CHAPTER 8 DIELECTRIC AND OPTICAL PROPERTIES OF SOLIDS

> *When life is true to the poles of nature, the streams of truth will roll through us in songs.*
>
> Ralph Waldo Emerson

8.1 INTRODUCTION

In this chapter we shall discuss dielectric and optical properties of solids and other phases of matter. These properties span an enormous range of frequencies, from the static to the ultraviolet region, and provide valuable information on the physical properties as well as the structure of matter.

After an elementary review, we shall relate the dielectric constant to the polarization properties of the molecules constituting a given substance. Then we shall consider the various sources of molecular polarization: dipolar, ionic, and electronic contributions. Finally we shall consider two important properties: piezoelectricity and ferroelectricity. Both are related to ionic polarizability.

8.2 REVIEW OF BASIC FORMULAS

Let us review some of the basic formulas which will be useful in the following sections. A concept most important in this chapter is that of the *electric dipole* and its *moment*. Think of an electric dipole as an entity composed of two opposite charges of equal magnitudes, q and $-q$, as in Fig. 8.1. The moment of this dipole is defined as

$$\mathbf{p} = q\mathbf{d}, \tag{8.1}$$

where $\mathbf{d}$ is the vector distance from the negative to the positive charge.† The electric moment is therefore equal to one of the charges times the distance between them.

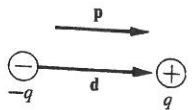

Fig. 8.1 An electric dipole.

An electric dipole produces an electric field, which may be calculated by applying Coulomb's law to find the fields of the two charges separately, and then adding the results. The field for the dipole is given by

$$\mathscr{E} = \frac{1}{4\pi\epsilon_0}\,\frac{3(\mathbf{p}\cdot\mathbf{r})\,\mathbf{r} - r^2\mathbf{p}}{r^5}, \tag{8.2}$$

which gives the field in terms of $\mathbf{r}$, the vector joining the dipole to the field point, and the moment $\mathbf{p}$. In deriving this expression, we have assumed that $r \gg d$, that is, expression (8.2) is valid only at points far from the dipole itself. In atoms and molecules this condition is well satisfied, since d, being of the order of an atomic diameter, is very small indeed.

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† Using the symbol $\mathbf{p}$ to denote the dipole moment should not lead to confusion with linear momentum, denoted by the same symbol, since linear momentum does not enter into this chapter.

When a dipole is placed in an external electric field, it interacts with the field. The field exerts a torque on the dipole which is given by

$$\boldsymbol{\tau} = \mathbf{p} \times \mathscr{E}, \tag{8.3}$$

where $\mathscr{E}$ is the applied field (Fig. 8.2). The magnitude of the torque is $\tau = p\mathscr{E}\sin\theta$, where θ is the angle between the directions of the field and the moment, and the direction of $\boldsymbol{\tau}$ is such that it tends to bring the dipole into alignment with the field. This tendency toward alignment is a very important property, and one which we shall encounter repreatedly in subsequent discussions.

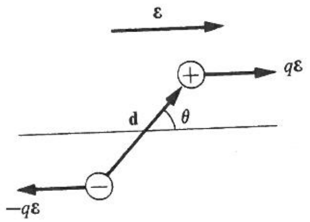

Fig. 8.2 The torque exerted on one dipole by an electric field. Vectors $q\mathscr{E}$ and $-q\mathscr{E}$ represent the two forces exerted by the field on the point charges of the dipole.

Another, and equivalent, way of expressing the interaction of the dipole with the field is in terms of the potential energy. This is given by

$$V = -\mathbf{p}\cdot\mathscr{E} = -p\mathscr{E}\cos\theta, \tag{8.4}$$

which is the potential energy of the dipole. We can see that the energy depends on θ, the angle of orientation, and varies between $-p\mathscr{E}$, when the dipole is aligned with the field, and $p\mathscr{E}$, when the dipole is opposite to the field. Because the energy is least when the dipole is parallel to the field, it follows that this is the most favored orientation, i.e., the dipole tends to align itself with the field. This is, of course, the same conclusion reached above on the basis of torque consideration.

In discussing dielectric materials, we usually talk about the *polarization* $\mathbf{P}$ of the material, which is defined as the dipole moment per unit volume. If the number of molecules per unit volume is N, and if each has a moment $\mathbf{p}$, it follows that the polarization is given by†

$$\mathbf{P} = N\mathbf{p}, \tag{8.5}$$

where we have assumed that all the molecular moments lie in the same direction.

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† In this chapter, the symbol N (not n) stands for the concentration, i.e. the number of entities (molecules, atoms, etc.) per unit volume.

When a medium is polarized, its electromagnetic properties change; this is expressed through the well-known equation

$$\mathbf{D} = \epsilon_0 \mathcal{E} + \mathbf{P}, \tag{8.6}$$

where $\mathbf{D}$ is the electric displacement vector and $\mathcal{E}$ the electric field in the medium.

It is also well known that the displacement vector $\mathbf{D}$ depends only on the *external* sources producing the external field, and is completely unaffected by the polarization of the medium.† It follows that the external field $\mathcal{E}_0$, that is, the field outside the dielectric, satisfies the relation

$$\mathbf{D} = \epsilon_0 \mathcal{E}_0. \tag{8.7}$$

When we compare this with (8.6), we find that

$$\mathcal{E} = \mathcal{E}_0 - \frac{1}{\epsilon_0}\mathbf{P}, \tag{8.8}$$

showing that the effect of the polarization is to modify the field inside the medium. In general, this results in a reduction of the field.

Equation (8.6) is usually rewritten in the form

$$\mathbf{D} = \epsilon \mathcal{E} = \epsilon_0 \epsilon_r \mathcal{E}, \tag{8.9}$$

where the *relative dielectric constant*

$$\epsilon_r = \epsilon/\epsilon_0 \tag{8.10}$$

expresses the properties of the medium. All the dielectric and optical characteristics of the substance are contained in this constant, and indeed much of this chapter is concerned with evaluating it under a variety of circumstances. Thus it follows that we can gain much information about a medium by measuring its dielectric constant. From this point on, we shall refer to the relative dielectric constant ϵ_r as simply the dielectric constant, since we rarely need to use the actual dielectric constant $\epsilon = \epsilon_0 \epsilon_r$.

Figure 8.3 shows a simple procedure for measuring dielectric constant. The plates of a capacitor are connected to a battery which charges the plates. When there is no dielectric inside the capacitor, the electric field produced by the charges is $\mathcal{E}_0$, which can be determined by measuring the potential difference V_0 across the capacitor, and using the relation

$$\mathcal{E}_0 = V_0/L, \tag{8.11}$$

where L is the distance between the plates. This relation should be familiar to the reader from his study of elementary physics. If a dielectric slab is now inserted between the plates, the field $\mathcal{E}_0$ induces the polarization of the medium—i.e., the lining up of the dipole moments along the field—which, in turn, modifies the field to a new value $\mathcal{E}$. This new field can be determined by measuring the new potential difference V by a voltmeter, and using the relation

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† See, for example, J. B. Marion (1965), *Classical Electromagnetic Radiation*, New York: Academic Press.

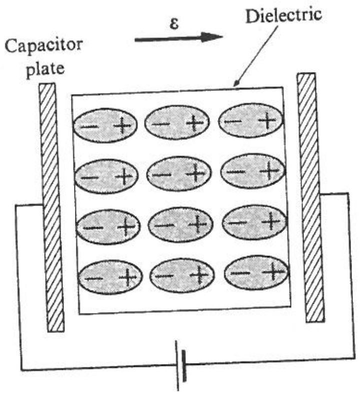

Fig. 8.3 Simple experimental setup for measuring dielectric constant. Note polarization of molecules in the solid.

$$\mathcal{E} = V/L. \tag{8.12}$$

The dielectric constant is given in terms of the fields $\mathcal{E}_0$ and $\mathcal{E}$ by the relation

$$\epsilon_r = \mathcal{E}_0/\mathcal{E}, \tag{8.13}$$

as can be seen by comparing (8.9) with (8.10). It follows, therefore, that

$$\epsilon_r = V_0/V, \tag{8.14}$$

where we used (8.11) and (8.12). We can thus obtain the dielectric constant by measuring the potential differences across the capacitor, with and without the presence of the dielectric, and taking their ratio.

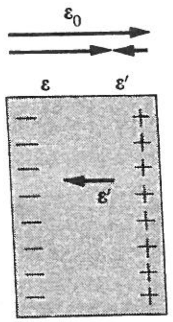

Fig. 8.4 The field $\mathcal{E}'$ due to polarization charges at the surfaces opposes external field $\mathcal{E}_0$. Resultant internal field is $\mathcal{E}$.

