PHYSICAL METHODS FOR MATERIALS CHARACTERISATION
2

Interaction of Radiation with Materials

2.1 RADIATION SOURCES

To characterise a microstructure it is necessary to perturb the material by interacting in some way with it. Indeed in order to see a surface we must bombard that surface with photons of wavelengths within the visible range and this in itself may alter the material. A typical example of damage caused by photons is the response of a photographic film. To achieve higher resolution and thereby magnification it is possible to use, for example, a scanning electron microscope where the photon source is replaced with electrons with an energy in the region of 10 to 30 keV. These are more damaging than photons since they penetrate a considerable distance on the atomic scale into the material. Many modern analytical instruments require high spatial resolution, while at the same time, high sensitivity for the detection of elements within the material. Often this involves bombarding the surface with ionised atoms of high energy which although extremely damaging, provides microstructural information that outweighs this disadvantage.

With any characterisation of a material the objective must be to obtain the maximum information whilst incurring the least amount of damage to the specimen. Thus, in general, initial examinations of a surface should be carried out using a low intensity beam of low energy photons. To obtain more information the source energy may have to be increased, for example with the use of X-rays initially and progressively through electrons to finally ions. There are, of course, situations where this simplistic approach may not hold; in the technique of Ion Scattering Spectroscopy (ISS), the ions reflect
from the surface and do not perturb it as much as a high energy photon or electron, so care must be taken when deciding how to examine a material. It is the purpose of this chapter to summarise the processes that occur when photons, electrons, ions and particles interact with materials. The various sources available will be considered, their properties described, and their potential uses outlined.

2.2 PENETRATION DEPTHS

The penetration depth or mean free path of the incident beam determines the depth and volume of material that will be sampled. In many cases the probe is one type of radiation but a second type is detected. This occurs in X-ray Photoelectron Spectroscopy (XPS) where the incident probe is a beam of X-ray photons but emitted electrons are detected, whereas this is reversed for the technique of Energy Dispersive X-ray Analysis (EDX). Generally the particle or radiation which has the shortest mean free path in the material will determine the volume analyzed. Whatever incident beam is selected we must be aware of its interaction with the material, what photons, electrons or other particles are ejected and how they, in turn, interact with the material. Only in this way can we use the emitted signals to gain an understanding of the material being examined.

2.2.1 Photons

Photons are discrete quanta of electromagnetic radiation. The photon is identified by the wavelength, $\lambda$, energy, $E$, and frequency, $v$, all of which are related by the equation

$$h v = E = h c / \lambda$$

(2.1)

where $h$ is the Planck constant and $c$ the velocity of light. The electromagnetic spectrum spans a vast range with wavelengths varying from $10^6$ m down to $10^{-14}$ m. The frequency, energy and wavelengths of the different types of electromagnetic radiation are illustrated in figure 2.1. If we are to use electromagnetic radiation for microstructural characterisation of materials a photon wavelength is needed that is of comparable size to the features being studied. This means that photon wavelengths greater than $10^{-4}$ m would result in an inadequate spatial resolution and we do not require radiation less than about $10^{-10}$ m.

The penetration of photons shows considerable and dramatic variations between different types of material and photon energy or wavelength. It is not possible or instructive to go into any detail regarding penetration depths
over the whole of the electromagnetic spectrum but some specific wavelengths that are important for interrogating the microstructure of materials. The long wavelength infra-red radiation is used to characterise materials by determining how specific wavelengths are absorbed, visible light is used in a variety of instruments mainly to obtain a visual image of the surface while at the shorter wavelength ultra-violet radiation is often used to obtain information concerning the electron distribution in the surface atoms. Some materials are opaque while others are transparent to this range of wavelengths. However, even the most opaque or highly reflecting of these materials will allow the radiation to penetrate at least a fraction of a wavelength below the surface. In the case of visible light, where the wavelength is approximately 500 nm, this penetrates an average of between 50 to 300 nm into the bulk so that any analysis performed or image obtained will average over several hundred atom layers.

After visible light, X-rays are probably the most utilised photon source for investigating the microstructure of materials. The whole subject of X-rays and their interaction with matter has been thoroughly treated by Cullity (1956). X-rays are produced by bombarding a metal target with high energy electrons to produce a band of ‘white’ radiation. The intensity of the X-rays within this band varies with the wavelength determined by the energy of
electrons incident on the target material, figure 2.2(a). Superimposed on the 'white' X-radiation are a series of discrete maxima whose wavelength and intensity is determined by the electron binding energies of the atom making up the metal target being bombarded. These characteristic X-ray photons, shown for a copper target in figure 2.2(b), result from electrons falling into holes created in core electron levels by the incident electron beam with the emission of a photon whose energy is given by replacing $E$ in equation 2.1 by $E_1 - E_2$, the energy difference between the electron shells.

The penetration of X-rays into a material shows less variation from one material to another than visible light and is easier to predict. The penetration distance varies both with wavelength and material and is typically several micrometres. The absorption coefficient, $\mu$, which increases with atomic number, determines the depth of penetration. The intensity of transmitted radiation, $I$, through a layer of material of thickness, $t$, is given by Peiser et al (1960):

$$I = I_0 \exp (-\mu t)$$  \hspace{1cm} (2.2)

where $I_0$ is the intensity of the incident X-ray beam.

