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Basics of Material Characterization Techniques

1.1 Introduction

In our daily life we come across different types of materials like metals, semiconductors, and ceramics. Scientific communities are continually exploring the nature of materials as well as their technological use, which requires understanding of some of the basic principles of physics and chemistry. The foremost thing about a material that is to be investigated is its structure and the related properties. The material is then fabricated to such a design that it results in exceeding the basic technological requirements. Checking the performance of the material is always a major focus in order to observe the behavior of the material under different conditions. The synthesis and characterization of materials play a crucial role for materials, research and nowadays a number of advanced instruments are available to understand the large range of mechanisms in materials. Since all characterization techniques are fundamental pillars in understanding the properties of a material, each characterization technique is based on some basic principles and some basic processes of physics. It is therefore worthwhile outlining the principles and processes that are being applied or used by different characterization techniques. Most characterization techniques involve the use of electromagnetic light, so information about the electromagnetic spectrum and related processes like reflection, refraction, absorption, transmittance, diffraction, interference, and dispersion are part of this chapter.

Apart from this, the solid form of materials is the most stable form, with minimum free energy, and a detailed information about the crystallography is provided, which is beneficial for understanding the structural properties of materials using techniques like X-ray diffraction. These are followed up in subsequent chapters. Similarly, different kinds of molecular motion and vibrations are also present in solids that, using Raman spectroscopy and infrared spectroscopy, also provide information about the materials providing information about the different motion in solids that form the initial stage for obtaining information and data. Some techniques such as electron microscopy also make use of electrons. This chapter provides details about electron–matter interactions and related consequences providing the morphology, topography, elemental composition, etc. Apart from these structural studies, dielectric studies of materials involve terms like dielectric constant

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Khalid Sultan.

and dielectric loss, which are also important parameters. The magnetic phenomenon involves magnetic terms and types of magnetism. All these terms are defined within this book.

1.2 Electromagnetic Spectrum

The electromagnetic spectrum envelops electromagnetic waves with a wide range of frequencies and hence a wide range of wavelengths and energy. The frequency range is divided into various parts and electromagnetic waves in each part have different names. Going from the low-frequency end of the electromagnetic spectrum to the high-frequency end we have radio waves, microwaves, infrared, visible light, ultraviolet (UV), X-rays, and gamma rays. Each type has different characteristics of production, interaction, and applications. Gamma rays, X-rays, and high-energy UV are called ionizing radiations because their photons have energy to ionize an atom. Some of the frequencies are responsible for spectroscopy, which is also based on the interaction of electromagnetic waves with matter. Before the 1800s, the term "light" was interpreted by a general reader and even a specialized person as visible light. In the 1800s, it was found that light contains not only the visible part but something more as evidenced by William Herschel's discovery of infrared light. The infrared region has three main parts, i.e., the far infrared, the mid-infrared, and the near infrared. The near-infrared region lies at the visible end of the electromagnetic spectrum. Similarly, in 1801 Johann Ritter identified the part of the spectrum that lies just beyond the violet end of visible light, which he termed deoxidizing rays. In the late nineteenth century, knowledge of these rays was well established and they were termed the UV rays. The UV region also consists of several parts, i.e., long-wave UV, medium-wave UV, and short-wave UV. James Clark Maxwell's equations provided information about the existence of an infinite number of frequencies of electromagnetic waves and thus predicted the entire electromagnetic spectrum. Heinrich Rudolf Hertz was the first to generate radio waves and microwave radiation. The study of X-rays was first carried out by Wilhelm Röntgen in 1895. X-ray spectroscopy was developed by Karl Manne Siegbahn, who was then awarded the 1924 Nobel Prize in Physics for his work. The discovery of gamma rays was made by Paul Villard in 1900 during an investigation of radioactivity and was said to be electromagnetic radiation, with the shortest wavelength and hence the highest energy as well as frequency. All parts of the spectrum are important and, as a result of their different characteristics, are used in different spectroscopic techniques [1]. The electromagnetic spectrum is shown in Figure 1.1.

