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Ashim K. Bain and Prem Chand

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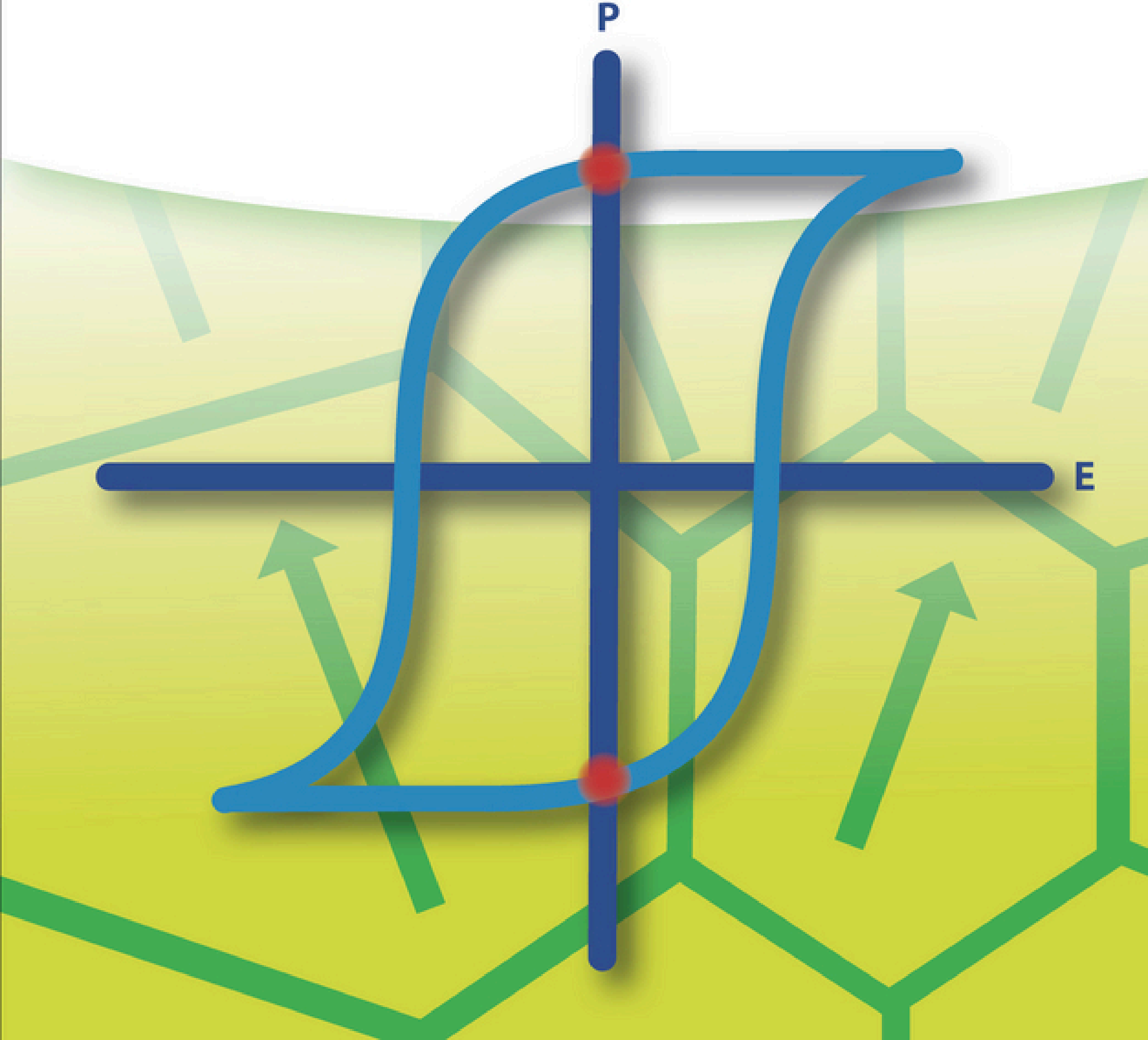
Principles and Applications



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Dielectric Properties of Materials

1.1 Energy Band in Crystals

In crystallography, a crystal structure is a unique arrangement of atoms, ions, or molecules in a crystalline solid. It describes a highly ordered structure, occurring due to the intrinsic nature of its constituents to form symmetric patterns. The crystal lattice can be thought of as an array of “small boxes” infinitely repeating in all three spatial directions. Such a unit cell is the smallest unit of volume that contains all of the structural and symmetry information to build up the macroscopic structure of the lattice by translation. The crystal structure and symmetry play a role in determining many of its physical properties, such as electronic band structure and optical transparency.

To discuss the behavior of electrons in a crystal, we consider an isolated atom of the crystal. If Z is the atomic number, the atomic nucleus has a positive charge Ze. At a distance r from the nucleus, the electrostatic potential due to the nuclear charge is (in SI units)

$$V(r) = \frac{Ze}{4\pi\varepsilon_0 r} \tag{1.1}$$

where ε_0 is the permittivity of free space. Since an electron carries a negative charge, the potential energy of an electron at a distance r from the nucleus is

$$E_\mathrm{p}\,(r) = -eV(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \tag{1.2}$$

$V(r)$ is positive, while $E_\mathrm{p}(r)$ is negative. Both $V(r)$ and $E_\mathrm{p}(r)$ are zero at an infinite distance from the nucleus. Figure 1.1a,b shows the variation of $V(r)$ and $E_\mathrm{p}(r)$, respectively, with r.

We now consider two identical atoms placed close together. The net potential energy of an electron is obtained as the sum of the potential energies due to the two individual nuclei. In the region between the two nuclei, the net potential energy is clearly smaller than the potential energy for an isolated nucleus (Figure 1.2).

The potential energy along a line through a row of equispaced atomic nuclei, as in a crystal, is diagrammatically shown in Figure 1.3. The potential energy between the nuclei is found to consist of a series of humps. At the boundary AB

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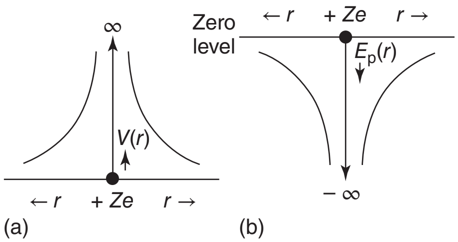

Figure 1.1 Variation of (a) potential in the field of a nucleus with distance and (b) potential energy of an electron with its distance from the nucleus.