Gamma rays have very high energies in the region of 50 keV to 50 MeV and wavelengths that are considerably less than X-rays and would typically be in the region of $10^{-2}$ nm (Seigbahn (1965)). When a gamma ray beam passes through a material, photons are removed from the beam in individual events, thus the number of gamma ray photons removed is proportional to the thickness traversed. Therefore the intensity of the gamma ray decays as:

$$I = I_0 \exp (-\mu x)$$  \hspace{1cm} (2.3)

where $\mu$ is the absorption coefficient and $x$ is the distance traversed by the beam. Gamma rays can penetrate considerable distances through materials.
Figure 2.3 The mean free path length of electrons (a) in stainless steel as a function of electron energy and (b) as a function of atomic number of the material being probed for 10 keV, 20 keV and 30 keV electrons (after Castaing 1960).

but the penetration distance tends to vary inversely with the atomic number. However, gamma rays will pass through the bulk of almost all practical specimens.

2.2.2 Electrons

The penetration depth of electrons varies dramatically with both the energy of the electron and the atomic number of the material that is being examined. Figure 2.3(a) reproduces the mean free path of electrons in stainless steel as a function of incident beam energy (Castaing (1960)). The mean free path length increases from a fraction of a micrometre, at energies in the region of 10 keV up to 2 μm at 30 keV. In figure 2.3(b) the mean free path of electrons is plotted as a function of atomic number for three incident electron energies 10, 20 and 30 keV. Here, even more dramatic changes can be seen, the mean free path of electrons in elements of low atomic number is very large and can be as great as 10 μm for elements with atomic number below 20 while elements with atomic numbers greater than 40 have short electron mean free paths generally less than 2 μm.

This clearly has important consequences for any microstructural characterisation since materials will invariably be composed of elements with
different atomic numbers; there may be precipitates such as carbides with low atomic mass in a matrix with a high mean atomic number and this will modify the images for each constituent. A situation often encountered when examining a metal alloy in the scanning electron microscope is that the surface images differently as the interrogating beam energy is changed and, indeed, different analyses can be obtained using the emitted characteristic X-rays. This is because the metal alloy specimen almost certainly has a thin oxide surface layer which can on occasions be further covered with a layer of carbon as a result of contamination. An example of this effect is shown in figure 2.4 where two images are obtained with incident beam energies of 900 eV and 20 keV (ETP(1990)) from colloidal silver and carbon on an aluminium substrate. The high energy electron beam produces an image in which the silver appears very bright and the carbon is poorly imaged. The low energy beam, on the other hand, produces a clear image from the carbon but a mottled image from the silver. The differences in the two images can be explained in terms of both the penetration of the electrons into the bulk and the backscattering of electrons by atoms of different atomic number. The low energy image is different from that obtained using the higher energy incident beam; the specimen is covered with a thin layer of carbon which is penetrated only by the higher energy electrons.

We have so far only considered the penetration of relatively high energy electrons, above 10 keV. However, many techniques detect electrons with energies much lower than this in the region 0 to 2 keV, where the effect of the material on the mean free path length, $\lambda$, of the electrons is much reduced, figure 2.5 (Seah and Dench (1979)). Clearly the mean free path length is very short over the whole of this energy region, varying from approximately 0.4 to 300 nm which is a hundred to a thousand times less than for high energy electrons. Moreover the mean free path of electrons for
elements with low atomic number is essentially the same as for elements with high atomic number and the mean free path increases, to a first approximation, as the square root of the electron energy over the range 0.1 to 2 keV. These changes in electron mean free path can be used in many ways to obtain additional microstructural information concerning a surface but it also indicates the great care that must be exercised when using electrons to probe a material.

Since an incident high energy electron beam is scattered as it penetrates a material, figure 2.6, the resolution will be influenced by the spread of electrons around the incident beam. Figure 2.7 is a plot of the intensity of the secondary electrons as a function of distance from the centre of 5 nm and 50 nm electron beams incident on aluminium and gold. The majority of the electrons come from the area of the incident beam, but a fraction emanate from an area around the incident beam (Seah (1986)). This is the result of electron processes taking place within the material; the scattered secondary electrons are detected up to 2 μm distant from the centre of the electron beam in the aluminium specimen but only 0.2 μm from the centre for the gold. However the intensity of these scattered electrons is lower in aluminium than gold. In general the scattered electrons will not significantly degrade the image except where the intensity of the scattered electrons makes a significant contribution to the total, as for gold with a 50 nm incident electron beam. However, the scattering of secondary electrons places an ultimate spatial resolution on images that can be obtained in the scanning electron microscope and it is for this reason that the images obtained have generally lower spatial resolution than images obtained using transmission electron microscopy.
Figure 2.6 Schematic diagram illustrating the volume of material that is probed by an incident electron beam together with the volumes from which X-rays and backscattered Auger and secondary electrons emanate.

Figure 2.7 The scattered electron distribution following bombardment of gold and aluminium by electron beams of 5 and 50 nm (Seah (1986)). (Reproduced with permission of J Wiley and Sons.)