Thus, based on the frequency, wavelength, and energy, which are fundamental factors in the spectrum, the electromagnetic radiations are divided into the following classes, regions, or bands:

a) gamma radiation,
b) X-ray radiation,
c) UV radiation,

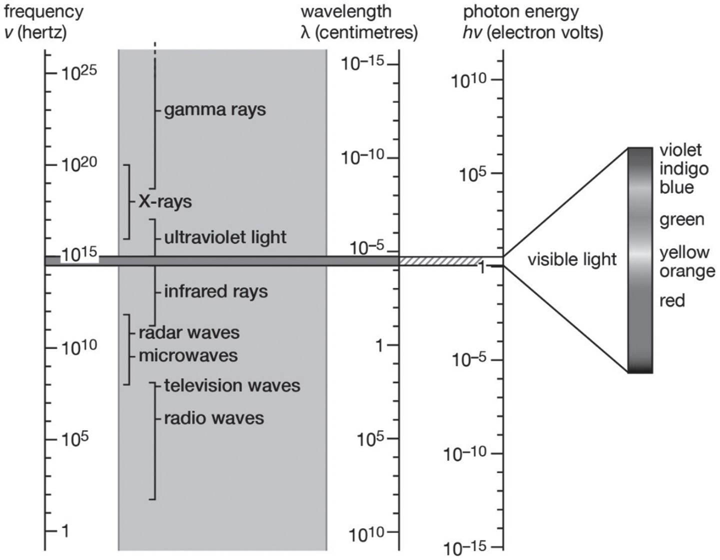


Figure 1.1 The electromagnetic spectrum.

d) visible radiation,
e) infrared radiation,
f) microwave radiation, and
g) radio waves.

These regions are given in increasing order of wavelength. It should also be noted that there is no well-defined boundary between the regions and they fade into each other.

Radio waves: These waves are released or received by antennas. The production of these waves involves the generation of an alternating current (AC) by a transmitter, which is an electric device available with an antenna. There is generation of oscillating electric and magnetic fields due to the oscillations of electrons in the antenna that lead to radiations that leave the antenna in the form of radio waves. Receiving these radio waves is associated with the coupling of oscillating electric and magnetic fields of waves with the electrons in the antenna. This causes the back-and-forth movement of electrons, thereby producing oscillating currents that are applied to radio receivers. These waves are used in the transmission of information in communication systems and in the Global Positioning System (GPS).

Microwaves: These waves are absorbed by polar molecules in addition to being released and received by short antennas. These are considered as radio waves of short wavelength with the characteristic of being used in radars and satellites. Microwaves have the capability to penetrate a material in order to deposit the energy well inside the surface. As a result they are used in microwave ovens.

Infrared radiation: The range of this frequency of radiation is approximately from 300 GHz to 400 THz. The far infrared part, ranging from 300 GHz to 300 THz, lies towards the microwave edge and is absorbed by the rotational modes of gas, the molecular motions in liquid, and phonons in solids. These are strongly absorbed by the water available in the atmosphere of Earth so are opaque to them, but there are certain frequencies that are allowed and are under study by astronomers. The mid-infrared part ranges from 30 THz to 120 THz. The hottest object or a blackbody radiator can emit radiations in this range while the skin of human beings also emits radiations of frequencies lying towards the lower end of this mid-region. As far as absorption of these radiations is concerned, they are absorbed by the vibration of molecules. The near-infrared part of this region ranges from 120 THz to 400 THz and lies towards the visible part of the electromagnetic spectrum. The higher frequencies are usually detected by photographic films and image sensors.

Visible light: The range of this frequency of radiations is approximately from 400 THz to 790 THz. This part of the electromagnetic spectrum is visible to human eyes and hence is called visible light. It is released and absorbed by electrons in an atom or in a molecule when going from one energy level to another. A rainbow shows the visible part of the electromagnetic spectrum, consisting of seven colors.

UV radiation: The wavelength range of these radiations of the electromagnetic spectrum is less than the visible part, but is considered to have the longest wavelength, with photons having such energy that they can ionize atoms. Shorter wavelength UV radiation and radiations having still smaller wavelengths, like X-rays and gamma rays, are known as ionizing radiations. UV also causes certain materials to glow, producing visible light, and the phenomenon is known as fluorescence.

X-ray: This is radiation that can interact with matter through the Compton effect. X-rays can be hard X-rays and soft X-rays, differing by the kind of wavelength. Shorter wavelength X-rays are called hard X-rays and can easily pass through different materials along with some absorption. The one most important use of these radiations is in diagnostic imaging. In material sciences, the X-rays diffraction phenomena has a major role in the identification of different compounds and samples. As far as the production of X-rays is concerned, they are released when there is a sudden deceleration of fast-moving electrons while interacting with the target anode.