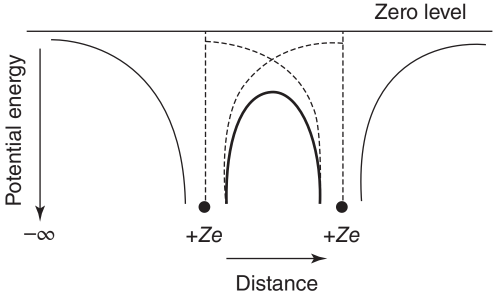

Figure 1.2 Potential energy variation of an electron with distance between two identical nuclei.

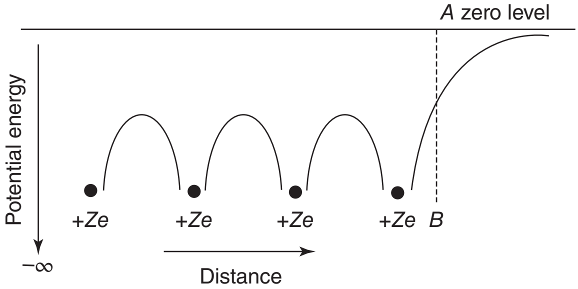

Figure 1.3 Potential energy of an electron along a row of atoms in a crystal.

of the solid, the potential energy increases and approaches zero at infinity, there being no atoms on the other side of the boundary to bring the curve down.

The total energy of an electron in an atom, kinetic plus potential, is negative and has discrete values. These discrete energy levels in an isolated atom are shown by horizontal lines in Figure 1.4a. When a number of atoms are brought close together to form a crystal, each atom will exert an electric force on its neighbors. As a result of this interatomic coupling, the crystal forms a single electronic system obeying Pauli's exclusion principle. Therefore, each energy level of the isolated atom splits into as many energy levels as there are atoms in the crystal, so that Pauli's exclusion principle is satisfied. The separation between the split-off energy levels is very small. A large number of discrete and closely spaced energy levels form an *energy band.* Energy bands are represented schematically by the shaded regions in Figure 1.4b.

The width of an energy band is determined by the parent energy level of the isolated atom and the atomic spacing in the crystal. The lower energy levels are not greatly affected by the interaction among the neighboring atoms and

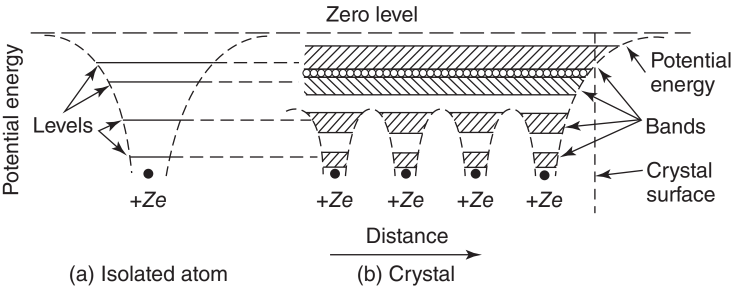

Figure 1.4 Splitting of energy levels of isolated atoms into energy bands as these atoms are brought close together to produce a crystal.

hence form narrow bands. The higher energy levels are greatly affected by the interatomic interactions and produce wide bands. The interatomic spacing, although fixed for a given crystal, is different for different crystals. The width of an energy band thus depends on the type of the crystal and is larger for a crystal with a small interatomic spacing. The width of a band is independent of the number of atoms in the crystal, but the number of energy levels in a band is equal to the number of atoms in the solid. Consequently, as the number of atoms in the crystal increases, the separation between the energy levels in a band decreases. As the crystal contains a large number of atoms ($\approx 1029\,\mathrm{m}^{-3}$), the spacing between the discrete levels in a band is so small that the band can be treated as continuous.

The lower energy bands are normally completely filled by the electrons since the electrons always tend to occupy the lowest available energy states. The higher energy bands may be completely empty or may be partly filled by the electrons. Pauli's exclusion principle restricts the number of electrons that a band can accommodate. A partly filled band appears when a partly filled energy level produces an energy band or when a totally filled band and a totally empty band overlap.

As the allowed energy levels of a single atom expand into energy bands in a crystal, the electrons in a crystal cannot have energies in the region between two successive bands. In other words, the energy bands are separated by gaps of *forbidden energy.*

The average energy of the electrons in the highest occupied band is usually much less than the zero level marked in Figure 1.4b. The rise of the potential energy near the surface of the crystal, as shown in Figure 1.4b, serves as a *barrier*, preventing the electrons from escaping from the crystal. If sufficient energy is imparted to the electrons by external means, they can overcome the surface potential energy barrier and come out of the crystal surface.

1.2 Conductor, Insulator, and Semiconductor

On the basis of the band structure, crystals can be classified into conductors, insulators, and semiconductors.

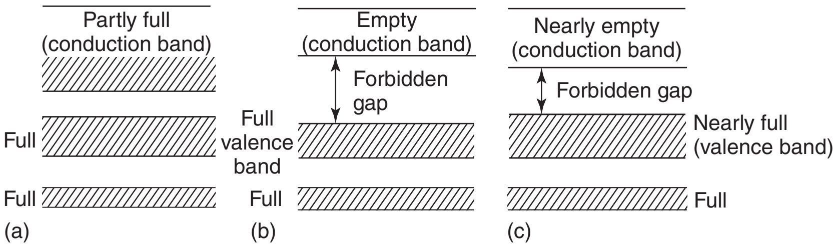

Figure 1.5 Energy band structure of (a) a conductor, (b) an insulator, and (c) a semiconductor.

1.2.1 Conductors

A crystalline solid is called a *metal* if the uppermost energy band is partly filled or the uppermost filled band and the next unoccupied band overlap in energy as shown in Figure 1.5a. Here, the electrons in the uppermost band find neighboring vacant states to move in and thus behave as free particles. In the presence of an applied electric field, these electrons gain energy from the field and produce an electric current, so that a metal is a good conductor of electricity. The partly filled band is called the *conduction band*. The electrons in the conduction band are known as *free electrons* or *conduction electrons*.

1.2.2 Insulators

In some crystalline solids, the forbidden energy gap between the uppermost filled band, called the *valence band*, and the lowermost empty band, called the *conduction band*, is very large. In such solids, at ordinary temperatures, only a few electrons can acquire enough thermal energy to move from the valence band into the conduction band. Such solids are known as *insulators*. Since only a few free electrons are available in the conduction band, an insulator is a bad conductor of electricity. Diamond having a forbidden gap of 6 eV is a good example of an insulator. The energy band structure of an insulator is schematically shown in Figure 1.5b.

1.2.3 Semiconductors

A material for which the width of the forbidden energy gap between the valence and the conduction band is relatively small (~1 eV) is referred to as a *semiconductor*. Germanium and silicon having forbidden gaps of 0.78 and 1.2 eV, respectively, at 0 K are typical semiconductors. As the forbidden gap is not very wide, some of the valence electrons acquire enough thermal energy to go into the conduction band. These electrons then become free and can move about under the action of an applied electric field. The absence of an electron in the valence band is referred to as a *hole*. The holes also serve as carriers of electricity. The electrical conductivity of a semiconductor is less than that of a metal but greater than that of an insulator. The band diagram of a semiconductor is given in Figure 1.5c.