At the same time a large number of electrons are produced with relatively low energy as the result of atoms being ionised by the removal of electrons from the valence band. In addition, a smaller fraction of atoms are ionised by the ejection of core level electrons and these atoms can rearrange and eject either photons (X-rays) or Auger electrons (see Chapter 6). Finally a number of incident electrons may be scattered back towards the specimen surface without losing a significant amount of energy. The Auger electrons are generally confined to energies in the range 0 to 2 keV and escape from
the surface only if they emanate from within the top few atom layers and laterally not beyond the incident beam diameter. Secondary electrons also have relatively low energies and, although produced by many of the electrons travelling within the subsurface volume, those that escape are restricted to the surface volume and to a relatively small distance laterally outside the diameter of the incident beam. It is these electrons that are used to form an image in the scanning electron microscope and as a result the image has a resolution essentially defined by the incident electron beam diameter. The backscattered electrons have high energies, large mean free paths and can originate from a greater depth in the material. They are scattered with components normal to the direction of the incident beam and, therefore, define a volume with a diameter that is much larger than that of the incident beam. Finally, the X-rays produced can penetrate much greater distances than electrons and potentially all the X-rays produced which travel towards the surface can escape. Thus X-rays originate from any point that the scattered electrons reach and this defines a volume of excitation.

2.2.3 Neutrons

Although a neutron is approximately one thousand times the mass of an electron and as a consequence is more particle like, it still possesses sufficient wave character to be diffracted by materials. However, since it does not possess an electric charge it is not affected by the electron cloud surrounding the nucleus and on passing through a material effectively interacts only with the atom nucleus. As a consequence neutron penetration distances are much greater than for electrons and even X-rays. The precise penetration depth depends on the atomic species being examined but for most materials neutrons will penetrate distances of several millimetres (Hutchings and Windsor (1986)). Neutrons can be used to study the microstructure within the bulk of a material.

2.2.4 Protons

The interaction of a proton beam with a material has many similarities to the electron but there are some important differences. The proton being charged is influenced by the electrostatic forces within the material but because the mass is 1836 times that of the electron a proton of a few MeV energy has a much greater momentum than electrons of say 50 keV. The proton loses a small fraction of momentum in each atom collision and will not be deviated significantly from the incident beam direction. Therefore protons will travel much further into a material than electrons of the equivalent energy with little scattering. The stopping power, S, is the term which defines the depth to which protons penetrate a material. The stopping power decreases with increasing proton energy and with increasing atomic
Figure 2.8 The stopping power for protons entering aluminium, nickel and silver as a function of incident energy \( (Ziegler \ et \ al \ (1985)) \).
(Reproduced with permission of Pergamon Press.)

number. A 2.5 MeV proton has a range of 55 \( \mu \text{m} \) \( (S = 123 \ \text{keV mg}^{-1} \ \text{cm}^{-2} ) \) in carbon and a range of 28 \( \mu \text{m} \) \( (S = 56 \ \text{keV mg}^{-1} \ \text{cm}^{-2} ) \) in silver. Figure 2.8 shows the stopping power as a function of proton incident energy for aluminium, nickel and silver \( (Ziegler \ et \ al \ (1985)) \). Protons are frequently used to excite X-rays in a technique known as Particle Induced X-ray Emission \( (\text{PIXE}) \) \( (Johansson \ and \ Campbell \ (1988)) \). (See Chapter 7.)

2.2.5 Ions/Atoms

It is natural to move on from protons to consider ions. Invariably if ions penetrate a material, so much damage occurs that it is more accurate to address the stopping distance rather than a penetration distance. It is perhaps instructive to describe what happens when either an atom or an ion impinges on a surface. At very low energies of a few eV an atom is simply reflected from the surface. When a primary ion of mass \( M_1 \) and energy \( E_1 \) impinges on a surface of atoms mass \( M_2 \) it will be reflected with a kinetic energy \( E_2 \) determined by the relative masses of the incident and surface atoms and the angle between the incident and reflected atom. Kinetic energy is transferred to the surface atom \( M_2 \) but the impinging ion does not penetrate into the surface (see Chapter 7). At higher energies the atom burrows into the material, causing atoms, atom clusters, ions and ion clusters to be ejected from the surface while, at the same time, atoms are knocked further into the material, figure 2.9. Here the incident ion of relatively high energy knocks surface atoms further into the material. These in turn collide with other atoms establishing a cascade process where atoms collide with one another and atoms move in both forward and backward directions. Some atoms, and atom clusters, will be ejected both in the ionised and neutral state together with some electrons. The original ion will
either come to rest within the body of the material or may be ejected as part of the scattering process. The distance penetrated is determined by the kinetic energy of the incident ion, the atomic number of the ion and the atomic number of the material. Figure 2.10 shows the penetration distance for krypton ions of energies from 5 keV to 50 keV impinging on germanium.
Figure 2.11 Schematic diagram illustrating the penetration of ions into a solid. \( R = \) range and \( x = \) penetration depth.

(Littmark and Hofer (1980)). Considerable effort has been devoted to the study of implantation of specific atom species into semiconductor materials because of the importance in silicon chip technology. In this example the krypton ions with energies of 5 keV do not penetrate deeper than 13 nm whereas those with 50 keV energy can be implanted to depths greater than 50 nm. Penetration distance and damage cannot be separated for ions.

When an ion enters a polycrystalline material it will follow a path which is not necessarily normal to the surface and travel a distance before coming to rest at a point, figure 2.11. The distance travelled by the ion is greater than the range \( R \) or the penetration depth \( x \), but cannot readily be measured. It is therefore customary to define the penetration depth, \( x \). The range along the direction of the incident beam is defined as the projected range \( R_p \). Naturally this will vary with the ion and the material but for ions in the energy range \( 0.002 \leq E \leq 0.1 \) keV (Schiot (1972)) is given by

\[
R_p = C_1(\mu)M_2\left[\left(\frac{Z_1^{2/3} + Z_2^{2/3}}{Z_1Z_2}\right)E\right]^{2/3}
\]

(2.4)

where \( M_2 \) is the atomic mass of the material, \( E \) the energy in keV, \( Z \) the atomic number and \( C_1(\mu) \) is obtained from experimental values shown in figure 2.12.

