} = (n + i\kappa) \frac{\omega}{c} . \quad (1.14)$$

On substituting eqn 1.14 into eqn 1.12, we obtain:

$$\begin{aligned}\mathcal{E}(z, t) &= \mathcal{E}_0 e^{i(\omega \tilde{n} z/c - \omega t)} \\ &= \mathcal{E}_0 e^{-\kappa \omega z/c} e^{i(\omega n z/c - \omega t)}.\end{aligned}\quad (1.15)$$

This shows that a non-zero extinction coefficient leads to an exponential decay of the wave in the medium. At the same time, the real part of  $\tilde{n}$  still determines the phase velocity of the wave front, as in the standard definition of the refractive index given in eqn 1.2.

The optical intensity of a light wave is proportional to the square of the electric field, namely  $I \propto \mathcal{E} \mathcal{E}^*$  (c.f. eqn A.40). We can therefore deduce from eqn 1.15 that the intensity falls off exponentially in the medium with a decay constant equal to  $2 \times (\kappa \omega/c)$ . On comparing this to Beer's law given in eqn 1.4 we conclude that:

$$\alpha = \frac{2\kappa\omega}{c} = \frac{4\pi\kappa}{\lambda}, \quad (1.16)$$

where  $\lambda$  is the free space wavelength of the light. This shows us that  $\kappa$  is directly proportional to the absorption coefficient.

We can relate the refractive index of a medium to its relative dielectric constant  $\epsilon_r$  by using the standard result derived from Maxwell's equations (cf. eqn A.31 in Appendix A):

$$n = \sqrt{\epsilon_r}. \quad (1.17)$$

This shows us that if  $n$  is complex, then  $\epsilon_r$  must also be complex. We therefore define the **complex relative dielectric constant**  $\tilde{\epsilon}_r$  according to:

$$\tilde{\epsilon}_r = \epsilon_1 + i\epsilon_2. \quad (1.18)$$

By analogy with eqn 1.17, we see that  $\tilde{n}$  and  $\tilde{\epsilon}_r$  are related to each other through:

$$\tilde{n}^2 = \tilde{\epsilon}_r \quad (1.19)$$

We can now work out explicit relationships between the real and imaginary parts of  $\tilde{n}$  and  $\tilde{\epsilon}_r$  by combining eqns 1.11, 1.18 and 1.19. These are:

$$\epsilon_1 = n^2 - \kappa^2 \quad (1.20)$$

$$\epsilon_2 = 2n\kappa, \quad (1.21)$$

and

$$n = \frac{1}{\sqrt{2}} \left( \epsilon_1 + (\epsilon_1^2 + \epsilon_2^2)^{\frac{1}{2}} \right)^{\frac{1}{2}} \quad (1.22)$$

$$\kappa = \frac{1}{\sqrt{2}} \left( -\epsilon_1 + (\epsilon_1^2 + \epsilon_2^2)^{\frac{1}{2}} \right)^{\frac{1}{2}}. \quad (1.23)$$

This analysis shows us that  $\tilde{n}$  and  $\tilde{\epsilon}_r$  are not independent variables: if we know  $\epsilon_1$  and  $\epsilon_2$  we can calculate  $n$  and  $\kappa$ , and *vice versa*. Note that if the medium is only weakly absorbing, then we can assume that  $\kappa$  is very small, so that eqns 1.22 and 1.23 simplify to:

$$n = \sqrt{\epsilon_1} \quad (1.24)$$

$$\kappa = \frac{\epsilon_2}{2n}. \quad (1.25)$$

These equations show us that the refractive index is basically determined by the real part of the dielectric constant, while the absorption is mainly determined by the imaginary part. This generalization is obviously not valid if the medium has a very large absorption coefficient.

The microscopic models that we will be developing throughout the book usually enable us to calculate  $\tilde{\epsilon}_r$  rather than  $\tilde{n}$ . The measurable optical properties can then be obtained by converting  $\epsilon_1$  and  $\epsilon_2$  to  $n$  and  $\kappa$  through eqns 1.22 and 1.23. The refractive index is given directly by  $n$ , while the absorption coefficient can be worked out from  $\kappa$  using eqn 1.16. The reflectivity depends on both  $n$  and  $\kappa$  and is given by

$$R = \left| \frac{\tilde{n} - 1}{\tilde{n} + 1} \right|^2 = \frac{(n - 1)^2 + \kappa^2}{(n + 1)^2 + \kappa^2}. \quad (1.26)$$

This formula is derived in eqn A.50. It gives the coefficient of reflection between the medium and the air (or vacuum) at normal incidence.