Figure 8.4 shows why the polarization of the medium reduces the electric field. The effect of the polarization produces net polarization charges situated at the faces of the dielectric, a positive charge on the right and a negative on the left. (The dipolar charges inside the medium cancel each other.) These charges create their own electric field which is directed to the left, and thus opposes the external field $\mathscr{E}_0$. When we add this polarization field to the external field $\mathscr{E}_0$, to obtain the resultant field $\mathscr{E}$, we find that $\mathscr{E} < \mathscr{E}_0$, as previously stated. When we combine this result with (8.12), we arrive at the useful conclusion that the dielectric constant of a medium is always larger than unity.[†]

8.3 THE DIELECTRIC CONSTANT AND POLARIZABILITY; THE LOCAL FIELD

Since the polarization of a medium—i.e., the alignment of the molecular moment—is produced by the field, it is plausible to assume that the molecular moment is proportional to the field. Thus we write

$$\mathbf{p} = \alpha\mathscr{E}, \tag{8.15}$$

where the constant α is called the *polarizability* of the molecule. The expression (8.15) is expected to hold good, except in circumstances in which the field becomes very large, in which case other terms must be added to (8.15) to form what is, in effect, a Taylor-series expansion of $\mathbf{p}$ in terms of $\mathscr{E}$. Equation (8.15) may be regarded as the first term in this expansion. (Higher-order terms lead to nonlinear effects.)

The polarization $\mathbf{P}$ can now be written as

$$\mathbf{P} = N\alpha\mathscr{E}, \tag{8.16}$$

which, when substituted into (8.6), yields

$$\mathbf{D} = \epsilon_0\mathscr{E} + N\alpha\mathscr{E} = \epsilon_0\left(1 + \frac{N\alpha}{\epsilon_0}\right)\mathscr{E}. \tag{8.17}$$

Comparing this result with (8.9), one finds

$$\epsilon_r = 1 + (N\alpha/\epsilon_0), \tag{8.18}$$

giving the dielectric constant in terms of the polarizability. This is a useful result in that it expresses the *macroscopic* quantity, ϵ_r, in terms of the *microscopic* quantity, α, thus forming a link between the two descriptions of dielectric materials.

The *electric susceptibility* χ of a medium is defined by the relation

$$\mathbf{P} = \epsilon_0\chi\mathscr{E}, \tag{8.19}$$

[†] This is not necessarily true at high frequencies (see Section 8.9).

which relates the polarization to the field. By comparing this equation with (8.16), we find that the susceptibility and polarizability are interrelated by

$$\chi = \frac{N\alpha}{\epsilon_0}, \tag{8.20}$$

and hence Eq. (8.18) may be written simply as

$$\epsilon_r = 1 + \chi. \tag{8.21}$$

Thus the departure of the dielectric constant from unity, the value for vacuum, is equal to the electric susceptibility.[†] (If several gaseous species are present, than the factor $N\alpha$ in (8.20) should be replaced by $\sum_i N_i\alpha_i$.)

Equation (8.18) may also be written in terms of the density of the medium by noting that $N = \rho N_A/M$, where ρ is the density, M the molar mass, and N_A Avogadro's number. Thus

$$\epsilon_r = 1 + (\rho N_A/\epsilon_0 M)\alpha. \tag{8.22}$$

This expression, indicating that ϵ_r increases linearly with density, holds in gases, in which density can be conveniently varied over a wide range. This fact lends support to the argument used in the derivation of (8.19), and in particular to (8.15).

Experiments do show, however, that Eqs. (8.18) or (8.22) do not hold well in liquids or solids, i.e., in condensed physical systems. This point is important to us here, as our primary interest lies in describing solid substances, and we must therefore seek a better expression for the dielectric constant than (8.18). The root of the difficulty lies in (8.15). It is implied here that the field acting on and polarizing the molecules is equal to the field $\mathscr{E}$, but a closer examination reveals that this is not necessarily so. If it develops that the polarizing field is indeed different from $\mathscr{E}$, relation (8.15) should then be replaced by

$$\mathbf{p} = \alpha\mathscr{E}_{\text{loc}}, \tag{8.23}$$

where $\mathscr{E}_{\text{loc}}$ is, by definition, the polarizing field—also called the *local field.*

To evaluate $\mathscr{E}_{\text{loc}}$ 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

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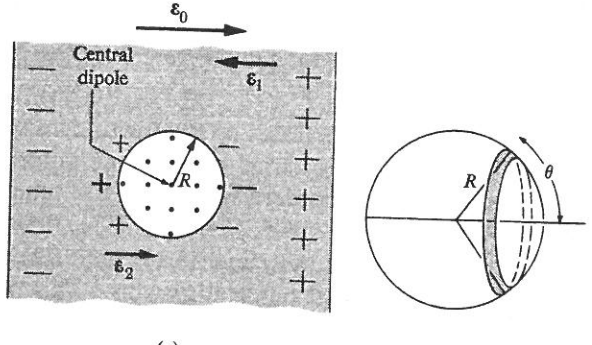
[†] Actual dielectric media are anisotropic, i.e., the value of ϵ_r, or χ, depends on the direction of the field. Thus the parameters ϵ_r and χ are tensor quantities of the second rank. In order to concentrate on the physical principles, we shall, however, ignore the anisotropy and regard the dielectric as an isotropic medium, in which case the dielectric constant is represented by a scalar, i.e., a single number.

concerned (Fig. 8.5). 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

$$\mathscr{E}_{\text{loc}} = \mathscr{E}_0 + \mathscr{E}_1 + \mathscr{E}_2 + \mathscr{E}_3, \tag{8.24}$$

where $\mathscr{E}_0$ is the external field, $\mathscr{E}_1$ the field due to the polarization charges lying at the external surfaces of the sample, $\mathscr{E}_2$ the field due to the polarization charges lying on the surface of the Lorentz sphere, and $\mathscr{E}_3$ the field due to other dipoles lying within the sphere. Note that the part of the medium between the sphere and the external surface does not contribute anything since, in effect, the volume polarization charges compensate each other, resulting in a zero net charge in this region.



(a) (b)

Fig. 8.5 (a) The procedure for computing the local field. (b) The procedure for calculating $\mathscr{E}_2$, the field due to the polarization charge on the surface of the Lorentz sphere.

Let us now evaluate the various fields which appeared above.

$\mathscr{E}_1$: This field, due to the polarization charges on the external surface, is also known as the *depolarization field*, since it is obviously opposed to the external field. The value of this field depends on the geometrical shape of the external surface, and for the simple case of an infinite slab is given by

$$\mathscr{E}_1 = -\frac{1}{\epsilon_0}\mathbf{P}, \tag{8.25}$$

which you may confirm by using Gauss' law. The depolarization fields for other geometrical shapes can be found in the references (Kittel, 1971), as well as in the problems.

$\mathscr{E}_2$: The polarization charges on the surface of the Lorentz cavity may be considered as forming a continuous distribution (recall that the cavity is large) whose density is $-P\cos\theta$. The field due to the charge at a point located at the center of the sphere is. according to Coulomb's law, given by

$$\mathscr{E}_2 = \int_0^{\pi}\left(-\frac{P\cos\theta}{4\pi\epsilon_0 R^2}\right)\cos\theta\,(2\pi R^2\sin\theta\,d\theta), \tag{8.26}$$

where the additional factor $\cos\theta$ is included because we are, in effect, evaluating only the component of the field along the direction of **P** (other components vanish by symmetry), and the factor $2\pi R^2\sin\theta\,d\theta$ is the surface element along the sphere (see Fig. 8.5b). Integration of (8.26) leads to the simple result

$$\mathscr{E}_2 = \frac{1}{3\epsilon_0}\mathbf{P}, \tag{8.27}$$

a field in the same direction as the external field.

$\mathscr{E}_3$: This field, which is due to other dipoles in the cavity, may be evaluated by summing the fields of the individual dipoles using (8.2). The result obtained depends on the crystal structure of the solid under consideration, but for the case of a cubic structure it may readily be shown that the sum vanishes. That is,

$$\mathscr{E}_3 = 0, \tag{8.28}$$

as the reader will be asked to show in the problem section. In other structures the dipolar field $\mathscr{E}_3$ may not vanish, and it should then be included in the rest of the discussion.

If the various fields are now substituted into (8.24), one finds that

$$\mathscr{E}_{\text{loc}} = \mathscr{E}_0 - \frac{2}{3\epsilon_0}\mathbf{P}, \tag{8.29}$$

which gives the polarizing field in terms of the external field and the polarization.

We may compare the value of $\mathscr{E}_{\text{loc}}$ obtained above with that of $\mathscr{E}$ in (8.8). We discover that

$$\mathscr{E}_{\text{loc}} = \mathscr{E} + \frac{1}{3\epsilon_0}\mathbf{P}, \tag{8.30}$$

which shows that $\mathscr{E}_{\text{loc}}$ is indeed different from $\mathscr{E}$, as we have suspected. The former field is, in fact, larger than the latter, so the molecules are more effectively polarized than our earlier discussions have indicated. Equation (8.30) is known as the *Lorentz relation*.

The difference between $\mathscr{E}$, which is known as the *Maxwell field*, and the Lorentz field $\mathscr{E}_{\text{loc}}$ may be explained as follows. The field $\mathscr{E}$ is a macroscopic quantity, and as such is an average field, the average being taken over a large number of molecules (Fig. 8.6). It is this field which enters into the Maxwell

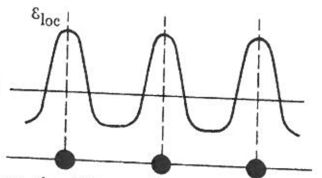


Fig. 8.6 The difference between the Maxwell field $\mathscr{E}$ and the local field $\mathscr{E}_{\text{loc}}$. Solid circles represent molecules.

equations, which, you will recall, are used for the macroscopic description of dielectric media. In the present situation the field $\mathscr{E}$ is a constant throughout the medium.