1.3 Fermi–Dirac Distribution Function

The free electrons are assumed to move in a field-free or equipotential space. Due to their thermal energy, the free electrons move about at random just like gas particles. Hence these electrons are said to form an *electron gas*. Owing to the large number of free electrons (~10^{23} cm^{-3}) in a metal, principles of statistical mechanics are employed to determine their average behavior. A useful concept is the *distribution function* that gives the probability of occupancy of a given state by the electrons. The *Fermi–Dirac* (FD) *distribution function* can be used to determine the energy distribution of free electrons in a metal. From statistical mechanics, the FD distribution function is found to be

$$f(E) = \frac{1}{1 + \exp\left[\frac{E-E_f}{k_B T}\right]} \tag{1.3}$$

where $f(E)$ is the occupation probability of a state with energy E, E_F is a characteristic energy (chemical potential) for a particular solid and is referred to as the *Fermi level*, T is the absolute temperature, and k_B is Boltzmann's constant ($k_B = 1.38 \times 10^{-23}$ J K^{-1}).

At the absolute zero of temperature, that is, at $T = 0$ K, Eq. (1.3) shows that $f(E) = 1$ for $E < E_F$ and $f(E) = 0$ for $E > E_F$. Thus all the energy states below E_F are occupied by the electrons, and all the energy states above E_F are completely empty. Hence *the Fermi energy* E_F denotes the maximum energy that can be occupied by the electrons at $T = 0$ K.

At temperatures greater than the absolute zero, $f\,(E) > 0$ for $E > E_F$, as shown in Figure 1.6. This means that at a finite temperature, some of the electrons in the quantum states below E_F acquire thermal energy to move into states above E_F.

When $E = E_F$, Eq. (1.3) shows that $f\,(E) = 1/2$ for $T > 0$. Thus the Fermi level is the energy level for which the probability of occupancy is 1/2 for a finite nonzero temperature. For most conductors, E_F is less than 10 eV. For a pure semiconductor and an insulator, the Fermi level lies near the middle of the forbidden energy gap, whereas for a conductor, the Fermi level lies within the conduction band (Figure 1.7a–c).

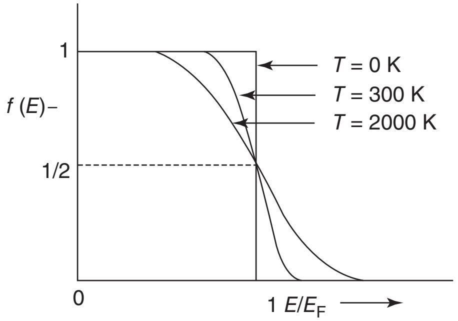

Figure 1.6 Plot of $f(E)$ against E/E_F for $T = 300$ and 2000 K.

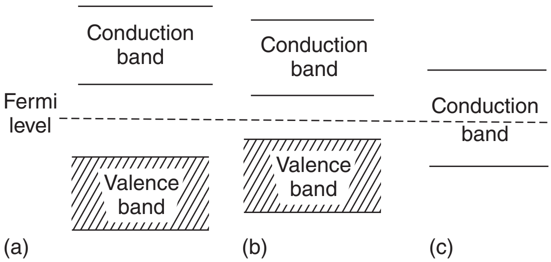

Figure 1.7 Schematic diagram showing the position of the Fermi level in (a) an insulator, (b) a semiconductor, and (c) a conductor.

1.4 Dielectrics

A dielectric material is a substance that is a poor conductor of electricity. On the basis of band structure, the dielectric materials have an energy gap of 3 eV or more. This large magnitude of energy gap precludes the possibility of electrons being excited from the valence band to the conduction band by thermal means. A dielectric is an electrical insulator that can be polarized by an applied electric field. When a dielectric is placed in an electric field, electric charges slightly shift from their average equilibrium positions, causing dielectric polarization. Because of dielectric polarization, positive charges are displaced toward the field and negative charges shift in the opposite direction. This creates an internal electric field that reduces the overall field within the dielectric itself. If a dielectric is composed of weakly bonded molecules, those molecules not only become polarized but also reorient so that their symmetry axis aligns to the field. The ideal dielectric material does not exhibit electrical conductivity when an electric field is applied. In practice, all dielectrics do exhibit some conductivity, which generally increases with increase in temperature and applied field.

The study of dielectric properties is concerned with the storage and dissipation of electric and magnetic energy in materials. In practice, most dielectric materials are solid. Examples include porcelain (ceramic), mica, glass, plastics, and the oxides of various metals. Dielectrics are employed as insulation for wires, cables, and electrical equipment, as polarizable media for capacitors, in apparatus used for the propagation or reflection of electromagnetic waves, and for a variety of artifacts, such as rectifiers and semiconductor devices, piezoelectric transducers, dielectric amplifiers, and memory elements.

Some liquids and gases can serve as good dielectric materials. Dry air is an excellent dielectric and is used in variable capacitors. Distilled water is a fair dielectric. A vacuum is an exceptionally efficient dielectric. Many of the traditional industrial dielectric materials are still in common use, and they compete well in some applications with newer materials regarding their electrical and mechanical properties, reliability, and cost. For example, oil-impregnated paper is still used for high-voltage cables. Various types of pressboard and mica, often as components of composite materials, are also in use. Elastomers and press-molded resins are also of considerable industrial significance. However, synthetic polymers such as polyethylene, polypropylene, polystyrene, polytetrafluoroethylene, polyvinyl chloride, polymethyl methacrylate, polyamide, and polyimide have become important, as has polycarbonate because it can be fabricated into very thin films. Generally, polymers have crystalline and amorphous regions, increasing crystallinity, causing increased density, hardness, and resistance to chemical attack but often producing brittleness. Many commercial plastics are amorphous copolymers, and often additives are incorporated in polymers to achieve certain characteristics or to improve their workability.

1.4.1 Polarization of Dielectrics

The factors contribute to the polarization of dielectric molecules: the formation of dipole moments and their orientation relatively to the electric field. If in a dielectric the molecules forming elementary dipole moments are composed of neutral particles such as atoms, the electric field shifts the electric charge of an atomic shell against the direction of field and the nucleus is moved in with the field. Thus the center of gravity of the positive and negative charges is displaced from the center of the atom, and an "induced dipole moment" is produced, as shown in Figure 1.8a. This part of polarization of molecules is called *electronic* (P_e). The electronic polarization is independent of temperature, but it is directly proportional to the field strength.