However for ions with energies \( 0.5 \leq E \leq 10 \) keV

\[
R_p = C_1(\mu)M_2\left[\left(\frac{Z_1^{2/3} + Z_2^{2/3}}{Z_2Z_2}\right)^{1/2}E\right]^{2/3}.
\]

(2.5)

If the ion enters a single crystal in a direction close to a low index crystallographic axis then the ion will be channelled into that direction so that there will be less deviation from the incident direction and the
penetration distance will be considerably enhanced compared with the polycrystalline case.

2.3 MATERIAL DAMAGE

2.3.1 Photons

Generally a photon source is regarded as the least damaging of the analytical probes, but the degree of damage is never zero and can in some instances be quite severe. The photon wavepacket will have a momentum determined by either the energy or wavelength. This momentum is clearly small for light quanta and other radiation sources of longer wavelengths such as infra-red radiation, microwaves etc. However, one only has to look at the results of leaving the Christmas pudding in a microwave oven too long to realise that the damage is not negligible. In general the damage caused by photons is the result of heating and the degree and extent is determined by the penetration of the photon source into the material, the energy of the radiation and the photon flux (Smith (1971)). X-ray beams can cause the surfaces of certain oxides to be reduced and laser beams can burn holes through metal by heating to temperatures that result in the instantaneous melting and evaporation in the immediate vicinity of the beam. Indeed this is the basis of one
technique (Laser Induced Mass Analysis (LIMA)) where a small volume of the material surface is vaporised by a pulsed laser beam and the evaporated material is then mass analysed. Figure 2.13 shows the effect of a laser beam used in a laser induced mass analyser on a metal surface. However, most photon sources selected cause very little damage and the surface being studied does not alter over very long periods of exposure. As a general rule, if the results for a microstructural investigation can be obtained using a photon source, then this should be used.

2.3.2 Electrons

While electrons are readily described as having a dual wave and particle character their mass allows a considerable momentum to be transferred, particularly when accelerated to several hundred keV in the transmission electron microscope. Again the resultant damage is related to the amount of energy or heat transferred to the material and to the thermal conductivity of the material. At low incident beam energies atom bonds do not break in the target material so that in general, metals and alloys can be examined without any significant degree of damage taking place. However in the case of oxides and polymeric materials the damage can be considerable. Indeed it is impossible to obtain a secondary electron image in the electron microscope from most polymeric materials before they degrade. The only way that images of these materials can be obtained is to coat the surface with a conducting material such as gold, but this renders any chemical determination almost impossible. Oxides are also damaged by the electron beam although if the oxide layer is thin and in contact with a metal substrate the damage is rarely so great that an image cannot be obtained. Figure 2.14 is an Auger electron spectrum obtained from the surface of a stainless steel which initially contained a thin silicon oxide SiO₂ layer (Wild (1985)). The top spectrum (a) was recorded using an electron beam of 10 keV and approximately 100 nanoamps current focused into a spot size of 100 nanometres but
rastered over an area of 200 μm × 200 μm. The spectrum is typical of that expected from SiO₂ with two peaks at 62 eV and 77 eV. The rastering of the beam was then turned off so that it was stationary when the second spectrum (b) was obtained. Here the spectrum is essentially that from silicon with a peak at 92 eV indicating that most of the oxide has been reduced by the influence of the electron beam. This result indicates oxide reduction caused by electron beam heating and reducing the oxide; the beam is not causing atom bond breaking.

A further dramatic demonstration of the heating effect of electrons is shown in figure 2.15 where a metal surface is examined under similar conditions to the previous example. The metal surface has oxide particles loosely adhering and the thermal conductivity between the particles and the metal is poor. In figure 2.15(a) the particle in the centre is rectangular in shape but after this image was recorded the electron beam was focused onto

Figure 2.14 The effect of a 10 keV electron beam focused on an SiO₂ layer on stainless steel showing reduction of the oxide to silicon (a) rastered beam (b) static beam (Wild (1985)). (Reproduced with permission of Pergamon Press.)
Figure 2.15 The heating effect of a 10 keV, $5 \times 10^{-9}$ A electron beam on an oxide particle when there is poor conductivity between the particle and the substrate.

the particle to obtain a chemical analysis. Following analysis the secondary electron image in (b) was recorded and this indicates that the oxide particle, which was a chromium iron oxide had melted and had thus been heated to a temperature in excess of 2800 K.

We have been considering the damaging effect of electrons in conventional instruments where the incident beam energy does not normally exceed 100 to 200 keV. However, there exist electron beam instruments which use considerably more energetic electrons and these can cause atoms to be displaced from normal lattice positions by the transfer of momentum (Madden et al (1979)). Such damage occurs in the million electron volt transmission electron microscope. Indeed such is the effect at this energy that the microscope is used to simulate the damage that is caused by fast neutrons in nuclear reactors. Figure 2.16 shows damage that has occurred in a thin foil specimen of stainless steel where voids and dislocation loops have formed by electron interactions.