On the other hand, the Lorentz field $\mathscr{E}_{\text{loc}}$ is a *microscopic* field which fluctuates rapidly within the medium. As the figure indicates, this field is quite large at the molecular sites themselves, and hence the molecules are more effectively polarized than they would be in the average field $\mathscr{E}$.

Let us now evaluate the dielectric constant. The polarization, according to (8.23) and (8.16), is given by

$$\mathbf{P} = N\alpha\mathscr{E}_{\text{loc}}, \tag{8.31}$$

which, when used in conjunction with (8.30), yields

$$\mathbf{P} = \left(\frac{N\alpha}{1 - \dfrac{N\alpha}{3\epsilon_0}}\right)\mathscr{E}. \tag{8.32}$$

This relation between $\mathbf{P}$ and $\mathscr{E}$ supersedes the earlier one, (8.16), and we note the fact that the denominator being less than unity contributes to the enhancement of the polarization; the enhancement is due to the local field correction. When the result (8.32) is substituted into (8.16) and (8.17), one finds the following expression for the dielectric constant

$$\epsilon_r = \frac{1 + \dfrac{2}{3\epsilon_0}N\alpha}{1 - \dfrac{N\alpha}{3\epsilon_0}}, \tag{8.33}$$

which is the relation we have been seeking. It is the generalization of (8.18) when the local field correction is taken into account.

In gases, in which the molecular concentration N is small, the expression (8.33) reduces to the earlier (8.18) without the field correction. This can be seen by noting that $(N\alpha/3\epsilon_0) \ll 1$ in the denominator of (8.33), since N is small, so that one may expand this denominator in powers of $(N\alpha/3\epsilon_0)$, which in first order reduces precisely to (8.18). This is expected, of course, because for small N the polarization $\mathbf{P}$ is also small, which, according to (8.27), means that the local field becomes more or less the same as the average field. In liquids and solids, however, the polarization is no longer small, and Eq. (8.33) has a wider range of applicability.

Equation (8.30) is also frequently rewritten in the form

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N\alpha}{3\epsilon_0}, \tag{8.34}$$

which is referred to as the *Clausius–Mosotti relation*. We can also write this equation as

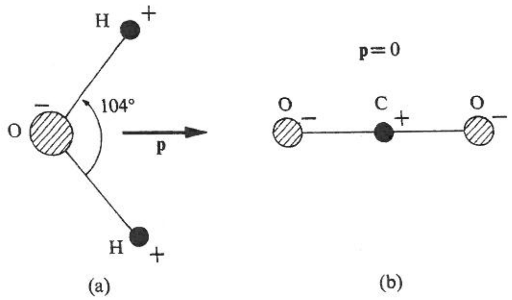
$$\frac{M}{\rho}\left(\frac{\epsilon_r - 1}{\epsilon_r + 2}\right) = \frac{N_A\alpha}{3\epsilon_0}, \tag{8.35}$$

which shows that the polarizability α may be determined from the measurable quantities M, ρ, and ϵ_r. The expression on the right (and on the left) is known as the *molar polarizability*.

8.4 SOURCES OF POLARIZABILITY

Let us now examine more closely the physical process which gives rise to polarizability. Basically, polarizability is a consequence of the fact that the molecules, which are the building blocks of all substances, are composed of both positive charges (nuclei) and negative charges (electrons). When a field acts on a molecule, the positive charges are displaced along the field, while the negative charges are displaced in a direction opposite to that of the field. The effect is therefore to pull the opposite charges apart, i.e., to polarize the molecule.

There are different types of polarization processes, depending on the structure of the molecules which constitute the solid. If the molecule has a *permanent moment*, i.e., a moment even in the absence of an electric field, we speak of a *dipolar* molecule, and a *dipolar* substance.



(a) (b)

Fig. 8.7 (a) The water molecule and its permanent moment. p = 1.9 debye units (1 debye = 10^{-29} coul·m). (b) CO_2 molecule.

An example of a dipolar molecule is the H_2O molecule in Fig. 8.7(a). The dipole moments of the two OH bonds add vectorially to give a nonvanishing net dipole moment. Some molecules are nondipolar, possessing no permanent moments; a common example is the CO_2 molecule in Fig. 8.7(b). The moments of the two CO bands cancel each other because of the rectilinear shape of the molecule, resulting in a zero net dipole moment.

The water molecule has a permanent moment because the two OH bands do not lie along the same straight line, as they do in the CO_2 molecule. The moment thus depends on the geometrical arrangement of the charges, and by measuring the moment one can therefore gain information concerning the structure of the molecule.

Despite the fact that the individual molecules in a dipolar substance have permanent moments, the net polarization vanishes in the absence of an external field because the molecular moments are randomly oriented, resulting in a complete cancellation of the polarization. When a field is applied to the substance, however, the molecular dipoles tend to align with the field, as stated in Section 8.2, and this results in a net nonvanishing polarization. This leads to the so-called *dipolar polarizability* which will be evaluated in Section 8.5.

If the molecule contains ionic bonds, then the field tends to stretch the lengths of these bonds. This occurs in NaCl, for instance, because the field tends to displace the positive ion Na^+ to the right (see Fig. 8.8), and the negative ion Cl^- to the left, resulting in a stretching in the length of the bond. The effect of this change in length is to produce a net dipole moment in the unit cell where previously there was none. Since the polarization here is due to the relative displacements of oppositely charged ions, we speak of *ionic polarizability*.

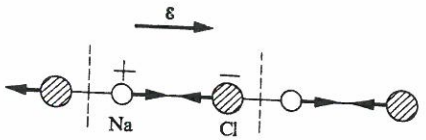


Fig. 8.8 Ionic polarization in NaCl. The field displaces the ions Na^+ and Cl^- in opposite directions, changing the length of the bond.

Ionic polarizability exists whenever the substance is either ionic, as in NaCl, or dipolar, as in H_2O, because in each of these classes there are ionic bonds present. But in substances in which such bonds are missing—such as Si and Ge—ionic polarizability is absent.

The third type of polarizability arises because the individual ions or atoms in a molecule are themselves polarized by the field. In the case of NaCl, each of the Na^+ and Cl^- ions are polarized. Thus the Na^+ ion is polarized because the electrons in its various shells are displaced to the left relative to the nucleus, as shown in Fig. 8.9. We are clearly speaking here of *electronic polarizability*.

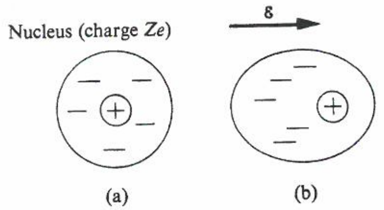


Fig. 8.9 Electronic polarization. (a) Unpolarized atom. (b) Atom polarized as a result of the field.

Electronic polarizability arises even in the case of a neutral atom, again because of the relative displacement of the orbital electrons.

In general, therefore, we may write for the total polarizability

$$\alpha = \alpha_e + \alpha_i + \alpha_d, \tag{8.36}$$

which is the sum of the various contributions; α_e, α_i, and α_d are the electronic, ionic, and dipolar polarizabilities, respectively. The electronic contribution is present in any type of substance, but the presence of the other two terms depends on the material under consideration. Thus the term α_i is present in ionic substances, while in a dipolar substance all three contributions are present. In covalent crystals such as Si and Ge, which are nonionic and nondipolar, the polarizability is entirely electronic in nature.

The relative magnitudes of the various contributions in (8.36) are such that in nondipolar, ionic substances the electronic part is often of the same order as the ionic. In dipolar substances, however, the greatest contribution comes from the dipolar part. This is the case for water, as we shall see.

The various polarizabilities may be segregated from each other because each contribution has its own characteristic features which distinguish it from the others, as we shall see in the remainder of this chapter. Dipolar polarizability, for instance, exhibits strong dependence on temperature, while the other two contributions are essentially temperature independent.

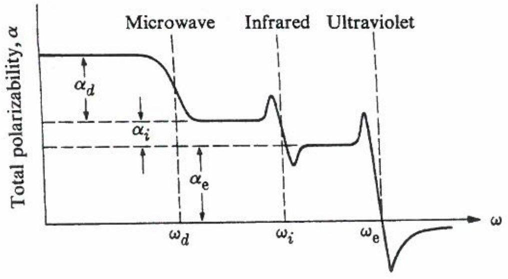


Fig. 8.10 Total polarizability α versus frequency ω for a dipolar substance.

Another important distinction between the various polarizabilities emerges when one examines the behavior of the ac polarizability that is induced by an alternating field. Figure 8.10 shows a typical dependence of this polarizability on frequency over a wide range, extending from the static all the way up to the ultraviolet region. It can be seen that in the range $\omega = 0$ to $\omega = \omega_d$, where ω_d (d for dipolar) is some frequency usually in the microwave region, the polarizability is essentially constant. In the neighborhood of ω_d, however, the polarizability decreases by a substantial amount. This amount corresponds precisely, in fact, to the dipolar contribution α_d. The reason for the disappearance of α_d in the frequency range $\omega > \omega_d$ is that the field now oscillates too rapidly for the dipole to follow, and so the dipoles remain essentially stationary.