If the molecule producing an elementary dipole moment is made of ions of opposite signs, the following process occurs when the dielectric is placed into an electric field: the positive ions leave their equilibrium positions and move in the direction of field, and the negative ions are displaced against the direction of field. This displacement of ions or their groups in a dielectric initiates an *ionic* polarization (P_i) of molecules, as shown in Figure 1.8b. The ionic polarization is also independent of temperature, but it depends on the binding energy of particles in the molecule and in the lattice of the dielectric.

The asymmetric distribution of charge between different atoms in a molecule produces permanent dipole moments in the molecules of a dielectric. Under the action of an electric field, these permanent dipoles are rotated into the direction of the field and thus contribute to polarization. In this case, we speak about the *orientational* polarization (P_o), as shown in Figure 1.8c. The orientational polarization is dependent on temperature. With increasing temperature, the thermal

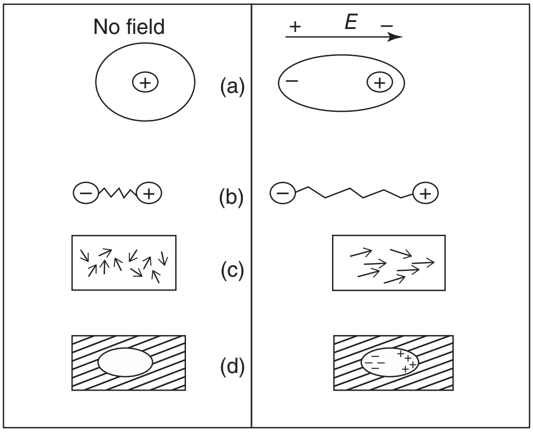

Figure 1.8 Polarization processes: (a) electronic polarization, (b) ionic polarization, (c) orientational polarization, and (d) space charge polarization.

energy tends to randomize the alignment of the permanent dipoles inside the materials.

In real dielectrics, free charges may exist, which, under the action of an electric field, move through the dielectric and are captured by various defects within the dielectric without coming into contact with the electrodes. The free charges then form regions with a surface or a space charge, which in turn produces a dipole moment, also contributing to the polarization of dielectric. This mechanism initiates a *space (surface)* charge polarization (P_s) inside the dielectric, as shown in Figure 1.8d. Like the orientational polarization, the space charge polarization is also a function of temperature; in most cases it increases with temperature.

The total polarization of a dielectric may simultaneously involve all the four mechanisms. If we assume that they are independent, we can write the total polarization of a dielectric material as the sum of the contributions from the four sources described earlier:

$$P_{\text{total}} = P_e + P_i + P_o + P_s \tag{1.4}$$

where the subscripts on the right refer to the four types: electronic, ionic, orientational, and space charge polarization.

1.4.2 Dispersion of Dielectric Polarization

The dielectric polarization process can be expressed as a function of temperature:

$$P(t) = P\left[1 - \exp\left(-\frac{t}{t_r}\right)\right] \tag{1.5}$$

where P is the maximum polarization attained upon application of the electric field and t_r is the relaxation time for a particular polarization process. The relaxation time t_r is the time taken for a polarization process to reach 63% of the maximum value.

The relaxation time varies widely with different polarization processes. There are a number of polarization mechanisms as shown in Figure 1.9. The most common, starting from high frequencies, are given in the following.

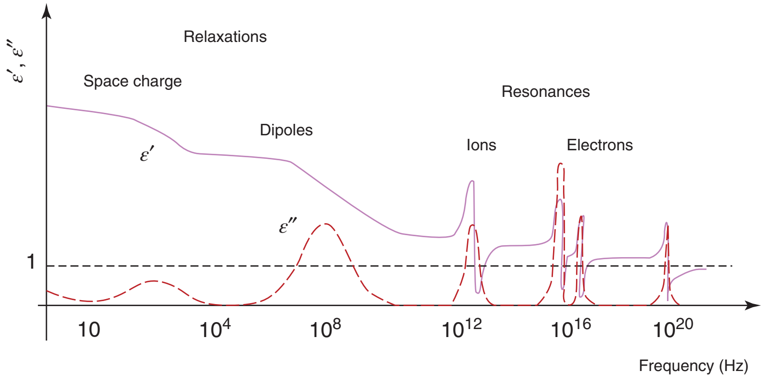

Figure 1.9 Frequency dependence of polarization dispersion.

1.4.2.1 Electronic Polarization

This process occurs in an atom when the electric field displaces the electron density relative to the nucleus it surrounds. Electronic polarization may be understood by assuming an atom as a point nucleus surrounded by spherical electron cloud of uniform charge density. Electrons have very small mass and are therefore able to follow the high-frequency fields up to the optical range. It is an extremely rapid process and is essentially complete at the instant the voltage is applied. Even when the frequency of the applied voltage is very high in the optical range ($\sim 10^{15}$ Hz), the electronic polarization occurs during every cycle of the applied voltage.

1.4.2.2 Ionic Polarization

This process is associated with the relative motions of cations and anions in an electric field. Ionic polarization is slower than electronic polarization, as the displacement involved here is that of much heavier ion, as compared with the electron cloud. The frequency with which ions can be displaced over a small fraction of the interatomic distance will be of the same order as the lattice vibration frequency ($\sim 10^{13}$ Hz). If an electric field of frequency in the optical range ($\sim 10^{15}$ Hz) is applied, the ions do not respond at all, as the time required by an ion for one vibration is 100 times longer than the period of the applied voltage. So, there is no ionic polarization at optical frequencies.

1.4.2.3 Orientation Polarization

It is slower than ionic polarization. The orientation polarization arises from the rotation of molecular dipoles in the field. It is easier for the polar molecules to reorient themselves in a liquid as compared with a solid. Orientation polarization occurs when the frequency of the applied voltage is in the audio range.

1.4.2.4 Space Charge Polarization

It is the slowest process, as it involves the diffusion of ions over several interatomic distances. The relaxation time for this process is related to the frequency of successful jumps of ions under the influence of the applied field. Space charge polarizations are often occur in the kilohertz range or even lower.

1.4.3 Molecular Theory of Induced Charges in a Dielectric

A dielectric contains no free charges; then how it is possible for an induced charge to appear on the surface of a dielectric when placed in an electric field? This can be explained by the molecular viewpoint of dielectric. The dielectrics are classified as polar and nonpolar. A nonpolar molecule is one in which the centers of gravity of positive and negative charges normally coincide, while a polar molecule is one where they do not coincide. Polar molecules therefore have permanent dipole moments. In the absence of an external field, these dipoles are oriented at random. But strong field orients more dipoles in the direction of the field. The charges of a nonpolar molecule suffer a small displacement when placed in an electric field.