Gamma rays: Gamma rays have the shortest wavelengths and were, discovered by Paul Ulrich Villard. These are considered to have the most energetic radiation, with no lower limit for their wavelength, and are usually used in the irradiation of food and seeds. In the field of astronomy these radiations have a role in the investigation of high-energy regions.

1.3 Fundamentals of Crystallography

The state of matter in which there is a regular arrangement of atoms is referred to as solid and the regularity is expressed by symmetry elements. In modern times the regularity of atoms can be studied with the help of high-resolution transmission electron microscopy. The arrangement and pattern of atoms connected through various interatomic forces can be expressed in terms of a unit whose repetition gives rise to crystals. In crystals, the set of points surrounding any given point is identical to those of all other points and constitutes a lattice, where each point is called a lattice point. A lattice in a crystal describes a translational symmetry. In the case of three dimensions, the unit cell is in the form of a parallelepiped such that the origin lies at the corner of the unit cell and the three axes are represented in terms of sides of the unit parallelepiped. The three axes are connected with each other through angles α, β, and γ, and the minimum separation between two adjacent lattice points along the three axes is expressed in terms of lattice parameters x, y, and z.

Consider a two-dimensional crystal having lattice parameters a and b such that the magnitudes of both a and b are different, as shown in Figure 1.2, where we observe that the mesh lines OB, O′B′, and O′′B′′ are parallel and thus constitute a set with regular spacing in between these mesh lines. Similarly, the same effect can be observed in mesh lines AB, A′B′, and A′′B′′. It has been determined that the spacing between parallel mesh lines depends not only on the lattice parameters $\boldsymbol{a}$ and $\boldsymbol{b}$ vectors but also on the angle between the $\boldsymbol{a}$ and $\boldsymbol{b}$ vectors. However, the case of the angle between the two sets depends on the ratio of magnitude of $\boldsymbol{a}$ and $\boldsymbol{b}$. It should be noted that the value of the angle between the corresponding faces is constant as long as all the crystals are of the same substance [2]. In this analogy of lines in a mesh, in the planes of a crystal the faces of the crystal are parallel to the planes of the lattice and the lattice planes have a high density. In this case, we also have a set of parallel planes whose spacing depends on the lattice parameters and axial angles. However, the angle between various lattice planes depends on the ratio of the axial angles and lattice parameters.

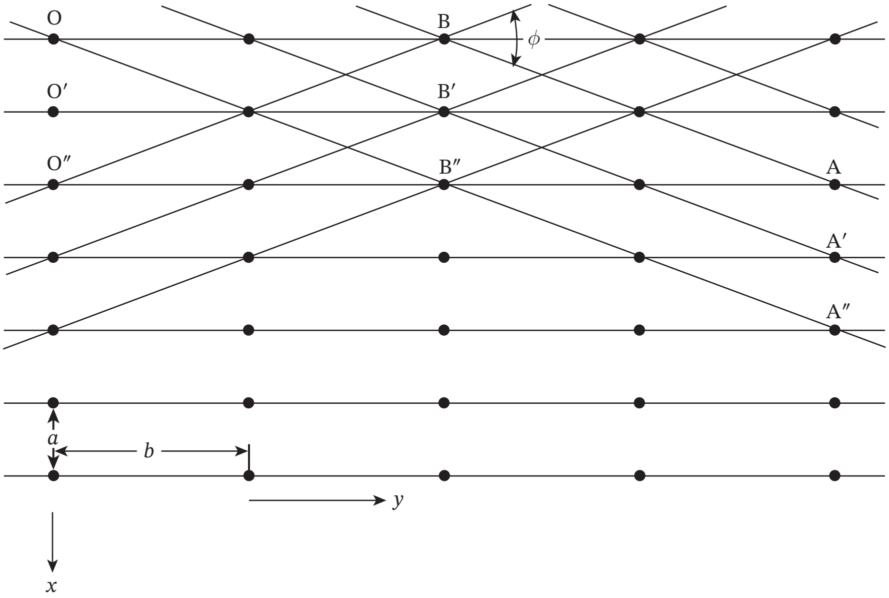


Figure 1.2 A two-dimensional crystal.

In a crystal the direction is expressed as a line. Let us assume two points P and P′ lying on a line with P at the origin, as shown in Figure 1.3. Using the concept of translation, the vector $\boldsymbol{r}$ joining P and P′ can be expressed in terms of $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ vectors along the x, y, and z directions, respectively, as

$$\boldsymbol{r} = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c} \tag{1.1}$$

The notation for direction is then represented by arrows and examples are shown in Figure 1.4.