The polarizability remains similarly unchanged in the frequency range ω_d to ω_i, and then plummets at the higher frequency. The frequency ω_i lies in the infrared region, and corresponds to the frequency of the transverse optical phonon in the crystal ω_t (Section 3.12). For the frequency range $\omega > \omega_t$, the ions with their heavy masses are no longer able to follow the very rapidly oscillating field, and consequently the ionic polarizibility α_i vanishes, as shown in Fig. 8.10.

Thus in the frequency range above the infrared, only the electronic polarizability remains effective, because the electrons, being very light, are still able to follow the field even at the high frequency. This range includes both the visible and ultraviolet regions. At still higher frequencies (above the electronic frequency ω_e), however, the electronic contribution vanishes because even the electrons are too heavy to follow the field with its very rapid oscillations.

We see, therefore, that the dielectric constant of a dipolar substance may decrease substantially as the frequency is increased from the static to the optical region. For example, the dielectric constant of water is 81 at zero frequency, while it is only 1.8 at optical frequencies.

The frequencies ω_d and ω_i, characterizing the dipolar and ionic polarizabilities, respectively, depend on the substance considered, and vary from one substance to another. However, their orders of magnitude remain in the regions indicated above, i.e., in the microwave and infrared, respectively. The various polarizabilities may thus be determined by measuring the substance at various appropriate frequencies.

Let us now evaluate the various polarizabilities, and show how measuring them may give us information about the internal microscopic structure of a given substance.

8.5 DIPOLAR POLARIZABILITY

We can obtain the expression for dipolar polarizability (also called *orientational polarizability*) by applying the basic formulas of Section 8.2 and some elementary statistical mechanics. Imagine that an electric field is applied to a dipolar system in which the dipoles are able to rotate freely, as in a gas or liquid. Before the field was applied, the dipoles were oriented randomly, resulting in a vanishing average polarization, but the presence of the field tends to align the dipoles, resulting in a net polarization in the direction of the field. It is this polarization that we wish to calculate.

Suppose the field is along the x-direction. The potential energy of the dipole is given, according to (8.4), by

$$V = -\mathbf{p}\cdot\mathscr{E} = -p\,\mathscr{E}\cos\theta, \tag{8.37}$$

where θ is the angle made by the dipole with the x-axis (Fig. 8.11). The dipole is no longer oriented randomly. The probability of finding it along the θ-direction is given by the distribution function

$$f = e^{-V/kT} = e^{p\mathscr{E}\cos\theta/kT}. \tag{8.38}$$

This expression is simply the Boltzmann factor, well known from statistical mechanics, with the potential energy being the orientational energy of (8.37). This distribution function, shown in Fig. 8.11(b), indicates that the dipole is more likely to lie along the field $\theta \simeq 0$ than in other directions, in agreement with the picture developed previously.

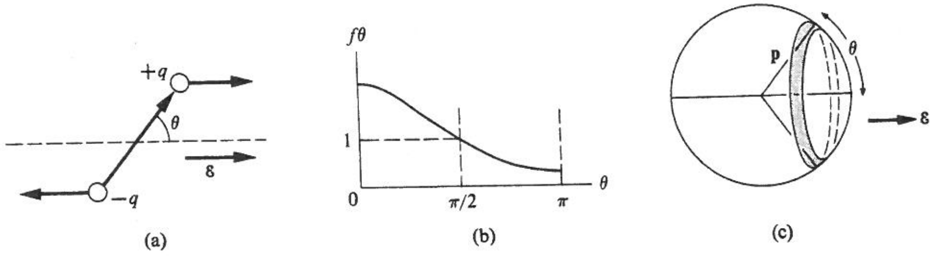


Fig. 8.11 (a) Aligning torque applied by the field to a dipole. (b) Distribution function $f(\theta)$ versus angle of orientation. (c) The integration over the solid angle defining the orientation of the dipole. Shaded area represents the element of the spherical shell specifying the orientation of the dipole.

The average value of p_x, the x-component of the dipole moment, is given by the expression

$$\bar{p}_x = \frac{\int p_x f(\theta)\,d\Omega}{\int f(\theta)\,d\Omega}, \tag{8.39}$$

where the integration is over the solid angle, whose element is $d\Omega$. By carrying out the integration over the whole solid angle range (Fig. 8.11c), we take into account all the possible orientations of the dipole. The function $f(\theta)$ is the distribution function of (8.38) with its dependence on θ indicated, and the denominator in (8.39) is included for a proper normalization of this distribution function. In evaluating expression (8.39), we use the formulas $p_x = p\cos\theta$, $d\Omega = 2\pi\sin\theta\,d\theta$

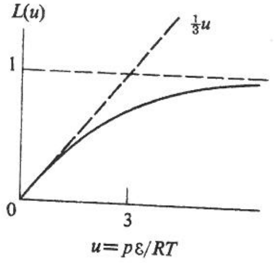


Fig. 8.12 The Langevin function $L(u)$ versus u.

(where the factor 2π arises from the integration over the azimuthal angle ϕ), $f(\theta)$ taken from (8.38), and the limits on the integrals $\theta = 0$ and $\theta = \pi$. Thus

$$\bar{p}_x = \int_0^\pi p \cos\theta \, e^{p\mathscr{E}\cos\theta/kT} \, 2\pi \sin\theta \, d\theta \bigg/ \int_0^\pi e^{p\mathscr{E}\cos\theta/kT} \, 2\pi \sin\theta \, d\theta,$$

which, when evaluated, yields†

$$\bar{p}_x = p\,L(u), \tag{8.40}$$

where

$$L(u) = \operatorname{Coth}(u) - \frac{1}{u} \quad \text{and} \quad u = \frac{p\mathscr{E}}{kT}. \tag{8.41}$$

The function $L(u)$, known as the *Langevin function*, is plotted in Fig. 8.12. Near the origin the function increases *linearly*, and one may show that $L(u) \simeq \frac{1}{3}u$. As u increases, the function continues to increase, monotonically, eventually saturating at the value unity as $u \to \infty$. The dipole moment $\bar{p}_x$, as a function of $p\mathscr{E}/kT$, has the same shape as Fig. 8.12, except for a change of the vertical scale by a constant p. Thus, for small values of the field, $\bar{p}_x$ increases linearly, while at very high field, $\bar{p}_x$ saturates at the maximum value p. This shows that at very high field the dipole points exactly along the field, which is a plausible result.

In most experimental situations, the ratio $u = p\mathscr{E}/kT$ is very small. For example, if we take $p \simeq 10^{-29}$ coul · m, $\mathscr{E} = 10^5$ V/m, and $T = 300$°K, we find $u \simeq 10^{-4}$, which is very small indeed compared with unity. Thus we may use the low-field approximation

$$\bar{p}_x = \frac{p^2}{3kT}\mathscr{E}. \tag{8.42}$$

---

† The evaluation of $\bar{p}_x$ is facilitated by noting the following point: If the integral in the denominator is denoted by Z, then it may be readily verified that the integral in the numerator is $[\partial/\partial(p\mathscr{E}/kT)]Z$. That is, the derivative of Z with respect to the quantity $p\mathscr{E}/kT$. Thus $\bar{p}_x = [\partial/\partial(p\mathscr{E}/kT)]Z/Z = [\partial/\partial(p\mathscr{E}/kT)] \log Z$. Therefore $\bar{p}_x$ may be evaluated by finding Z, taking its logarithm, and carrying out the indicated integration. The actual value one finds for Z is $4\pi \sinh(p\mathscr{E}/kT)/(p\mathscr{E}/kT)$.

That is, the net dipole moment is directly proportional to the field, and inversely proportional to the temperature.

The result (8.42) may also be obtained from the following physical argument. As we know, the effect of a field is to align the dipoles, whereas the effect of temperature is to oppose this and to randomize the direction of the dipoles. Therefore one may write

$$\bar{p}_x = p\,\frac{\text{orientational energy}}{\text{thermal energy}}.$$

If we substitute the values orientational energy $= p\mathscr{E}$ and thermal energy $\simeq kT$, we obtain

$$\bar{p}_x = p\frac{p\mathscr{E}}{kT} = \frac{p^2\mathscr{E}}{kT},$$

which is the same as (8.42), except for the numerical factor $\frac{1}{3}$, which is of the order of unity. We see therefore that at low field orientational energy is much less than thermal energy, and consequently the net dipole moment $\bar{p}_x$ is only a small fraction of its maximum value p. On the other hand, at high field, orientational energy dominates thermal energy, and consequently the net moment $\bar{p}_x$ is very close to its maximum value, that is, $\bar{p}_x \simeq p$.

Dipolar polarizability, on the basis of (8.42), is given by

$$\alpha_d = \frac{p^2}{3kT}. \tag{8.43}$$

When this is substituted into the Clausius-Mosotti relation (8.35), one finds that

$$\frac{M}{\rho}\left(\frac{\epsilon_r - 1}{\epsilon_r + 2}\right) = \frac{N_{\mathrm{A}}}{3\epsilon_0}\left(\alpha_{ei} + \frac{p^2}{3kT}\right), \tag{8.44}$$

where α_{ei} is the combined polarizability due to both electronic and ionic contributions. This polarizability is essentially temperature independent, as we shall see in later sections.

If we plot the molar polarizability $(M/\rho)[(\epsilon_r - 1)/(\epsilon_r + 2)]$ versus the inverse temperature, $1/T$, we should obtain a straight line the slope of which is proportional to p^2, and its intercept should be proportional to α_{ei}. This graph therefore leads to the determination of both the molecular dipole moment and the nondipolar polarizability, both of which are very useful quantities.