The molecules are said to become polarized by the field and are called *induced dipoles*. So, the dielectrics, both polar and nonpolar, behave in the same way

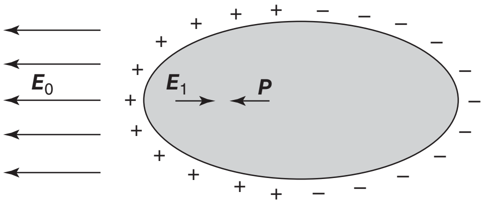

Figure 1.10 The depolarization field $\boldsymbol{E}_1$ is opposite to $\boldsymbol{P}$. The fictitious surface charges are indicated: the field of these charges is $\boldsymbol{E}_1$ within the ellipsoid.

under the influence of an external electric field. We can imagine that these dipoles in the applied electric field can have excess negative charges on one surface and positive charges on the opposite surface as shown in Figure 1.10.

These charges are not free, but each is bound to a molecule lying on or near the surface. The net charge per unit volume within the rest of the dielectric medium is zero. The electric field $\boldsymbol{E}_1$ set up by the induced charge always opposes the applied field $\boldsymbol{E}_0$. The resultant field $\boldsymbol{E}$ is the vector sum of these two. That is,

$$\boldsymbol{E} = \boldsymbol{E}_0 + \boldsymbol{E}_1 \tag{1.6}$$

The field $\boldsymbol{E}_1$ is called the *depolarization field*, for within the body, it tends to oppose the applied field $\boldsymbol{E}_0$ as shown in Figure 1.10. The resultant field $\boldsymbol{E}$ points to the same direction as $\boldsymbol{E}_0$ but is smaller in magnitude. This leads to the conclusion that if a dielectric is placed in an electric field, the induced surface charges appear, which tend to weaken the original field within the dielectric. Thus we can define the relative dielectric constant or relative permittivity ε as the ratio of the magnitude of the applied field $\boldsymbol{E}_0$ to the resultant field $\boldsymbol{E}$. Then,

$$\frac{\boldsymbol{E}_0}{\boldsymbol{E}} = \frac{V_0}{V} = \varepsilon \tag{1.7}$$

where V_0 is the potential difference without any medium and V is the same with a dielectric medium in between the capacitor plates.

Therefore, for same charges Q, the ratio of capacitance with dielectric C and capacitance without dielectric (for free space) C_0 will be

$$\frac{C}{C_0} = \frac{(Q/V)}{(Q/V_0)} = \frac{V_0}{V} = \frac{\boldsymbol{E}_0}{\boldsymbol{E}} = \varepsilon \tag{1.8}$$

From the given definition of ε, the dielectric constant or permittivity for free space is unity. Obviously ε is a dimensionless quantity.

1.4.4 Capacitance of a Parallel Plate Capacitor

If a constant voltage V_0 is applied to a plane condenser with a vacuum capacity C_0, a charge Q of density $\sigma = Q/A$ is set up on the condenser with area A and distance of separation d between the plates (Figure 1.10). From the application of Gauss's law, we know that the electric field intensity between two plates with a vacuum is $E = \sigma/\varepsilon_0$.

The potential difference V_0 is the work done in carrying a unit charge from one plate to the other. Hence

$$V_0 = Ed = \left(\frac{\sigma}{\varepsilon_0}\right) d = \left(\frac{Qd}{\varepsilon_0 A}\right) \tag{1.9}$$

Rearranging the relation (1.9), we can write

$$\frac{Q}{V_0} = \left(\frac{\varepsilon_0 A}{d}\right) \tag{1.10}$$

The capacitance C_0 can be written as

$$C_0 = \frac{Q}{V_0} = \left(\frac{\varepsilon_0 A}{d}\right) \tag{1.11}$$

We already know that for same charges Q, the ratio of capacitance with dielectric C and without dielectric (for free space) C_0 is

$$\frac{C}{C_0} = \varepsilon \tag{1.12}$$

Rearranging relations (1.11) and (1.12), we can write

$$C = \varepsilon C_0 = \varepsilon\varepsilon_0 \left(\frac{A}{d}\right) \tag{1.13}$$

Relation (1.13) can be expressed in the rationalized form in the SI system by the formula

$$C = \varepsilon C_0 = \varepsilon\varepsilon_0 \left(\frac{A}{d}\right) = \varepsilon(8.854 \times 10^{-12}) \left(\frac{A}{d}\right) F \tag{1.14}$$

where d is in meters and A in square meters. Normalized units in the *cgs* electrostatic system can be expressed by the formula

$$C = \varepsilon \left(\frac{1}{4\pi}\right) \left(\frac{A}{d}\right) \text{cm} \tag{1.15}$$

where d is in centimeters and A in square centimeters.

1.4.5 Local Field in a Dielectric

We now develop an expression for the local field at a general lattice site, not necessarily of cubic symmetry. To evaluate E_{loc}, we must calculate the total field acting on a certain typical dipole, this field being due to the external field as well as all *other* dipoles in the system. This was done by Lorentz as follows: the dipole is imagined to be surrounded by a spherical cavity whose radius R is sufficiently large that the matrix lying outside it may be treated as a continuous medium as far as the dipole is concerned (Figure 1.11a). The interaction of our dipole with the other dipoles lying inside the cavity is, however, to be treated microscopically, which is necessary since the discrete nature of the medium very close to the dipoles should be taken into account. The local field, acting on the central dipole, is thus given by the sum

$$E_{\text{loc}} = \boldsymbol{E}_0 + \boldsymbol{E}_1 + \boldsymbol{E}_2 + \boldsymbol{E}_3 \tag{1.16}$$

where $\boldsymbol{E}_0$ is the external field; $\boldsymbol{E}_1$ is the depolarization field, that is, the field due to the polarization charges lying at the external surfaces of the sample; $\boldsymbol{E}_2$ is the field due to the polarization charges lying on the surface of the Lorentz sphere

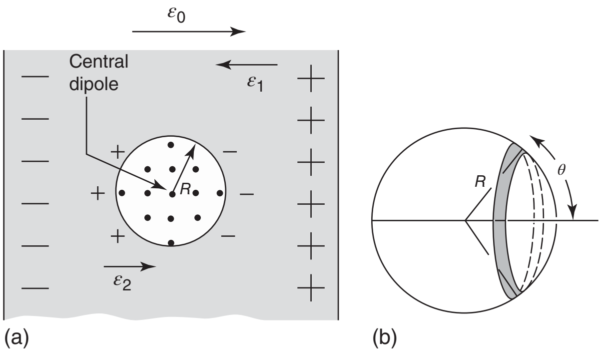

Figure 1.11 (a) The procedure for computing the local field. (b) The procedure for calculating $\boldsymbol{E}_2$, the field due to the polarization charge on the surface of the Lorentz sphere.