2.3.3 Ions and Atoms

When ions or atoms penetrate a material they either interact in essentially a totally non-damaging manner as in Ion Scattering Spectroscopy (ISS) (Nichus and Baner (1975)) where they interact elastically with the surface or they cause severe damage. Ion damage is effected by displacing atoms from their normal lattice positions and a minimum energy is required by the ion to exceed the binding energy of the atom. In addition a certain amount of energy is required to displace the atom and this varies with the direction of the incident ion relative to the crystallographic directions of the material. However, the threshold displacement energy is some ten times the energy
required to break the atom bonds. If the ion has sufficient energy to displace an atom then the total damage caused will be related to the ion energy and the flux. At a low flux the damage regions are isolated one from the other since the ion produces a region of amorphous material surrounded by regions containing large numbers of defects. As the flux increases so these regions overlap and an amorphous layer is found. The processes involved in these ion cascade events are described by Benninghoven et al (1987) and Sigmund (1981).

An example of the damage caused by ions penetrating into a material is shown in figure 2.17 (Ward and Fisher (1992)). Here a transmission electron micrograph is reproduced showing the damage in Type 316 stainless steel following bombardment with 4 MeV iron ions at 813 K. Here each iron ion causes five displacements in the stainless steel. Ion penetration depth varies with ion energy and with ion species. Ions will be stopped over a range of distances and the penetration distance is normally defined as the maximum in the implantation profile, i.e. the stopping distance for the largest number of ions.

2.4 RESOLUTION

In the earlier sections of this chapter we discussed the penetration of various types of radiation into materials. This determines the depth resolution and will have a distinct bearing on the spatial resolution that is obtainable for investigating microstructural features. The resolution normal to the direction of the incident beam, frequently referred to as spatial resolution is
Figure 2.17 Damage caused in type 316 stainless steel following bombardment with 4 MeV iron ions at 813 K. Each incident ion displaces five stainless steel ions on average (Ward and Fisher (1992)) (Courtesy A Ward).

influenced by the diameter of the incident beam, the wavelength of the incident radiation and the mean free path of the incident beam in the material. An image of an object can be obtained in two basic ways. One method is to illuminate the object over its entire surface by using a suitable source of radiation (photons, electrons or ions) and then use a lens arrangement to form an image by focusing the radiation that is either reflected or emitted from the object. This is achieved such that a point on the object is focused to an equivalent point on an image plane. In such systems the spatial resolution is determined by the lens system and the wavelength of the emitted or reflected radiation. In general, optical microscopes, certain X-ray microscopes and some ion microscopes operate in this way. The second method is to direct a very narrow beam of radiation on to the object and to detect either the absorbed or reflected radiation. The incident beam is rastered over the object surface and changes that occur in absorption and reflection allow an image of the surface to be built-up. In these cases the spatial resolution is determined by the diameter of the incident beam, the wavelength of the incident radiation, and the scattering of the incident radiation within the object surface. Most electron and ion optical instruments form their image in this way although the advent of lasers has meant that some light microscopes also use this method. Details of the resolution achieved for the specific techniques is discussed in the following chapters where each technique is discussed.
2.5 LOSS PROCESSES

The previous part of this chapter has been concerned primarily with processes which describe how photons, electrons, neutrons, atoms and ions interact with, and can be used to give, images of the surface and bulk materials. We now move on to describe the interactions of these particles with the material and how processes transfer energy to the material under investigation. This energy transfer is used to determine information concerning the type of atom, its environment or chemical state. Any process that involves the incident beam surrendering some energy is described as a loss process. We will now consider the loss processes that are currently utilised to characterise the microstructure of a material. Most, although not all, of the techniques mentioned briefly here will be described in more detail in later chapters.

2.5.1 Photons

2.5.1(a) Very long wavelengths (>1 mm) (including radio and micro-waves)
A molecule with either a magnetic nucleus or an unpaired electron will have nuclear and electron energy levels that can be influenced by a magnetic field. The magnetic field, \( B \), causes the electron to take up new quantized values of \( \pm (1/2) \left( \frac{h}{2\pi} \right) \), where \( h \) is the Plank constant, and with each of these is associated an energy level, one above and the other below the original energy level. The separation of these energy levels is \( \mu_0 B \), where \( \mu_0 \) is the magnetic dipole moment, and this is linearly dependent on the magnitude of the applied magnetic field, \( B \). By combining a magnetic field with an appropriate electromagnetic radiation, transitions between the two energy levels can be induced. With magnetic fields that can be applied routinely to materials it is necessary to use radio-frequency waves to excite the nuclear magnetic resonance (NMR) (Akitt (1983) and Cudby and Williamson (1990)) and microwaves to excite the electron spin resonance (ESR) (Symons (1978)) and electron paramagnetic resonance (EPR) (Thomson (1990)). The magnetic moments of certain nuclei also interact with the unpaired electron to produce additional fine structure on the major resonance. This technique has been used extensively to study kinetics processes in organic material reactions and to follow catalytic reactions. NMR has been used to determine the structure of organic materials, and degradation in microstructure of resins, rubbers and other hydrocarbons under certain conditions.