Such a plot is shown in Fig. 8.13 for several gaseous substances. We can see that the linear behavior predicted by (8.44) is borne out experimentally.

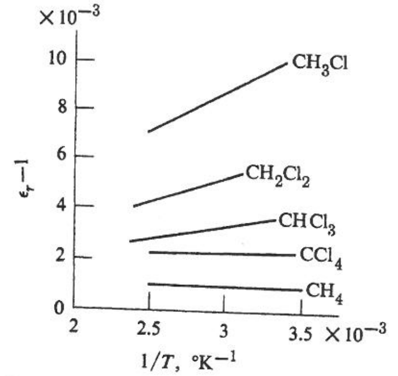


Fig. 8.13 Total susceptibility $\chi = \epsilon_r - 1$ versus $1/T$ for several gaseous substances. (Note that denominator on left side of Eq. (8.44) is $\epsilon_r + 2 \simeq 3$ for these gaseous materials.)

The graph indicates that the molecules CH_3Cl, CH_2Cl_2, and $CHCl_3$ are all dipolar, while the molecules CCl_4 and CH_4, whose graphs are horizontal, are nonpolar (no permanent moment). Indeed it is easy to understand why the methane molecule CH_4 is nondipolar. Its structure, as shown in Fig. 8.14, is such that the hydrogen atoms are located at the corners of a regular tetrahedron, with the carbon atom at the center. There are four bonds joining the carbon to each of the hydrogen atoms, and although each of these bonds has an electric moment, the total dipole moment of the molecule vanishes because of the symmetric arrangement of the bonds. Note, however, that when one of the hydrogen atoms is replaced by a chlorine atom, the resulting CH_3Cl molecule, no longer symmetrical, acquires a permanent moment, in agreement with Fig. 8.13.

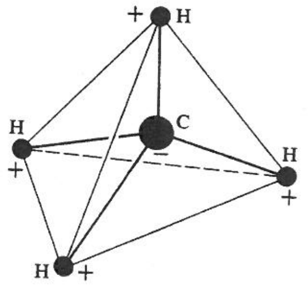


Fig. 8.14 Geometrical structure of the methane molecule (CH_4).

Table 8.1 gives dipole moments for various molecules, measured in the manner indicated above. The moments are expressed in terms of the *Debye unit*, which is equal to 10^{-29} coul · m. This convenient microscopic unit corresponds to a dipole of charge $q = 10^{-19}$ coul ($= e/1.6$) and length 10^{-10} m ($= 1$ Å). Since the distances encountered in molecules are of the order of angstroms, and the charges of the order of e, the moments encountered are of the order of the Debye unit.

Table 8.1

Permanent Dipole Moments of Some Dipolar Molecules

Substance	Dipole moment, debyes	Substance	Dipole moment, debyes
HF	1.91	NH_3	1.5
HCl	1.1	CH_3Cl	1.97
HBr	0.8	CH_2Cl	1.59
HI	0.38	$CHCl_3$	0.95
NO	0.1	H_2O	1.9
CO	0.1	H_2S	1.10
NaI	4.9	SO_2	1.6
KCl	6.3		

8.6 DIPOLAR DISPERSION

Let us now discuss ac dipolar polarizability. When an electric field oscillates, the dipoles in the system tend to follow the field, flipping back and forth as the field reverses its direction during each cycle. However, a dipole experiences some friction due to its collision with other molecules in the system. This means that some energy is absorbed from the field, and we speak of *dielectric loss*. This energy appears eventually in the form of heat, which raises the temperature of the substance. Therefore studying the ac polarizability and the dielectric loss gives information on the interaction between the molecules in the medium.

The equation we shall use to describe the motion of the dipolar polarization is

$$\frac{dp_d(t)}{dt} = \frac{1}{\tau}\left[p_{ds}(t) - p_d(t)\right], \qquad (8.45)$$

where $p_d(t)$ is the actual dipolar moment at the instant t, while $p_{ds}(t)$ is the saturated (or equilibrium) value of the moment, which would be the value approached by $p_d(t)$ if the field were to retain its instantaneous value for a long time. We have assumed that the rate of increase of $p_d(t)$ is proportional to the departure of this moment from its equilibrium value, and the quantity τ is called the *relaxation time*, also referred to as the *collision time*.

Let us illustrate the meaning of (8.45) in a very simple situation. Suppose that a static field is applied at the instant $t = 0$. In that case, $p_{ds}(t) = \alpha_d \mathscr{E} = p_0$ (p_0 is the permanent moment of the molecule), because this is the value reached

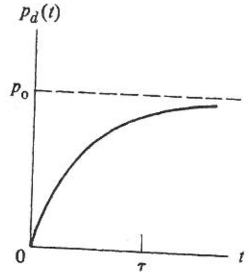


Fig. 8.15 Instantaneous dipole moment $p_d(t)$ versus time t in a static electric field.

by the moment long after the application of the field, where α_d is the static polarizability calculated in Section 8.5. Equation (8.45) now reduces to

$$\frac{dp_d}{dt} + \frac{p_d(t)}{\tau} = \frac{p_0}{\tau}, \tag{8.46}$$

which, as a first-order linear differential equation, can be readily solved, yielding

$$p_d(t) = p_0(1 - e^{-t/\tau}). \tag{8.47}$$

Thus the moment rises toward its equilibrium value in an exponential fashion (Fig. 8.15), much like the direct-current rise in an R–L electrical circuit (of time constant τ) when the battery has just been connected.

Suppose, on the other hand, that the medium has been placed in a static field for a sufficiently long interval for the moment to have achieved its equilibrium value p_0, and let this field be suddenly removed at $t = 0$. In applying (8.45), we now take $p_{ds} = 0$, since this is the equilibrium value, and the equation now leads to the solution

$$p_d(t) = p_0 e^{-t/\tau}, \tag{8.48}$$

showing that the moment *relaxes* to its equilibrium value of zero polarization exponentially, where the rate of relaxation is determined by the relaxation time τ. The situation is the same as that of the current decay in an R–L circuit, of time constant τ, when the switch has just been opened.

Let us now apply (8.45) to the case of an ac field

$$\mathcal{E}(t) = A\, e^{-i\omega t}. \tag{8.49}$$

The equilibrium moment is given by

$$p_{ds}(t) = \alpha_d(0)\mathcal{E}(t) = \alpha_d(0)A\, e^{-i\omega t}, \tag{8.50}$$

where $\alpha_d(0)$ is the static dipolar polarizability discussed in Section 8.5. Clearly the expression (8.50) is the value which would be reached by $p_d(t)$ if the field were

to remain equal to $\mathcal{E}(t)$ at all subsequent times (that is, for $t' > t$). Equation (8.45) now reduces to

$$\frac{dp_d(t)}{dt} + \frac{p_d(t)}{\tau} = \frac{\alpha_d(0)}{\tau}\mathcal{E}(t). \tag{8.51}$$

Since the driving term on the right is varying harmonically in time, as indicated by (8.49), we try a solution of the form

$$p_d(t) = \alpha_d(\omega)\mathcal{E}(t) = \alpha_d(\omega)A\, e^{-i\omega t}, \tag{8.52}$$

where $\alpha_d(\omega)$ is, by definition, the ac polarizability. When this is substituted into (8.51), one readily arrives at

$$\alpha_d(\omega) = \frac{\alpha_d(0)}{1 - i\omega\tau}. \tag{8.53}$$

It can be seen that the ac polarizability is now a complex quantity, indicating that the polarization is no longer in phase with the field. This gives rise to energy absorption, as we shall see shortly.

To derive the corresponding expression for the dielectric constant $\epsilon_r(\omega)$, we write

$$\epsilon_r(\omega) = 1 + \chi_e(\omega) + \chi_d(\omega),$$

where $\chi_e(\omega)$ and $\chi_d(\omega)$ are the electronic and dipolar susceptibilities, respectively. We have assumed for simplicity that the ionic contribution is sufficiently small to be negligible, and we have also ignored the local field correction, i.e., we have used (8.18). Now in the frequency region in which dipolar dispersion is significant—i.e., the microwave region—the electronic susceptibility is constant because the electrons, being so light, can respond to the field essentially instantaneously. We may therefore write the above equation as

$$\epsilon_r(\omega) = n^2 + \chi_d(\omega), \tag{8.54}$$

where $n^2 = 1 + \chi_e$ is the optical dielectric constant and n is the index of refraction.

The dipolar contribution $\chi_d(\omega) = \epsilon_r(\omega) - n^2$ does not follow the field instantaneously. There is a phase lag, as implied by the complex polarizability of (8.53). Since χ_d is proportional to α_d (see 8.20), it follows that $\chi_d(\omega)$ has the same complex form as $\alpha_d(\omega)$ in (8.53), and one may then write (8.54) in the form

$$\epsilon_r(\omega) = n^2 + \frac{\epsilon_r(0) - n^2}{1 - i\omega\tau}, \tag{8.55}$$

where the numerator on the right gives the static value of the dipolar susceptibility, that is, $\chi_d(0) = \epsilon_r(0) - n^2$. Equation (8.55) is the expression we have been seeking for the dielectric constant. This quantity is clearly frequency dependent, signifying that the medium exhibits *dispersion*.