(Figure 1.11b), which is known as *Lorentz field*; and $\boldsymbol{E}_3$ is the field due to other dipoles lying within the sphere.

It is important to note that the part of the medium between the sphere and the external surface does not contribute anything since the volume polarization charges compensate each other, resulting in a zero net charge in this region. The contribution $\boldsymbol{E}_1 + \boldsymbol{E}_2 + \boldsymbol{E}_3$ to the local field is nothing but the total field at one atom caused by the dipole moments of all the other atoms in the specimen. Dipoles at distances greater than perhaps 10 lattice constants from the reference site make a smoothly varying contribution. It is convenient to let the interior surface be spherical.

1.4.5.1 Lorentz Field, E_2

The polarization charges on the surface of the Lorentz cavity may be considered as forming a continuous distribution. The field due to the charge at a point located at the center of the sphere is, according to Coulomb's law, given by

$$\boldsymbol{E}_2 = \frac{4\pi}{3}\boldsymbol{P} \tag{1.17}$$

1.4.5.2 Field of Dipoles inside Cavity, E_3

The field $\boldsymbol{E}_3$ due to the dipoles within the spherical cavity is the only term that depends on the crystal structure. For a reference site with cubic surroundings in a sphere, $E_3 = 0$ if all the atoms may be replaced by point dipoles parallel to each other. The total local field at a cubic site is then

$$\boldsymbol{E}_{\text{loc}} = \boldsymbol{E}_0 + \boldsymbol{E}_1 + \frac{4\pi}{3}\boldsymbol{P} = \boldsymbol{E} + \frac{4\pi}{3}\boldsymbol{P} \tag{1.18}$$

This is known as *the Lorentz relation*: the field acting at an atom in a cubic site is the macroscopic field $\boldsymbol{E}$ of plus $4\pi\boldsymbol{P}/3$ from the polarization of the other atoms in the specimen.

1.4.6 Molecular Description of Polarization

The interpretation of the polarization vector $\boldsymbol{P}$ describing the electric field inside a dielectric as an electric dipole for unit volume enables us to progress from the macroscopic to a molecular description of the dielectric. In the molecular concept, the resulting dipole moment $\boldsymbol{p}$ of a unit volume of a dielectric is set up by composing the elementary dipole moments of the smallest aggregates forming the elementary dipoles, which are called *molecules of a dielectric.*

The elementary dipole moment of a molecule $\boldsymbol{p}$ of a dielectric is thus proportional to the intensity of the local field $\boldsymbol{E}_{\text{loc}}$ acting on the molecule:

$$\boldsymbol{p} = \alpha \boldsymbol{E}_{\text{loc}} \tag{1.19}$$

The constant of proportionality α is called the *molar polarizability.* For a nonspherical atom, α will be a tensor. The polarization of a crystal may be expressed approximately as the product of the polarizabilities of the atoms times the local electric field:

$$\boldsymbol{P} = \sum_i N_i \boldsymbol{p}_i = \sum_i N_i \alpha_i \boldsymbol{E}_{\text{loc}}(i) \tag{1.20}$$

where N_i is the concentration, α_i is the polarizability of atoms i, and $\boldsymbol{E}_{\text{loc}}(i)$ is the local field at atom sites i.

We want to relate the dielectric constant to the polarizabilities; the result will depend on the relation that holds between the macroscopic electric field and the local electric field. If the local field is given by the Lorentz relation (1.18), then

$$\boldsymbol{P} = \left(\sum_i N_i \alpha_i\right)\left(\boldsymbol{E} + \frac{4\pi}{3}\boldsymbol{P}\right) \tag{1.21}$$

The polarization is induced by electric field, and therefore it is a function of electric field. The relationship is written in the following way:

$$P = \chi \boldsymbol{E} \tag{1.22}$$

where χ is called the *dielectric susceptibility.* In general χ is a tensor and depends on the electric field. The dielectric constant ε of an isotropic or a cubic medium relative to vacuum is defined in terms of the macroscopic field $\boldsymbol{E}$:

$$\varepsilon = \frac{\boldsymbol{E} + 4\pi \boldsymbol{P}}{\boldsymbol{E}} = 1 + 4\pi\chi \tag{1.23}$$

We solve for $\boldsymbol{P}$ to find the susceptibility

$$\chi = \frac{\boldsymbol{P}}{\boldsymbol{E}} = \frac{\sum_i N_i \alpha_i}{1 - \frac{4\pi}{3}\sum_i N_i \alpha_i} \tag{1.24}$$

Using relation (1.23), we can then write the expression in terms of the dielectric constant:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3}\sum_i N_i \alpha_i \tag{1.25}$$

This is *the Clausius–Mossotti relation.* This relates the dielectric constant to the electronic polarizability but only for crystal structures for which the Lorentz local field (Eq. (1.18)) holds. Since $\varepsilon = n^2$, we can rewrite Eq. (1.25) in the form

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3}\sum_i N_i \alpha_i \tag{1.26}$$

This is the Lorentz–Lorenz equation. It connects the index of refraction with the polarizability.

1.4.7 Dielectrics Losses

When an electric field acts on any matter, the latter dissipates a certain quantity of electric energy that transforms into heat energy. This phenomenon is known as the *loss of power*, meaning an average electric power dissipated in matter during a certain interval of time. As a rule, the loss of power in a specimen of a material is directly proportional to the square of the electric voltage applied to the specimen.

If a metal conductor is first connected to direct voltage and then to alternating voltage, the acting magnitude of which is equal to direct voltage, the loss of power P in watts will be the same in both cases in conformity with the Joule–Lenz law and equal to

$$P = \frac{V^2}{R} \tag{1.27}$$

where V is the voltage in volts and R is the resistance of the conductor in ohms.

As distinct from conductors, most of the dielectrics display a characteristic feature: under a given voltage, the dissipation of power in the dielectrics depends on the voltage frequency; the expense of power at an alternating voltage is markedly higher than at a direct voltage, rapidly grows with an increase in frequency, voltage, and capacitance, and also depends on the material of the dielectric.

The power losses in a dielectric under the action of the voltage applied to it are commonly known as *dielectric losses*. This is the general term determining the loss of power in an electrical insulation both at a direct and an alternating voltage. Dielectric losses at a direct voltage can be found from relation (1.27) where R stands for the resistance of the insulation, while the losses under the alternating voltage are determined by more intricate regularities. Actually the dielectric losses mean the losses of power under an alternating voltage.