2.5.1(b) Long wavelengths
As considered in Chapter 1, materials are composed of atoms bonded together where the distance between the ions is determined by a balance
between the attractive long range interactions of the ions with charge \( +q \) and the repulsive short range interactions between the ion cores. If given sufficient energy the atoms are able to vibrate and this process can be visualised by imagining the atoms as hard spheres connected by springs. The simplest case is to consider two atoms connected together and by applying Hooke's law for elastic expansion under a force, the frequency of vibration of the two atoms, \( \nu \), is given by:

\[
\nu = \frac{1}{2\pi c} \left[ \frac{F_c}{M_0} \right]^{1/2}
\]  

(2.6)

where \( c \) is the velocity of light, \( F_c \) is the force constant of the atom bond and \( M_0 \) is the reduced mass of the system given by

\[
M_0 = \frac{M_1 M_2}{M_1 + M_2}
\]  

(2.7)

where \( M_1, M_2 \) are the masses of the two atoms. When a material is illuminated with light then the wavelengths which correspond to the vibrational frequencies are absorbed. This simplistic approach produces surprisingly good agreement between theory and experiment with the vibration frequencies for say a hydrogen atom bound to carbon being fairly well predicted. As the complexity of the molecule increases so the number of vibration frequencies increases. A non-linear molecule containing \( n \) atoms has \( 3n \) degrees of freedom and \( 3n - 6 \) vibrational modes each with a characteristic band frequency. As the molecule becomes more complicated, with atoms bound to more than one atom and when there are nonlinear chains of atoms, vibrations can take place in directions with components normal to the bond direction. The vibrations in the direction of the bond are referred to as stretching vibrations while those normal to the bond direction are known as bending or deformation vibrations. Figure 2.18 illustrates some of the different ways a molecule can vibrate (Cross (1960)). These vibrations may be determined by observing the absorption of infra-red radiation either in the transmission or reflection mode. This, in turn, permits substances to be identified and molecular structure to be determined and allows reaction kinetics to be studied. Infra-red spectroscopic techniques (Herzberg (1945) and Wilson et al (1955)) use radiation with wavelengths from approximately 1 \( \mu \text{m} \) (wavenumber \( 10^4 \text{ cm}^{-1} \)) to 1 mm (wavenumber \( 10 \text{ cm}^{-1} \)) to study these vibrational absorption bands. The wavenumber has been quoted here because it is conventional, in infra-red spectroscopy, to refer to the wavenumber rather than the wavelength; the wavelength, \( \lambda \), and wavenumber, \( \eta \), are related by \( \eta = 1/\lambda \). Increasingly lasers are being used to provide the source of infra-red radiation with the advantage that high intensities are confined to relatively small areas with the associated improved spatial resolution.
2.5.1 Intermediate wavelengths (including visible and ultraviolet light)

As wavelength is decreased so the energy available to excite an atom increases until a stage is reached where it becomes possible to raise electrons from their ground state to higher electron orbitals (Rao (1961)). The binding energies of electrons in atoms are specific to a particular element and by determining the difference in energy between two electron levels, by measuring absorption lines, it is possible to identify the type of atom. Consider the hydrogen atom illustrated in figure 2.19 which contains a series of energy levels where electrons may be present or absent. The energy levels are filled from the lowest level in pairs, one with spin up and one with spin down, until all the lowest levels are filled. Energy may then be given to the electrons in the outermost orbits which may be excited to higher levels. The effect of this on a beam of white light is to absorb light of frequency, $\nu$, since:

$$h\nu = E_1 - E_2$$

where $E_1$ and $E_2$ are the initial and final electron levels.

Thus a beam of white light when passed through a gas or material will have a series of missing wavelengths corresponding to the difference in electron binding energies of the atoms. By measuring the wavelengths of the absorption band the atom type can be identified. Absorption bands have been catalogued according to the lowest energy level which takes place in the absorption. Those in which the quantum number of the lowest level is 1 are referred to as the Lyman series, for $n = 2$ the Balmer, $n = 3$ the Paschen and $n = 4$ the Brackett. The atom that has been excited by an electron being
transferred to a higher orbital will subsequently decay to the original ground state by the emission of light. The decay may be by a direct transition to the original electron energy level or it may be by a series of transitions. Thus a spectrum is observed which contains a number of discrete lines. Figure 2.20 shows an absorption spectrum for hydrogen and the Balmer series of absorption bands which gradually close together as the quantum number \( n \) increases. In practice, visible and ultra-violet radiation is used to study the electron energy levels of the outer shell electrons and the vibrational levels between atoms because the energy supplied by the incident radiation is insufficient to excite core level electrons from most elements to the next highest state.

When light is incident on a material certain resonance frequencies are absorbed in raising the molecules to an excited state. When the molecules decay that same frequency may be re-emitted in a random direction and

![Energy levels and possible transitions in the hydrogen atom.](image)

**Figure 2.19** Energy levels and possible transitions in the hydrogen atom.

![The hydrogen spectrum showing characteristic absorption bands.](image)

**Figure 2.20** The hydrogen spectrum showing characteristic absorption bands.
not necessarily in the direction of the incident beam (Baranska et al. 1987, Clark and Hester (1983, 1984, 1985) and Andrews and McCoustra (1990)). This is known as Rayleigh scattering. However, the material illuminated will contain energy levels at both higher and lower energies than the energy level of the initially excited state. These energy levels may be unfiled because they too may have been excited to higher levels. The molecules may, therefore, decay by the excited electron falling into one of these other energy levels effecting emission of radiation at both higher and lower frequencies than the Rayleigh line. These lines are known as Stokes (at lower energies than Rayleigh) and anti-Stokes (at higher energies than the Rayleigh line) while the effect is known as the Raman effect, figure 2.21. The effect is most easily observed if a material is illuminated with an intense beam of radiation. Therefore, lasers are used to illuminate materials in the technique of Laser Raman Spectroscopy which provides information concerning the vibrational spectra and hence the strength of the bond between atoms (Baranska et al. 1987)).