This dielectric constant, being a complex quantity, can be written as

$$\epsilon_r(\omega) = \epsilon_r'(\omega) + i\epsilon_r''(\omega), \tag{8.56}$$

yielding for the real and imaginary parts

$$\epsilon_r'(\omega) = n^2 + \frac{\epsilon_r(0) - n^2}{1 + \omega^2\tau^2}, \tag{8.57a}$$

and

$$\epsilon_r''(\omega) = \frac{\epsilon_r(0) - n^2}{1 + \omega^2\tau^2}\,\omega\tau, \tag{8.57b}$$

which are known as *Debye's equations*.

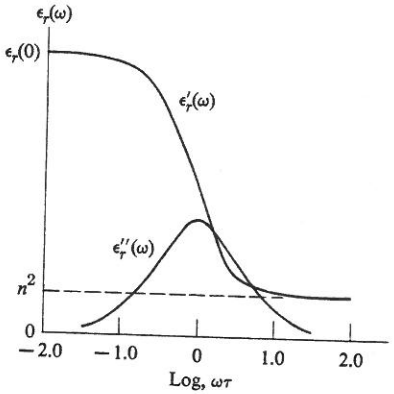


Fig. 8.16 Real and imaginary parts $\epsilon_r'(\omega)$ and $\epsilon_r''(\omega)$ versus log $(\omega\tau)$ for a dipolar substance.

Figure 8.16 plots the components of the dielectric constant versus log $\omega\tau$. Note that the real part $\epsilon_r'(\omega)$ is a constant, equal to $\epsilon_r(0)$ for all frequencies at which $\omega \ll 1/\tau$ (the quantity $1/\tau$ is often called the *collision frequency*), a frequency range which usually covers all frequencies up to the microwave region. As the frequency increases to such an extent that $\omega \gtrsim 1/\tau$, the real part $\epsilon_r'(\omega)$ decreases, and eventually reaches the value n^2, the high-frequency dielectric constant. This confirms the statements made in Section 8.5.

Figure 8.16 also shows that the imaginary part, $\epsilon_r''(\omega)$, achieves its maximum, equal to $(\epsilon_r(0) - n^2)/2$, at the frequency $\omega = 1/\tau$, and decreases as the frequency departs from this value in either direction. The curve decreases to half its maximum value when

$$\omega\tau = (1 + \omega^2\tau^2)/4,$$

which gives the frequencies $\omega = 0.27/\tau$ and $\omega = 3.73/\tau$, the two values corresponding respectively to the low and high frequencies of the $\epsilon_r''(\omega)$ curve. The function $\epsilon_r''(\omega)$ is appreciable over a frequency range of more than one order of magnitude, the range being centered around the collision frequency $1/\tau$.

The rate of energy loss in the system may be calculated as follows: The polarization current density is

$$J = \frac{dP}{dt}, \tag{8.58}$$

and therefore the rate of joule heating per unit volume is given by

$$Q = J\mathcal{E}. \tag{8.59}$$

The polarization vector is given in terms of the dielectric constant by the relation

$$\begin{aligned} P(t) &= \epsilon_0\,[\epsilon_r(\omega) - 1]\,\mathcal{E}(t) \\ &= \epsilon_0\,[(\epsilon_r'(\omega) - 1) + i\epsilon_r''(\omega)]\,\mathcal{E}(t), \end{aligned} \tag{8.60}$$

which can also be written as

$$P(t) = \epsilon_0\,\epsilon_r^*(\omega)\,e^{i\phi}\,\mathcal{E}(t), \tag{8.61}$$

where $\epsilon_r^*(\omega) = [(\epsilon_r(\omega) - 1)^2 + \epsilon_r''^2(\omega)]^{1/2}$ and ϕ is an angle given by

$$\tan\phi = \frac{\epsilon_r''(\omega)}{\epsilon_r'(\omega) - 1}. \tag{8.62}$$

It is evident from (8.61) that the polarization lags behind the field by an angle ϕ (recall that $\mathcal{E}(t) \sim e^{-i\omega t}$).

The density of the polarization current is now given according to (8.58) and (8.61) by

$$\begin{aligned} J &= -\,i\omega\epsilon_0\epsilon_r^*(\omega)\,e^{i\phi}\,\mathcal{E}(t) \\ &= \omega\epsilon_0\epsilon_r^*(\omega)\,e^{i(\phi-\pi/2)}\,\mathcal{E}(t), \end{aligned} \tag{8.63}$$

which precedes the field by a phase angle $\phi' = (-\phi + \pi/2)$. [Draw the figure.] If we now substitute this value into (8.59) and determine the time average, we obtain

$$\begin{aligned} Q &= \tfrac{1}{2}\,|J|\,|\mathcal{E}|\cos\phi' \\ &= \tfrac{1}{2}\,\epsilon_0\omega\epsilon_r^*(\omega)\sin\phi\,|\mathcal{E}|^2 \\ &= \tfrac{1}{2}\,\epsilon_0\omega\epsilon_r''(\omega)\,|\mathcal{E}|^2, \end{aligned} \tag{8.64}$$

where we have used (8.62) in the last equation. Note that the loss rate is proportional to $\omega\,\epsilon_r''(\omega)$, that is, essentially to $\epsilon_r''(\omega)$. Thus the loss rate is greatest near the collision frequency.

Measuring the dielectric constant enables us to determine the relaxation time, as we have just seen. This time depends on the interaction between the dipolar molecule and the fluid in which it rotates. Debye has shown that, when we treat the surrounding medium as a viscous fluid, the relaxation time for a spherical molecule is given by

$$\tau = \frac{4\pi\eta R^3}{kT}, \tag{8.65}$$

where η is the viscosity of the fluid and R the radius of the molecule. For water at room temperature, $\eta \simeq 0.01$ poise, $R \simeq 2$Å, leading to $\tau \simeq 2.5 \times 10^{-11}$s, in approximate agreement with experiment.

The time τ increases as the temperature is lowered both because of T in the denominator and because viscosity increases as temperature decreases. For example, the relaxation time in ice at -20°C is of the order of 10^{-7}s, which is five orders of magnitude greater than the value at room temperature. Table 8.2 lists relaxation times for a few simple liquids at room temperature.

Table 8.2

Relaxation Times at 20°C

Substance	τ
Water	9.5×10^{-11}
Alcohol	13
Chloroform	7.5
Acetone	0.33
Chlorobenzene	0.12
Toluene	0.75
t-butyl chloride	0.48

The relaxation times in solids are much longer than in liquids, because the dipoles in solids are more rigidly constrained against rotation, as we shall see in Section 8.7.

8.7 DIPOLAR POLARIZATION IN SOLIDS

We derived the result (8.43) for dipolar polarizability on the basis of a model in which the molecular dipole moment may rotate continuously and freely, except for occasional collisions with the surrounding medium. Such a model is applicable in gases and liquids, but not in solids, because in solids the molecular moment does not rotate freely. It is constrained to a few *discrete* orientations determined by the interaction of this dipole with neighboring ones. A dipole may

hop back and forth between these various discrete orientations in a manner which depends on the temperature and the electric field, but it is not *a priori* obvious that the resulting polarizability would be governed by an expression similar to (8.43). What is the actual behavior of the dipolar polarizability in a solid?

The answer depends on the particular solid and on the range of temperature. In some solids, dipolar moments seem indeed to be frozen in their orientations, and are unaffected by the field. In these solids, the dipolar polarizability vanishes altogether. In other solids, however, applying a field results in transitions between the orientations in such a manner as to result in a net polarization. One then often finds that the polarizability shows essentially the same behavior as (8.43).

Consider, for instance, the case of hydrogen sulfide (H_2S). The melting point of this substance is $T_m = 188$°K, yet, as Fig. 8.17 demonstrates, the dielectric constant continues to rise as the temperature is lowered, just as it does in the liquid state. The rise continues until a temperature $T_0 = 103$°K is reached, at which the dielectric constant drops appreciably, from 20 to 3. Below this it remains constant. Although for the low-temperature range $T < T_0$ the dipoles indeed seem to be frozen, in the intermediate range $T_0 < T < T_m$ the dipoles are able to polarize, even though the substance is in the solid state. It is this ability to polarize that we now wish to explore.

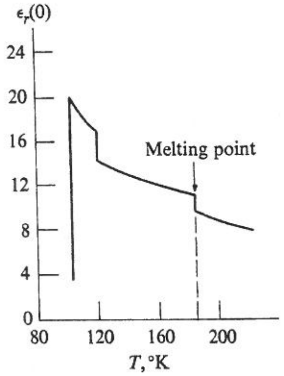


Fig. 8.17 Static dielectric constant $\epsilon_r(0)$ for H_2S versus temperature. [After Smyth and Walls]

Consider the following model which, despite its oversimplifications, illustrates the basic concepts involved. We assume that each dipole of the lattice has only two possible orientations, either to the right or to the left. The potential curve is shown in Fig. 8.18, in which the potential energy is plotted versus the orientation angle of a dipole. The bottom of the potential wells correspond to the two allowed orientations. Intermediate orientations are forbidden because of the high potential energy involved.