In cases where the value of any of the u, v, and w is negative, it is expressed in terms of bar. Moreover, P lies at the origin and in the case where u, v, and w are also integers, the P′ will lie on the lattice point such that the produced PP′ represents a row of lattice points and is called a rational line and accordingly we have a rational plane. To designate a plane let us consider that a plane from the set cuts the three

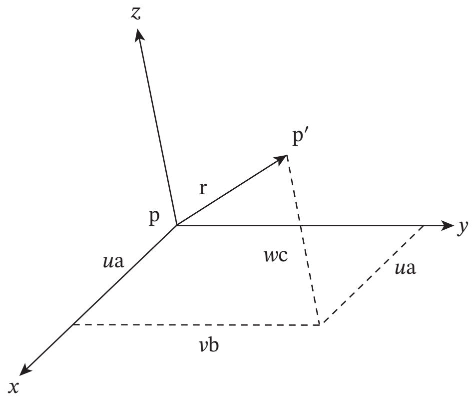


Figure 1.3 Representation of $\boldsymbol{r}$ in terms of $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$.

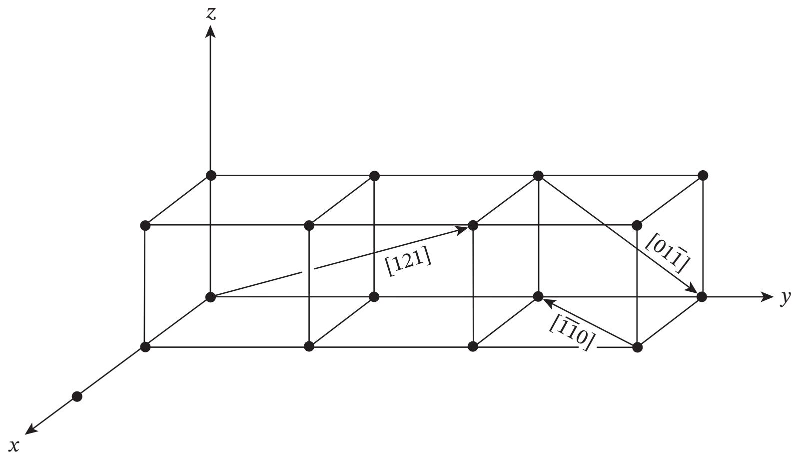


Figure 1.4 Example showing directions.

axes x, y, and z at A, B, and C respectively. Suppose that the origin lies at the lattice point and $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ represent the separation between lattice points that are adjacent to each other. Here we define Miller indices (hkl) for a set of planes such that

$$\mathrm{OA} = \frac{a}{h}$$

$$\mathrm{OB} = \frac{b}{k}$$

$$\mathrm{OC} = \frac{c}{l}$$

The reason behind the introduction of Miller indices in crystal structures is that it simplifies calculations.

Now the basic idea for a description pertains to the explanation of solids in terms of the Bravais lattice that pertains to the periodic arrangement in solids where a unit is repeated. In actual fact, these units can be an atom or group of atoms but the Bravais lattice depends on the geometry of the structure, whatever the unit is. A Bravais lattice can be understood in terms of the following definitions:

- An infinite arrangement of lattice points is such that the array and orientation are the same from every point the arrangement is viewed.
- A Bravais lattice has all points such that the position vector $\boldsymbol{R}$, for $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, and $\boldsymbol{a}_3$, does not lie on the same plane:

$$\boldsymbol{R} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3 \tag{1.2}$$

- Here n_1, n_2, and n_3 take integer values. This means that a point $\Sigma n_i\boldsymbol{a}_i$ can be obtained if moved in the direction of $\boldsymbol{a}_i$ through n_i steps, each of length a_i.

The vector $\boldsymbol{a}_i$ is called a primitive vector and is responsible for the generation of a lattice. In physics, it is said to span the lattice [3]. A two-dimensional Bravais lattice is shown in Figure 1.5, where $\boldsymbol{P} = \boldsymbol{a}_1 + 2\boldsymbol{a}_2$ and $\boldsymbol{Q} = -\boldsymbol{a}_1 + \boldsymbol{a}_2$, and a simple cubic three-dimensional representation of a Bravais lattice is shown in Figure 1.6.