2.5.1(d) Short wavelengths (10⁻¹² to 10⁻⁹ m) (including X-rays and ultraviolet excitation)

In the previous section we considered the absorption of infra-red and light radiation which has an intermediate wavelength and hence low energy and does not have sufficient energy to excite core level electrons to higher orbits. However, as the wavelength of the incident radiation is decreased so the
number of energy levels available for excitation increases and electrons positioned closer to the nucleus of the atom may be excited. The energy of light and ultraviolet radiation is sufficient to excite energy levels in materials of low atomic number but for higher atomic number elements it is capable of exciting only outer shell and valence electrons. However, if the material is bombarded with X-rays then many of the core shell electrons can be excited and will, in most cases, be given sufficient energy to be ejected from the atom (see the photoelectric effect below). The atom then rearranges with the electrons falling into the hole created by the initial excitation and energy is released as a photon or by the emission of an Auger electron (see below). The energy of this photon is determined by the difference in the electron energy levels $E_1$, $E_2$ by the expression $h\nu = E_1 - E_2$. This is the basis of X-ray Fluorescence Spectroscopy (XRF) where the material is bombarded with a beam of X-rays and the emitted X-ray energy is measured using a either a wavelength dispersive or energy dispersive analyser.

In the previous section we have described how photons may excite electrons to higher energy levels. However, as the energy of the photon increases it may supply sufficient energy to the electron such that it overcomes the work function of the material and ejects the electron into the vacuum. This is known as the photoelectric effect. The energy of the ejected photon is given by:

$$E = h\nu - E_B - \Phi$$

(2.9)

where $E_B$ is the electron binding energy of the ejected photoelectron and $\Phi$ is the work function of the material. If the energy of the incident photon is known, the energy of the photoelectron is measured then the work function allows the binding energy of the electron in the atom to be determined.

Therefore an atom can be identified and this is the basis of ultra-violet photoelectron spectroscopy (UPS) (Williams (1977)) and X-ray photoelectron spectroscopy (XPS) (Briggs and Seah (1990) and Rivière (1990)) described in Chapter 5. Following ionisation of the atom by the incident photon, the atom will decay to the ground state either by the emission of a photon or by ejecting an electron. In the first case an electron in a higher orbital will fall into the hole created by the initial ionisation event with the emission of a photon of a wavelength determined by the difference in energy of the two electron energy levels while in the second case an Auger electron is ejected. Emissions of longer wavelengths resulting from a sequence of decays is also possible as the atom rearranges. The process in which an X-ray ionises the atom and an X-ray photon is emitted is known as X-ray Fluorescence (XRF).

In 1925 Pierre Auger (1925) was studying cosmic ray tracks in a Wilson Cloud Chamber and realised that certain tracks could be explained only if the ionised atom was decaying by emitting another electron. This process has since become known as the Auger effect and the emitted electron as the
Auger electron. Here the atom is ionised and rearranges with an electron from an outer electron shell falling into the hole created by the initial ionisation, but, instead of the energy being emitted as a photon, it is transferred to a third outer shell electron that is then ejected. The energy of the ejected Auger electron is determined by the binding energies of the electrons which take part in the process and is given approximately by the equation:

$$E_{\text{Auger}} = E_1 - E_2 - E_3 - \Phi$$  \hspace{1cm} (2.10)

where $E_1, E_2, E_3$, are the energies of the electron shells taking part and $\Phi$ is the work function.

2.5.1(e) Very short wavelengths ($<10^{-12}$ m $\gamma$-rays)

In 1958 R L Mossbauer (1958 and 1964) discovered nuclear gamma ray resonance in a solid and this technique has become a popular method for studying both composition and crystal structure. The basic principle of the method involves processes that occur when an atom emits a gamma ray (Long (1984), Frauenfelder (1962) and Wertheim (1964)). When atoms decay by the emission of either a photon or an electron, momentum is transferred to the emitted particle and to conserve momentum in the system the atom must recoil in the opposite direction. This is manifested by induced lattice vibrations or heating within the material. However, the quantum theory predicts that the energy states within an atom are not continuous but increase in discrete steps. If an atom is, say, in a ground state it can increase to the next level only if it receives an amount of energy equal to, or greater than the difference between the ground state and the next energy level. The momentum of the photon emitted from the atom may be less than the quantum of energy required to excite the lowest energy level to the next highest. As a consequence there is a finite probability that the gamma ray will not lose energy and the event will be recoil free. Similarly a gamma ray has a finite probability that it will be absorbed in a recoil free event by an atom. If energy is not lost by emission or absorption then the associated lines may overlap to allow nuclear gamma ray resonance. In the event that the emission and absorption lines do not overlap it is possible to bring them into coincidence by moving the emitter or absorber relative to one another and utilising the Doppler shift to vary the frequency of the gamma ray. This technique, described in more detail in Chapter 5 is used to identify the environment of atoms in materials in which the Mossbauer effect occurs. While iron is the most commonly studied metal there are many others which have been utilised.

2.5.2 Electrons

In many respects the loss processes involving electrons have many similarities with higher energy photon loss processes. When an electron

impinge excite a atom su lose a di the two the inci be dete in a tecl and Mi incident energy Mi incident energie: microsc atomic

2.5.2(a)

We hav electron atom w photons inner el outer od release od photon measure dispersi to dete spectro:

2.5.2(b)

There is emission the pho from a process the ene outer od electron 2.10. Ti photon
impinges on an atom in a material it may interact with that atom to either excite an electron in the atom to a higher orbital or give an electron in the atom sufficient energy to escape. In the former case the incident electron will lose a discrete amount of energy equal to the difference in binding energy of the two electron energy shells involved. By measuring the amount of energy the incident electron has lost the difference in electron binding energies may be determined. This is utilised to identify the atoms causing the energy loss in a technique known as electron energy loss spectroscopy (EELS) (Ibach and Mills (1982), Joy (1979)). If the electron is ejected, however, the incident electron will lose energy that is equal to or greater than the binding energy of the electron in the atom. Thus the energy loss spectrum of the incident electron appears as a series of edges with tails to higher electron energies. It is frequently used in conjunction with the transmission electron microscope to determine the presence and concentration of elements of low atomic number.