In the absence of an external field, the dipole is equally likely to point in the left or right direction, and as a result the net polarization is zero in this equilibrium situation. When a field is applied to the right, however, the well to the right is lowered by an amount $+p\mathscr{E}$, as shown by the dashed line in the figure, since it corresponds to a dipole orientation parallel to the field, that is, $\theta = 0$ in (8.5). At the same time, the well to the left is raised by an amount $p\mathscr{E}$, corresponding to $\theta = \pi$. The two wells are no longer equivalent, and since the left well is now higher, it is populated to a lesser extent than the right well. Hence the net polarization.

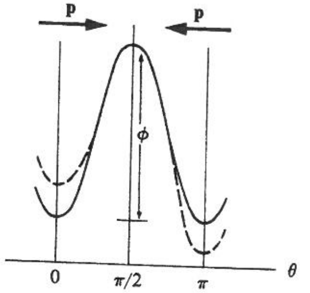


Fig. 8.18 Potential of a dipole in a solid versus orientation angle θ. The height of the barrier ϕ is called the activation energy. Solid curve represents the situation in absence of field; dashed curve the situation in presence of field.

When we denote the probability of the leftward orientation by w, it follows that

$$\frac{w}{1-w} = e^{-2p\mathscr{E}/kT}, \tag{8.66}$$

where the term on the right is the Boltzmann factor, corresponding to a potential difference $2p\mathscr{E}$ (note that $1 - w$ is the probability of the rightward orientation). Solving for w, we find that

$$w = \frac{e^{-2p\mathscr{E}/kT}}{1 + e^{-2p\mathscr{E}/kT}},$$

which, in the condition $p\mathscr{E} \ll kT$ which usually prevails, reduces to

$$w \simeq \tfrac{1}{2} e^{-2p\mathscr{E}/kT}. \tag{8.67}$$

The net moment along the field direction, the x-direction, is

$$\bar{p}_x = p(1 - w) - pw = p(1 - 2w), \tag{8.68}$$

which, by use of (8.67), leads to

$$\bar{p}_x = p(1 - e^{-2p\mathscr{E}/kT}). \tag{8.69}$$

If one expands the exponential in powers of the field, retaining terms up to the first power only, which is justified insofar as $p\mathscr{E} \ll kT$, one finds

$$p_x = \frac{2p^2\mathscr{E}}{kT}, \tag{8.70}$$

leading to a dipolar polarizability

$$\alpha_d = \frac{2p^2}{kT}. \tag{8.71}$$

This, except for a numerical factor, is of the same form as the result (8.43) obtained on the basis of the model of continuous rotation.

The two-orientation model explains, in principle at least, the decrease in dipolar polarizability with temperature in H_2S (Fig. 8.17). At low temperatures the field is able to orient all the dipoles to point to the right, but as the temperature increases the dipole can flip its orientation more readily (the necessary energy is supplied by thermal excitation), and the polarizability diminishes.

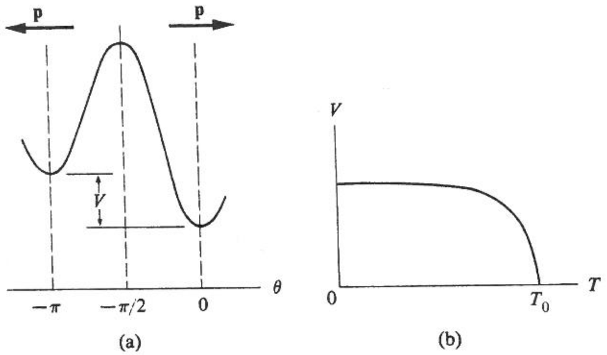


Fig. 8.19 (a) Potential energy versus orientation angle θ in an asymmetric potential barrier. (b) Variation of potential V with temperature.

The model we have used to describe the solid does not, however, explain the apparent freezing of the molecular dipoles for $T < T_0 = 103°\text{K}$ in Fig. 8.17, but this can be rectified by a slight change in the model. Suppose that the potential curve versus the orientation is as shown in Fig. 8.19(a). Here again the dipole has only two possible orientations, but the rightward orientation is favored because it is lower than the leftward by a potential V. If $V \gg kT$, then all the dipoles point to the right, in the absence of the field. Even when the field is applied, the dipoles remain frozen in their original orientation, unaffected by the field (unless the field is very strong).

To explain the behavior of H_2S, the potential must depend on the temperature in a manner somewhat like that shown in Fig. 8.19(b). The potential is large and constant at low temperature, but it vanishes as T approaches and passes T_0.† In this manner, polarization is inhibited below the transition temperature T_0, but it is allowed for the range $T > T_0$.

The model we used in connection with Fig. 8.18 may also be used to study dielectric dispersion in solids. Thus the *jumping frequency* ν may be written

$$\nu = \nu_D e^{-\phi/kT}, \tag{8.72}$$

where ν_D is of the order of the Debye frequency, $\nu_D \simeq 10^{13}$ Hz, and ϕ is the activation energy‡ (see Fig. 8.18). The relaxation time (the jumping period) is therefore

$$\tau \simeq \frac{1}{\nu_D} e^{\phi/kT}, \tag{8.73}$$

which is to be used in conjunction with the dispersion equations (8.57) to describe dispersion in solids.

8.8 IONIC POLARIZABILITY

We turn now to ionic polarizability. We discussed this subject in Section 3.12 in connection with the optical properties of lattice vibrations, and therefore we shall be content here with quoting the results of that section, and with a brief discussion of their relation to our present purpose. We found there that the frequency-dependent dielectric constant is given by

$$\epsilon_r(\omega) = \epsilon_r(\infty) + \frac{\epsilon_r(0) - \epsilon_r(\infty)}{1 - (\omega^2/\omega_t^2)}, \tag{8.74}$$

where ω_t is the frequency of the optical phonon and $\epsilon_r(0)$, $\epsilon_r(\infty)$ are, respectively, the static dielectric constant and the dielectric constant at high frequency $(\omega \gg \omega_t)$.

In (8.74) the first term on the right, $\epsilon_r(\infty)$, contains only the electronic polarizability, which is constant in the infrared region, where this expression is useful. The second term on the right is the ac polarizability, the quantity $[\epsilon_r(0) - \epsilon_r(\infty)]$ being the static ionic susceptibility, and the frequency dependence shown was derived in Section 3.12 from the equations of motion of the ions. We ignored the local field correction in (8.74), since in calculating the dielectric constant we have simply added the electronic and the ionic susceptibilities.

Equation (8.74) may also be rewritten in another form by recalling that $\epsilon_r(\infty) = n^2$, where n is the optical index of refraction, and the result is

$$\epsilon_r(\omega) = n^2 + \frac{\epsilon_r(0) - n^2}{1 - (\omega^2/\omega_t^2)}. \tag{8.75}$$

The dielectric constant $\epsilon_r(\omega)$ is plotted versus ω in Fig. 8.20. For $\omega \ll \omega_t$, $\epsilon_r(\omega) = \epsilon_r(0)$, the static dielectric constant, which is expected, since at low frequency the ions are able to respond to the ac field essentially instantaneously. However, in the range $\omega \gg \omega_t$, $\epsilon_r(\omega) \simeq n^2$; the ionic contribution has vanished because the field now oscillates too rapidly for the massive ions to follow.

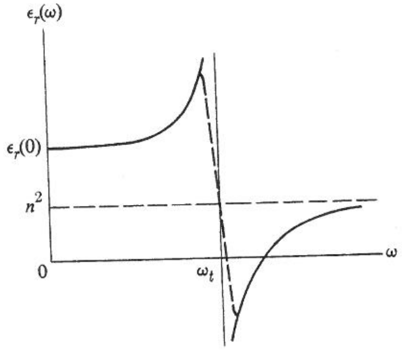


Fig. 8.20 Dielectric constant $\epsilon_r(\omega)$ versus ω, showing dispersion in infrared region due to optical phonons in an ionic crystal. Dashed curve indicates removal of divergence due to collisions of ions.

The optical dielectric constant n^2 may therefore be appreciably smaller than the static dielectric constant $\epsilon_r(0)$, due to the absence of the ionic contribution. In NaCl, for example, $n^2 = 2.25$, while $\epsilon_r(0) = 5.62$. Table 8.3 illustrates this point further for several alkali halide crystals.

Table 8.3

Static and Optical Dielectric Constants for Some Ionic Crystals

Substance	$\epsilon_r(0)$	$\epsilon_r(\infty) = n^2$
LiF	9.27	1.90
LiC	11.0	2.7
NaCl	5.62	2.32
KCl	4.64	2.17
RbCl	5.10	2.18

---

† The dependence of the potential on temperature, shown in this figure, is not as arbitrary (or strange) as it may seem at first. Actually this potential is a "cooperative" interaction, due to all the dipoles in the substance. As the temperature rises more and more dipoles are able to flip over, and there are fewer and fewer dipoles in the original orientation which produces the restraining potential.

‡ The exponential increase of γ with temperature, given in (8.72), is due to the fact that the dipole is able to flip only if the ion (or ions) involved has sufficient energy to go over the potential barrier ϕ in Fig. 8.18.

We note from Fig. 8.20 that the substance exhibits great dispersion near the optical phonon frequency ω_t. This leads to strong optical absorption and reflection in the infrared region, as discussed in Section 3.12.