1.4.7.1 Dielectric Loss Angle

The phase diagram of currents and voltages in a capacitor energized by an alternating voltage is shown in Figure 1.12. If the power were not dissipated at all in the dielectric of the capacitor (ideal dielectric), the phase of current I through the capacitor would be ahead of the phase of voltage V by 90° and the current

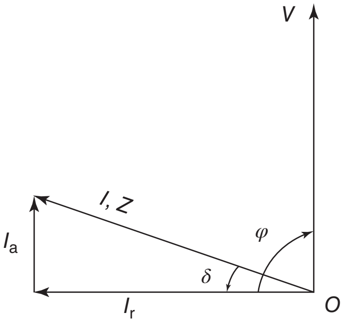

Figure 1.12 Phase diagram of current and voltage in a capacitor with a dielectric material.

would be purely reactive. In actual fact, the phase angle φ is slightly less than 90°. The total current I through the capacitor can be resolved into two components – active I_a and reactive I_r currents.

Thus, the phase angle describes a capacitor from the viewpoint of losses in a dielectric. Since the phase angle φ is very close to 90° in a capacitor with a high-quality dielectric, the angle δ (i.e., $\delta = 90° - \varphi$) is a more descriptive parameter, which is called the *dielectric loss angle*. The tangent of the angle is equal to the ratio of the active currents to the reactive currents:

$$\tan\delta = I_\mathrm{q}/I_r \tag{1.28}$$

or the ratio of active power P (power loss) to the reactive power P_r:

$$\tan\delta = P/P_\mathrm{r} \tag{1.29}$$

The dielectric loss angle is an important parameter for the dielectric materials. This parameter is usually described by the loss tangent $\tan\delta$. Sometimes the quality factor of an insulation portion is determined, that is, the value reciprocal of the loss tangent:

$$Q = \frac{1}{\tan\delta} = \tan\varphi \tag{1.30}$$

The values of $\tan\delta$ for the best electrical insulating materials employed in high-frequency and high-voltage engineering practice are of the order of thousands and even tenths of thousands of fractions.

1.4.7.2 Total and Specific Dielectric Losses

The value of dielectric losses P in an insulating material having a capacitance C is described from relation (1.27) as

$$P = VI_\mathrm{a} = VI_\mathrm{r}\tan\delta$$

Inserting the intensity of the capacitive current through an insulation portion with a capacitance of C,

$$I_\mathrm{r} = V\omega C \tag{1.31}$$

Since $\omega = 2\pi f$, the angular frequency, the dielectric losses P can be expressed as

$$P = V^2\omega C\tan\delta = 2\pi fCV^2\tan\delta \tag{1.32}$$

Inserting the value of effective length $\Lambda = A/d$ in Eq. (1.32) and replacing ε_0 by its numerical value

$$\varepsilon_0 \approx \frac{10^{-9}}{36\pi}\ F/m$$

the expression of dielectric losses can be formulated as

$$P = 5.56\times 10^{-11} V^2 f\Lambda\varepsilon\ \tan\delta \tag{1.33}$$

Formulas (1.32) and (1.33) have a broad field of application. They hold for any size and shape of an insulated portion.

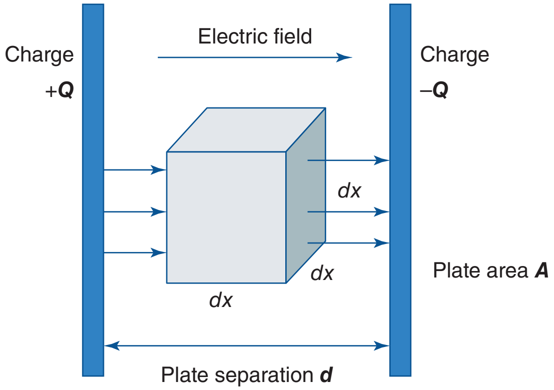

Figure 1.13 Electric field pierces a cube with edge *dx* in an insulated portion.

The knowledge of total amount of dielectric losses in the insulated portion is not enough, and it is necessary to study the distribution of dielectric losses at the separate points of insulation. Let us consider a cube with edge dx inside the insulated portion in which we are interested so that the lines of forces pierce the cube entering and leaving it through two opposite faces in the direction perpendicular to these faces (Figure 1.13).

The capacitance of the capacitor formed by the cube, according to relation (1.13) with $d = dx$ and $A = (dx)^2$, is

$$C = \varepsilon\varepsilon_0 \left(\frac{A}{d}\right) = \varepsilon\varepsilon_0 dx$$

and the voltage across the cube is $V = E\,dx$. Inserting these values into Eq. (1.32), we get

$$dP = E^2\omega\varepsilon_0\varepsilon\ \tan\delta\ (dx)^3 \tag{1.34}$$

where the specific dielectric losses are the losses per unit volume of the dielectric:

$$p = \frac{dP}{dV} = \frac{dP}{(dx)^3}$$

where $V = (dx)^3$ is the volume of the cube. So, the specific dielectric losses p are expressed as

$$p = E^2\omega\varepsilon_0\varepsilon\ \tan\delta \tag{1.35}$$

Now substituting $\omega = 2\pi f$ and replacing ε_0 by its numerical value in Eq. (1.35),

$$\varepsilon_0 \approx \frac{10^{-9}}{36\pi}\ F/m$$

We have the following expression for specific dielectric losses:

$$p = 5.56 \times 10^{-11} E^2 f \varepsilon\ \tan\delta \tag{1.36}$$

Formulas (1.35) and (1.36) are suitable for any pattern of field that possesses unlike properties at different places. The product $\varepsilon \tan\delta$ is called the *dielectric loss index (factor).*

1.4.8 Dielectrics Breakdown

At high electric fields, a material that is normally an electrical insulator may begin to conduct electricity – that is, it ceases to act as a dielectric. This phenomenon is known as *dielectric breakdown*. The mechanism behind dielectric breakdown can best be understood using band theory.

Essentially, there are two "bands" in every material that the electrons within the material may occupy – the valence band and the higher energy conduction band (Figure 1.14). Electrons in the valence band can be conducted as being bound in place, whereas electrons in the conduction band may act as mobile charge carriers. In dielectrics, the two bands are separated by a certain energy gap E_g, corresponding to the energies that are forbidden to the electrons. Since the valence band is lower in energy, electrons will preferentially occupy this band. Therefore, in a dielectric under normal conditions, the conduction band will be empty. If an electron in the valence band is supplied with energy greater than or equal to E_g, for example, from a high energy photon, it may be promoted to the conduction band.