In a transparent material such as glass in the visible region of the spectrum, the absorption coefficient is very small. Equations 1.16 and 1.21 then tell us that  $\kappa$  and  $\epsilon_2$  are negligible, and hence that both  $\tilde{n}$  and  $\tilde{\epsilon}_r$  may be taken as real numbers. This is why tables of the properties of transparent optical materials generally list only the real parts of the refractive index and dielectric constant. On the other hand, if there is significant absorption, then we will need to know both the real and imaginary parts of  $\tilde{n}$  and  $\tilde{\epsilon}_r$ .

In the remainder of this book we will take it as explicitly assumed that both the refractive index and the dielectric constant are complex quantities. We will therefore drop the tilde notation on  $n$  and  $\epsilon_r$  from now on, except where it is explicitly needed to avoid ambiguity. It will usually be obvious from the context whether we are dealing with real or complex quantities.

### Example 1.2

The complex refractive index of germanium at 400 nm is given by  $\tilde{n} = 4.141 + i 2.215$ . Calculate for germanium at 400 nm: (a) the phase velocity of light, (b) the absorption coefficient, and (c) the reflectivity.

#### Solution

(a) The velocity of light is given by eqn 1.2, where  $n$  is the real part of  $\tilde{n}$ . Hence we obtain:

$$v = \frac{c}{n} = \frac{2.998 \times 10^8}{4.141} \text{ m s}^{-1} = 7.24 \times 10^7 \text{ m s}^{-1}.$$

(b) The absorption coefficient is given by eqn 1.16. By inserting  $\kappa = 2.215$  and  $\lambda = 400 \text{ nm}$ , we obtain:

$$\alpha = \frac{4\pi \times 2.215}{400 \times 10^{-9}} \text{ m}^{-1} = 6.96 \times 10^7 \text{ m}^{-1}.$$

(c) The reflectivity is given by eqn 1.26. Inserting  $n = 4.141$  and  $\kappa = 2.215$  into this, we obtain:

$$R = \frac{(4.141 - 1)^2 + 2.215^2}{(4.141 + 1)^2 + 2.215^2} = 47.1 \%.$$

We will see in Chapter 10 that the restrahlen absorption is caused by the interaction between the light and the optical phonons.

### Example 1.3

Salt (NaCl) absorbs very strongly at infrared wavelengths in the ‘restrahlen’ band. The complex dielectric constant at  $60\mu\text{m}$  is given by  $\tilde{\epsilon}_r = -16.8 + i 91.4$ . Calculate the absorption coefficient and the reflectivity at this wavelength.

#### Solution

We must first work out the complex refractive index using eqns 1.22 and 1.23. This gives:

$$n = \frac{1}{\sqrt{2}} \left( -16.8 + ((-16.8)^2 + 91.4^2)^{\frac{1}{2}} \right)^{\frac{1}{2}} = 6.17$$

and

$$\kappa = \frac{1}{\sqrt{2}} \left( +16.8 + ((-16.8)^2 + 91.4^2)^{\frac{1}{2}} \right)^{\frac{1}{2}} = 7.41.$$

We then insert these values into eqns 1.16 and 1.26 to obtain the required results:

$$\alpha = \frac{4\pi \times 7.41}{60 \times 10^{-6}} \text{ m}^{-1} = 1.55 \times 10^6 \text{ m}^{-1},$$