2.5.2(a) Ionisation with photon emission
We have described the effect of excitation or ionisation on the incident electron, but following the initial excitation, processes take place within an atom which are identical to those described in the section dealing with photons. Clearly in the excited or the ionised condition the atom contains an inner electron shell with a hole and the atom can relax by an electron from an outer orbital falling into this hole. When this occurs an amount of energy is released, equal to \( E_1 - E_2 \), as a photon. By determining the energy of the photon the type of atom may be identified. The photon energy may be measured using a Li drifted silicon crystal in a technique known as energy dispersive X-ray spectroscopy (EDX) (Chapter 6) or by using single crystals to determine the wavelength and hence wavelength dispersive X-ray spectroscopy (WDX) (Gilfrich (1974)).

2.5.2(b) Ionisation with Auger electron emission
There is another way in which the ionised atom can decay, that is with the emission of an Auger electron in exactly the same manner as described for the photon ionised atom. In this process the atom relaxes by an electron from a higher orbital falling into the hole created by the initial ionisation process in the same manner as electron fluorescence. However, instead of the energy being released as a photon, it is transferred to an electron in an outer orbital which may have sufficient energy to escape from the atom. This electron is known as the Auger electron and has an energy given by equation 2.10. The probability, \( W \), that the atom will decay with the emission of a photon or an electron is given by (Burhop (1952)):

\[
W = (1 - \alpha Z^{-\beta})^{-1}
\]  (2.11)
2.6 ATOM AND ION PROCESSES

We now turn to the interaction of atoms and ions with materials. Compared to the photon and electron beams an atom or ion is massive and the wave nature may effectively be ignored and the atom or ion can be treated by Newtonian mechanics.

2.6.1 Scattering

Ions with very low energy can be elastically scattered from a material surface as shown schematically in figure 2.23. If the incident ion has a mass $M_1$ and an energy $E_1$ and is scattered through an angle $\theta$ such that after deflection by atoms of mass $M_2$, it will lose energy. The energy of the deflected ion, $E_2$, is, for the case when $M_2 > M_1$, given by:

$$E_2 = \frac{M_1 \cos \theta + (M_2^2 - M_1^2 \sin^2 \theta)^{1/2}}{M_2 + M_1} E_1.$$  \hfill (2.12)

When ions of higher energy impinge on a surface considerable damage occurs by inelastic scattering. The ion will embed into the surface, knocking atoms of the material in random directions. Some of the initial momentum will be transferred to ions, or ion clusters, in a backwards direction. A
Figure 2.23 Elastic scattering of ions of mass $M_1$ by a surface composed of atoms of mass $M_2$.

proportion of these are ejected from the surface together with electrons. The electron current can be detected in a similar manner to the scanning electron microscope and an image built up or the ions can be mass analysed and the composition and chemical form of the material determined. Atoms will be ionised and will decay with the emission of photons and Auger electrons which may be detected and analysed in exactly the same manner as for photon and electron ionisation described above.

2.7 EFFECT OF HIGH ELECTRIC FIELDS

There are a few techniques that utilise the effects of high electric fields to obtain microstructural information concerning materials. In order for electrons to leave an atom they have to surmount a potential barrier, $V$. If an electrostatic potential is applied to the specimen both the shape and height of the barrier are modified as shown in figure 2.24. The field at certain points can be made very large by appropriate specimen design such that electrons can be induced to leave the surface in a technique known as field emission microscopy (FEM) (Muller (1956)) and in related techniques atoms near the surface may be ionised and accelerated to form an image in field ion microscopy (FIM) (Kane (1979), Muller and Tsong (1969) and Panitz (1982)) while individual atoms may be induced to desorb from the surface and are subsequently identified using a mass spectrometer in the atom probe microscope (Muller et al (1968)).

When two conducting materials are separated by an insulator the insulator acts as a barrier to the flow of electrons. This is because the electron
shells in the insulator are completely full or empty and the requirement for conduction that one or more electron shells be only partially full is not satisfied. If an electron from a full shell can surmount the potential barrier then the material acts as a conductor. There is a finite probability that an electron that does not have sufficient energy to surmount the potential barrier may ‘tunnel’ through it. A similar phenomenon occurs with electron tunnelling through a thin insulating layer. If the distance between two conductors is sufficiently small, typically 1 nm, then there is a significant probability that the electron will pass through the barrier. This phenomenon, known as electron tunnelling, is utilised in the scanning tunnelling microscope (STM) (Bessenbacher et al (1989)) and can be used to identify surface features to a subatomic spatial resolution.

2.8 ACOUSTIC PHENOMENA

Before leaving this chapter acoustic waves should be mentioned. These waves travel through a solid medium by exciting vibrations in the material. Imperfections in the lattice, such as strain fields, particles, voids and cracks will interact with the acoustic wave and by detecting the scattered wave, information relating to the imperfection can be obtained. Acoustic waves range from the relatively long sound waves to the much shorter ultrasonic waves. The long wavelength waves will penetrate many centimetres into a