Another concept in solid-state physics is of a reciprocal lattice. Let us try to understand this. If we have a set of points in a Bravais lattice and accordingly a plane wave of the form $e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$, then all wave vectors $\boldsymbol{K}$ that produce periodicity of a given Bravais lattice are called a reciprocal lattice of a Bravais lattice, such that

$$e^{i\boldsymbol{K}\cdot(\boldsymbol{r}+\boldsymbol{R})} = e^{i\boldsymbol{K}\cdot\boldsymbol{r}} \tag{1.3}$$

is satisfied for any $\boldsymbol{r}$ and all $\boldsymbol{R}$ in a Bravais lattice.

There are seven types of crystal systems, which will be defined and are shown in Figure 1.7.

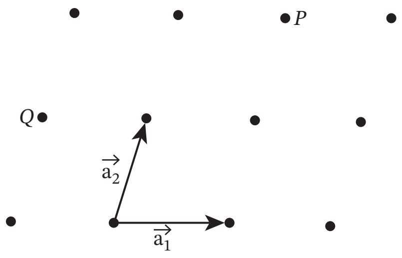


Figure 1.5 Two-dimensional Bravais lattice.

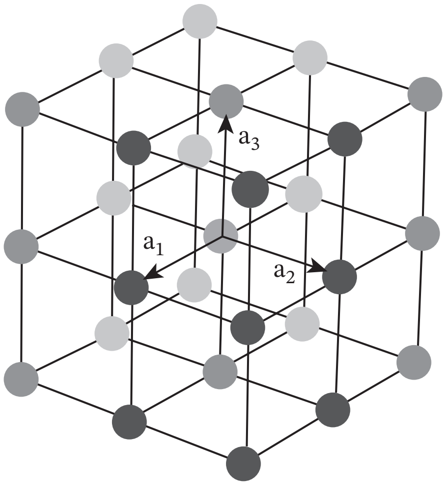
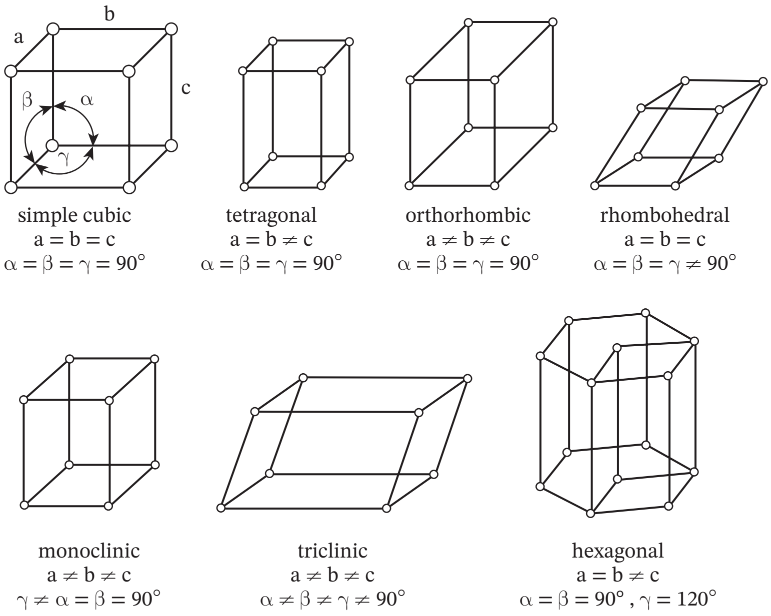


Figure 1.6 Simple cubic Bravais lattice.



simple cubic
$a = b = c$
$\alpha = \beta = \gamma = 90°$

tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

monoclinic
$a \neq b \neq c$
$\gamma \neq \alpha = \beta = 90°$

triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

hexagonal
$a = b \neq c$
$\alpha = \beta = 90°, \gamma = 120°$

Figure 1.7 Crystal systems.