and

$$R = \frac{(6.17 - 1)^2 + 7.41^2}{(6.17 + 1)^2 + 7.41^2} = 76.8 \%$$

## 1.4 Optical materials

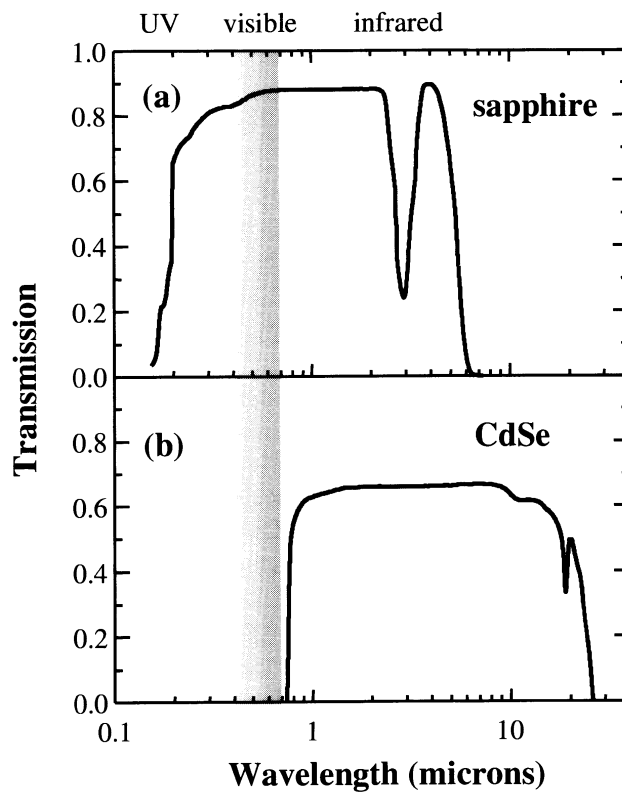
We will be studying the optical properties of many different types of solid state materials throughout this book. The materials can be loosely classified into five general categories:

- Crystalline insulators and semiconductors
- Glasses
- Metals
- Molecular materials
- Doped glasses and insulators.

Before delving into the details, we give here a brief overview of the main optical properties of these materials. This will serve as an introduction to the optical physics that will be covered in the following chapters.

### 1.4.1 Crystalline insulators and semiconductors

Figure 1.4(a) shows the transmission spectrum of crystalline sapphire ( $\text{Al}_2\text{O}_3$ ) from the infrared to the ultraviolet spectral region. The spectrum for sapphire shows the main features observed in all insulators, although of course the details will vary considerably from material to material. The principal optical properties can be summarized as follows:



**Fig. 1.4** (a) Transmission spectrum of a sapphire (Al<sub>2</sub>O<sub>3</sub>) crystal of thickness 3 mm. (b) Transmission spectrum of a CdSe crystal of thickness 1.67 mm. After [1].

- (1) Sapphire has a high transmission in the wavelength range 0.2–6  $\mu\text{m}$ . This defines the **transparency range** of the crystal. The transparency region of sapphire includes the whole of the visible spectrum, which explains why it appears colourless and transparent to the human eye.
- (2) Within the transparency range the absorption coefficient is very small, and the refractive index may be taken to be real with no imaginary component. The value of the refractive index is approximately constant, and is equal to 1.77 in sapphire.
- (3) The transmission coefficient in the transparency range is determined by the reflectivity of the surfaces through eqn 1.6. The reflectivity in turn is determined by the refractive index through eqn 1.26. For sapphire with  $n = 1.77$ , this gives  $R = 0.077$ . Hence we find  $T = (1 - R)^2 = 0.85$ .
- (4) The dip in the transmission in the infrared around 3  $\mu\text{m}$ , and the sharp drop in the transmission for  $\lambda > 6 \mu\text{m}$ , is caused by vibrational absorption. This absorption mechanism is analogous to the infrared absorption due to vibrations in polar molecules. The vibrational excitations of a crystal lattice are called phonon modes, and so the vibrational absorption in a solid is usually called phonon absorption or lattice absorption. This absorption mechanism will be discussed in Chapter 10.
- (5) The transmission drops sharply in the ultraviolet spectral region for  $\lambda < 0.2 \mu\text{m}$  due to absorption by bound electrons. The onset of the absorption is called the **fundamental absorption edge**. The wavelength of the fundamental edge is determined by the band gap of the insulator. The

Sapphire gemstones tend to be blue. This is caused by the presence of chromium, titanium and iron impurities in the Al<sub>2</sub>O<sub>3</sub> crystal. Pure synthetic Al<sub>2</sub>O<sub>3</sub> crystals are colourless.

Sapphire actually transmits in the far infrared spectral region when the frequency is well below that of the optical phonons.