An electric field of sufficient strength can supply enough energy to promote many electrons to the conduction band at once. Since electrons in the conduction band act as charge carriers, the material now conducts charge rather than storing it. For each material, there is a characteristic field strength needed to cause dielectric breakdown. This is referred to as the *breakdown field* or *dielectric strength*. Typically values of the dielectric strength lie in the range 10^6–10^9 V m^{-1}. The exact value of the dielectric strength depends on many factors – most obviously, the size of the energy gap but also the geometry and microstructure of the sample and the conditions it is subjected to.

The dielectric breakdown is associated with the formation in a dielectric crystal of a conducting path in which the current density is substantially higher than the average for the specimen. The Joule heat generated because of the high-density current in the path leads to the destruction of the material, including melting; the appearance of an air channel as a result of volatilization; and the extensive

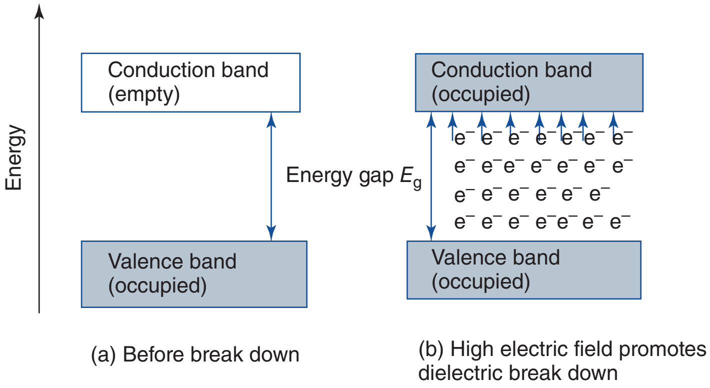

Figure 1.14 (a) Band structure before dielectric breakdown, and (b) band structure after dielectric breakdown.

formation of crystal defects or cracking. Thus, dielectric breakdown is an irreversible phenomenon. Dielectric breakdown is often associated with the failure of solid or liquid insulating materials used inside high-voltage transformers or capacitors in the electricity distribution grid, usually resulting in a short circuit or a blown fuse. It can also occur across the insulators that suspend overhead power lines, within underground power cables or lines arcing to nearby branches of trees.

2

Microscopic Properties of Materials

This chapter is an introduction to lattice vibrations – phonons – from a simple microscopic point of view. The basic principles can be set out within a model of a one-dimensional (1D) crystal.

2.1 Phonon

In condensed-matter physics, phonon is a unit of vibrational energy that arises from oscillating atoms within a crystal. Any solid crystal, such as ordinary table salt (sodium chloride), consists of atoms bound into a specific repeating three-dimensional spatial pattern called a *lattice*. Because the atoms behave as if they are connected by tiny springs, their own thermal energy or outside forces make the lattice vibrate. This generates mechanical waves that carry heat and sound through the material. A packet of these waves can travel throughout the crystal with a definite energy and momentum, so in quantum mechanical terms the waves can be treated as a particle, called a *phonon*. A phonon is a definite discrete unit or quantum of vibrational mechanical energy, just as a photon is a quantum of electromagnetic or light energy.

Phonons and electrons are the two main types of elementary particles or excitations in solids. Whereas electrons are responsible for the electrical properties of materials, phonons determine such parameters as the speed of sound within a material and how much heat it takes to change its temperature.

2.1.1 One-Dimensional Monatomic Chain

Our model consists of identical atoms connected by springs, shown in Figure 2.1. In equilibrium, the atoms are uniformly spaced at a distance a, and we now look for oscillations about the equilibrium position. We assume that the crystal is harmonic, so that the spring restoring force is linearly dependent upon the extension. Then, if we denote the displacement of the nth atom (which is at the point $r_n = n_\mathrm{a}$) to be u_n, its equation of motion is

$$m\frac{\partial^2 u_n}{\partial t^2} = K(u_{n+1} - u_n) + K(u_{n-1} - u_n) \tag{2.1}$$

Ferroelectrics: Principles and Applications, First Edition. Ashim Kumar Bain and Prem Chand.

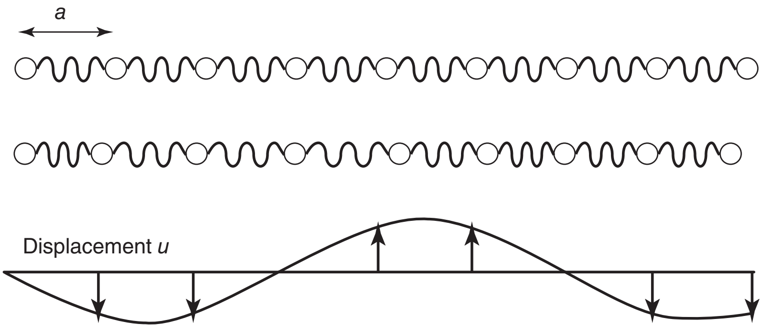

Figure 2.1 A one-dimensional linear chain. The atoms are shown in their equally spaced equilibrium conditions in the top row and with a periodic distortion below. The bottom figure plots the displacements u_n as arrows, and the curve shows how this is a sine wave of period $6a$ in this case. (Reproduced with permission of PB Littlewood and Premi Chandra.)

We guess that the solution is a wave of the form

$$u_n(t) = u_0 \cos[qr_n - \omega(q)t] \tag{2.2}$$

Here the wavelength of the wave is $\lambda = 2\pi/q$, and the period is $T = 2\pi/\omega(q)$; to check that this is a solution and to determine the frequency, we substitute it in the equation of motion. This is left as an exercise, and a few lines of algebra will show that the solution Eq. (2.2) exists, provided that

$$m\omega^2(q) = 2K[1 - \cos(q^a)] = 4K\sin^2\left(\frac{q^a}{2}\right) \tag{2.3}$$

so that

$$\omega(q) = 2\sqrt{\frac{K}{m}}\ \sin\left(\frac{q^a}{2}\right) \tag{2.4}$$

Equation (2.3) is called a *dispersion relation* – the relation between the frequency of the mode and its wave vector or equivalently the relationship between the wavelength and the period. The wave vector q is inversely related to the wavelength; note that for long-wavelength modes (i.e., $q \to 0$), the relationship is linear, namely,

$$\omega(q) = \sqrt{\frac{K}{m}}\,(q^a) \tag{2.5}$$

which is the same as for a wire with tension K_a and density $m/a.$ In the long-wavelength limit, we have compressive sound waves that travel with a velocity $v = a(K/m)^{1/2}$. Because this kind of wave behaves like a sound wave, it is generally called an *acoustic mode.*

The dispersion is not linear for larger values of q and is in fact periodic (Figure 2.2). The periodicity can easily be understood by reference to Eq. (2.2). Suppose we choose $q = 2\pi/a$. Note then that

$$qr_n = \frac{2\pi}{a} \times na = 2\pi n \tag{2.6}$$