1) **Cubic system:** In this system all angles are equal to 90º and all of the axes are equal, such that we write

$$a = b = c$$

$$\alpha = \beta = \gamma = 90^{\circ}$$

2) **Tetragonal system:** In this system all angles are equal to 90º and two axes are equal such that one axes is unequal to both of the equal axes. In this case we write

$$a = b \neq c$$

$$\alpha = \beta = \gamma = 90^{\circ}$$

3) **Orthorhombic system:** In this system all three axes are at right angles but are unequal, such that

$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^{\circ}$$

4) **Rhombohedral system:** In this system all three axes are equal and no angle is equal to 90º, such that

$$a = b = c$$

$$\alpha = \beta = \gamma \neq 90^{\circ}$$

5) **Monoclinic system:** In this system all three axes are not equal and two angles are equal to 90º and one angle is not equal to 90º, such that

$$a \neq b \neq c$$

$$\alpha = \gamma = 90^{\circ}$$

$$\beta \neq 90^{o}$$

6) **Triclinic system:** In this system all three axes are unequal in length and none of the angles between these axes is equal to 90º In other words, we write parameters *a*, *b*, and *c* as

$$a \neq b \neq c$$

$$No\ angle = 90^{\circ}$$

7) **Hexagonal system:** In this system two angles are equal to 90º and one angle is equal to 120°. Similarly, the two axes are equal and one axis is unequal to both equal axes, such that

$$a = b \neq c$$

$$\alpha = \beta = 90^{\circ}$$

$$\gamma = 120^{\circ}$$

1.4 Molecular Vibrations

A molecule consists of atoms that move relative to one another in such a way that the center of mass remains unaltered. The frequency of vibration is generally less than 10^{13} Hz. If a molecule is polyatomic in nature then the vibrational motion is described in terms of normal modes of vibration. These modes of vibration are not dependent on each other instead the different parts constituting a molecule are influenced by each normal mode of vibration.

For a molecule that is nonlinear and has N atoms in total, the total number of normal modes of vibration are $3N - 6$, but this number of modes becomes $3N - 5$ if the molecules are linear. For a molecule with N atoms there should be $3N$ degrees of freedom corresponding to translation, vibration, and rotation. When the molecule is nonlinear in structure, it has three rotational degrees of freedom, while in the case of a linear molecule it has only two rotational degrees of freedom. Thus, the vibrational modes will be obtained by subtracting the translational and rotational degrees of freedom from $3N$ total degrees of freedom. Consider a diatomic molecule, which is always linear, to have only one possible mode of vibration that corresponds to the compressing and stretching of bonds joining the two atoms of the molecule. Let the molecule absorb an energy $\Delta E = h\upsilon$, which as a result causes it to become excited vibrationally. If one quantum of this energy is absorbed in the ground state, this will lead to fundamental vibration. Similarly, absorption of multiple quanta of energy causes excitement of first, second, and higher overtones.

To probe the vibrational states of a molecule, a number of techniques can be used. The first and foremost technique is infrared spectroscopy. This is because the energy required for the vibrational transitions lies in the infrared region of the electromagnetic spectrum. However, Raman spectroscopy can also be applied in the study of vibrations.

1.5 Magnetism in Solids

Magnetic materials in solids are very important because of their role in scientific development and industrial growth. The primary source of magnetism in materials is motion of electrons. Based on the behavior of these materials in response to an externally applied magnetic field, these materials can be classified into the following types:

1) **Diamagnetic materials:** When placed in an external magnetic field, these materials become magnetized in a direction opposite to that of the applied field. Diamagnetic substances do not possess any permanent magnetic moment but have the ability to expel the magnetic lines of an externally applied field. They have a temperature-independent negative value of magnetic susceptibility.
2) **Paramagnetic materials:** These substances possess a permanent magnetic moment. When they are placed in an external magnetic field the random

magnetic moment becomes aligned in the direction of the magnetic field. In the absence of a magnetic moment, the material possesses a zero net magnetic moment. These materials have a positive but small value of magnetic susceptibility.

3) **Ferromagnetic materials:** These materials have magnetization even in the absence of an external magnetic field and that magnetization is called spontaneous magnetization. Spontaneous magnetization exists up to the temperature known as the Curie temperature. After the Curie temperature the substance becomes paramagnetic because a further increase in temperature causes thermal agitations, as a result of which there would be randomization in the magnetic moments. In ferromagnetic materials each atom acts as a tiny magnet pointing in the same direction.
4) **Antiferromagnetic materials:** These materials have magnetic moments of adjacent atoms that are antiparallel to each other. This behavior has been seen in mangenese oxide (MnO), in which the moments of adjacent atoms are antiparallel to each other in the absence of an external magnetic field and hence the net magnetization is zero. When a field is applied a small value of magnetization appears, which increases with an increase in temperature up to a specific temperature, called the Neel temperature. After this, magnetization decreases and the substance becomes paramagnetic.
5) **Ferrimagnetic substances:** These substances are the same as antiferromagnetic substances except that the adjacent antiparallel magnetic moments are unequal in magnitude. In other words, we may say that two sublattices have different values of magnetization. These materials also result in ferrites, which have high resistivity and anisotropic properties [4].

1.6 Optical Properties of Solids

Understanding the optical properties of solids involves the investigation of the energy band structure, lattice vibrations, excitons, etc. Experimental study requires the observation of reflectivity, transmission, scattering, absorption, etc., and arrives at results for the dielectric constant and conductivity, for example. These properties have a direct dependence on the energy band structure [5].

Let us introduce complex optical conductivity and complex dielectric constant with the help of Maxwell's equation and with the assumption of zero charge density, given by:

$$\nabla \times \boldsymbol{H} - \frac{1}{c}\frac{\partial \boldsymbol{D}}{\partial t} = \frac{4\pi}{c}\boldsymbol{j} \tag{1.4}$$

$$\nabla \times \boldsymbol{E} + \frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t} = 0 \tag{1.5}$$

$$\nabla \cdot \boldsymbol{D} = 0 \tag{1.6}$$

$$\nabla \cdot \boldsymbol{B} = 0 \tag{1.7}$$

Constitutive equations are given by

$$\boldsymbol{D} = \varepsilon \boldsymbol{E}$$

$$\boldsymbol{B} = \mu \boldsymbol{H}$$

$$\boldsymbol{j} = \sigma \boldsymbol{E} \tag{1.8}$$

From this equation the parameter ε defines the complex dielectric function. The field variables $\boldsymbol{E}$ and $\boldsymbol{H}$ can be given by

$$\nabla^2 \boldsymbol{E} = \frac{\varepsilon\mu}{c^2}\frac{\partial^2 \boldsymbol{E}}{\partial t^2} + \frac{4\pi\sigma\mu}{c^2}\frac{\partial \boldsymbol{E}}{\partial t} \tag{1.9}$$

$$\nabla^2 \boldsymbol{H} = \frac{\varepsilon\mu}{c^2}\frac{\partial^2 \boldsymbol{H}}{\partial t^2} + \frac{4\pi\sigma\mu}{c^2}\frac{\partial \boldsymbol{H}}{\partial t} \tag{1.10}$$

In optical fields we define the solution of the equations for $\boldsymbol{E}$ in the form

$$\boldsymbol{E} = \boldsymbol{E}_0 e^{i(\boldsymbol{K}\cdot\boldsymbol{r} - \omega t)} \tag{1.11}$$

where $\boldsymbol{K}$ is the propagation constant and ω is the frequency of light. The real part of $\boldsymbol{K}$ is the wave vector and the imaginary part represents the attenuation within the material. By substitution of this solution into the above equation for $\boldsymbol{E}$, we obtain

$$-K^2 = -\frac{\varepsilon\mu\omega^2}{c^2} - \frac{4\pi i\sigma\mu\omega}{c^2} \tag{1.12}$$

For no loss, K becomes K_0 and is a real quantity, such that

$$K_0 = \frac{\omega}{c}\sqrt{\varepsilon\mu} \tag{1.13}$$

For loss, we can express K as

$$K_0 = \frac{\omega}{c}\sqrt{\varepsilon_{complex}\mu} \tag{1.14}$$

Here the complex dielectric constant is defined as

$$\varepsilon_{complex} = \varepsilon + \frac{4\pi i\sigma}{\omega} = \varepsilon_1 + i\varepsilon_2$$

$$\varepsilon_{complex} = \frac{4\pi i\sigma}{\omega}\left[\sigma + \frac{\varepsilon\omega}{4\pi i}\right] = \frac{4\pi i}{\omega}\sigma_{complex} \tag{1.15}$$

References

1 Ball, D.W. (2007). The electromagnetic spectrum: A history. *Spectroscopy* 22: 14.

2 Kelly, A. and Knowles, K.M. (2012). *Crystallography and Crystal Defects*. John Wiley & Sons.

3 Ashcroft, N. and Mermin, D. (1976). *Solid State Physics*. Harcourt College Publisher.

4 Globus, A., Packard, H., and Kagan, V. (1977). Distance between magnetic ions and fundamental properties in ferrites. *Le Journal de Physique Colloques* 38 (C1): C1–163.

5 Dressel Haus, M.S. (2018). *Optical Properties of Solids in Solid State Physics*. Springer.