We also observe from Fig. 8.20 that the dielectric constant diverges at $\omega = \omega_t$. This divergence is attributable to the ionic susceptibility, and is expected since, as the signal frequency becomes equal to the natural frequency of the system ω_t, a *resonance* condition is satisfied, and the response of the system becomes infinitely large. In practice such a divergence is not observed, of course, because of collisions experienced by the ions. These collisions arise from several mechanisms which cause scattering of the optical phonons in the crystal, e.g., anharmonic interaction, scattering by defects, etc., as discussed in Section 3.9. The effect of collision is to round off the dielectric constant, as indicated by the dashed line in Fig. 8.20, so that even though this constant is still quite large near the resonance frequency, the troublesome divergence has been removed.

8.9 ELECTRONIC POLARIZABILITY

Now that we have discussed dipolar and ionic polarizabilities, let us look at electronic polarizability and dispersion. We shall give a classical treatment first as a preliminary to the quantum discussion to follow.

Classical treatment

To find the static polarizability, we assume that the electrons form a uniform, negatively charged sphere surrounding the atom. It can be shown through the laws of electrostatics that when a field $\mathscr{E}$ is applied to this atom, the nucleus is displaced from the center of the sphere by a distance

$$x = \left(\frac{4\pi\epsilon_0 R^3}{Ze}\right)\mathscr{E}, \tag{8.76}$$

where R is the radius of the sphere (the atomic radius), and Ze the nuclear charge (see the problem section). The atom is thus polarized, and the dipole moment, $p = Zex$, yields the electronic polarizability

$$\alpha_e = 4\pi\epsilon_0 R^3. \tag{8.77}$$

If we substitute the typical value $R = 10^{-10}$ m, we find that $\alpha_e \simeq 10^{-41}$ farad · m^2, in an order of magnitude which has actual polarizabilities given in Table 8.4.

To find the ac polarizability, we assume that the electrons in the atom experience an elastic restoring force corresponding to a resonant frequency ω_0.†

---

† Although an electron interacts with a bare nucleus according to the Coulomb law, the classical screening of the nucleus by other electrons results in a harmonic-like force between the electron and the nucleus.

Table 8.4

Electronic Polarizabilities for Some Inert Gases and Closed-Shell Alkali and Halogenic Ions (in units of 10^{-40} farad m^2).

Inert gases		Alkali cores		Halogenic closed-shell	
He	0.18	Li^+	0.018	F^-	0.76
Ne	0.35	Na^+	0.20	Cl^-	2.65
Ar	1.74	K^+	0.86	Br^-	3.67
Kr	2.2	Rb^+	1.34	I^-	5.5
Xe	3.6	Cs^+	2.20		

When the ac field is polarized in the x-direction, the appropriate equation of motion for the electron is

$$m\frac{d^2x}{dt^2} + m\omega_0^2 x = -e\mathscr{E}. \tag{8.78}$$

Assuming an ac field $\mathscr{E} = \mathscr{E}_0 e^{-i\omega t}$, one can readily solve for x and the polarization. The polarizability is found to be

$$\alpha_e(\omega) = \frac{e^2/m}{\omega_0^2 - \omega^2}. \tag{8.79}$$

If there are Z electrons per atom and N atoms per unit volume, the resulting electric susceptibility is

$$\chi_e(\omega) = \frac{NZe^2/\epsilon_0 m}{\omega_0^2 - \omega^2}, \tag{8.80}$$

and the index of refraction is given by

$$n^2(\omega) = 1 + \frac{NZe^2/\epsilon_0 m}{\omega_0^2 - \omega^2}. \tag{8.81}$$

Figure 8.21 plots the function $n^2(\omega)$ versus ω, and shows strong dispersion at the resonance frequency ω_0. Such behavior is typical of all resonant systems, and reflects the strong interaction between the driving field and the system when the frequency-matching condition is satisfied, that is, when $\omega \simeq \omega_0$. The annoying divergence at $\omega = \omega_0$ can be removed by including a collision term in Eq. (8.78), as we did in Section 4.11. [Indeed, the results thus obtained should be the same as those in Section 4.11, if we set $\omega_0 = 0$, that is, if we treat the electrons as free particles.] Note that at high frequencies, that is, $\omega_0 \ll \omega$, $n^2(\omega) \to 1$, as for a vacuum, because at such high frequencies the electrons cannot follow the rapid oscillations of the field.

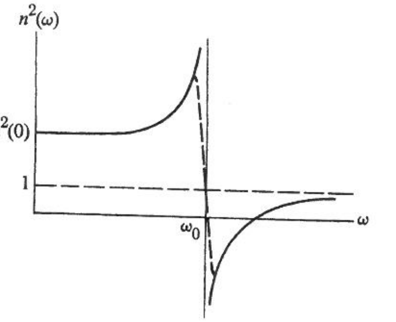


Fig. 8.21 Square of index of refraction $n^2(\omega)$ versus frequency, illustrating dispersion in ultraviolet region due to motion of electrons.

Quantum theory

The motion of an electron in an atom is governed by quantum laws, and hence an accurate treatment of electronic polarizability necessitates the use of quantum mechanics (a brief review of the subject is given in the Appendix). Suppose that the energy spectrum of an atom consists of two levels only, the ground state E_0 and the excited level E_1. It can then be shown (Van Vleck, 1932), that the electronic polarizability is given by

$$\alpha_e(\omega) = \frac{e^2}{m}\frac{f_{10}}{\omega_{10}^2 - \omega^2}, \tag{8.82}$$

where $\omega_{10} = (E_1 - E_0)/\hbar$, the Einstein frequency for the two levels, and f_{10} is a quantity expressing the coupling between the two wave functions ψ_0 and ψ_1 by the incident electric field; f_{10} is referred to as the *oscillator strength*, and is usually of the order of unity. Note that the quantum result (8.82) is quite similar to the classical expression (8.79). The static polarizability, $\alpha_e(0) = (e^2 f_{10}/m\omega_{10}^2)$ from (8.82), can also be similarly related to α_e of (8.77).

In an atom containing many excited levels, expression (8.82) is generalized to

$$\alpha_e(\omega) = \frac{e^2}{m}\sum_{j\neq 0}\frac{f_{j0}}{\omega_{j0}^2 - \omega^2}, \tag{8.83}$$

where $\omega_{j0} = (E_j - E_0)/\hbar$, and j refers to the j^{th} excited level. The system now has a number of resonance frequencies, and strong dispersion appears near each of them.

We can now see why $\alpha_e(\omega)$ is independent of temperature. Since $E_j - E_0$ is typically of the order of a few electron volts, the thermal energy kT is too small to excite the electrons to the higher levels; thus in the absence of the field the electrons all lie in the ground level, which is the level to be used as the initial state in (8.83).

Interband transition in solids

The expression (8.83) for $\alpha_e(\omega)$ is applicable to a single, isolated atom. It is thus useful in the dielectric treatment of gases, since a gas may be considered as an aggregate of independent atoms. However, the result (8.83) is not applicable to a solid, since a solid's energy spectrum consists of continuous bands rather than discrete levels, and the electron states are represented by delocalized Bloch functions (Section 5.2) rather than localized atomic orbitals.

The quantum treatment which led to (8.83) can also be modified to yield the appropriate expression for the case of a solid. It is convenient to begin the discussion with ϵ_r'', the imaginary component of the dielectric constant, which represents the absorption of the EM wave by the system, as discussed in Section 4.11. It can be shown (Greenway, 1968) that ϵ_r'' is given by

$$\epsilon_r''(\omega) = \frac{A}{\omega^2}\int ds \frac{f_{cv}(\mathbf{k})}{\nabla[E_c(\mathbf{k}) - E_v(\mathbf{k})]}, \tag{8.84}$$

where $E_v(\mathbf{k})$ and $E_c(\mathbf{k})$ are the energies of the valence and conduction bands, respectively, and $\mathbf{k}$ is the wave vector of the electron which absorbs the photon and transfers from the valence to the conduction band. The integral in (8.84) is over a surface contour in the Brillouin zone which conserves the energy

$$E_c(\mathbf{k}) - E_v(\mathbf{k}) = \hbar\omega. \tag{8.85}$$

[The momentum conservation is guaranteed because $\mathbf{k}$ has the same value in both bands, as shown in Eq. (8.84). The photon's momentum is negligibly small (Section 3.4).] The quantity $f_{cv}(\mathbf{k})$ is the band-to-band oscillator strength, as in Eq. (8.82).

Figure 8.22 illustrates the application of (8.84) to a direct-gap semiconductor. The integration region consists of a sphere surrounding the origin, part of which is shown in the figure. It can be shown (see the problem section) that $E_c(\mathbf{k}) - E_v(\mathbf{k}) = E_g + \hbar^2k^2/2\mu$, where E_g is the energy gap and $\mu = m_e m_h/(m_e + m_h)$ is the electron–hole reduced mass. Substituting this into (8.84), and carrying out the integration, one finds

$$\epsilon_r''(\omega) = \frac{B}{\omega^2}(\hbar\omega - E_g)^{1/2}, \tag{8.86}$$

where $B = \pi(2\mu/h^2)^{3/2} f_{cv} A$. This expression is valid for $E_g < \hbar\omega$ [$\epsilon_r''(\omega) = 0$ for $\hbar\omega < E_g$, as discussed in Section 6.12], and shows that $\epsilon_r''(\omega)$ increases parabolically with ω near the absorption edge; that is, $\epsilon_r''(\omega) \sim (\hbar\omega - E_g)^{1/2}$, as noted in Section 6.12.

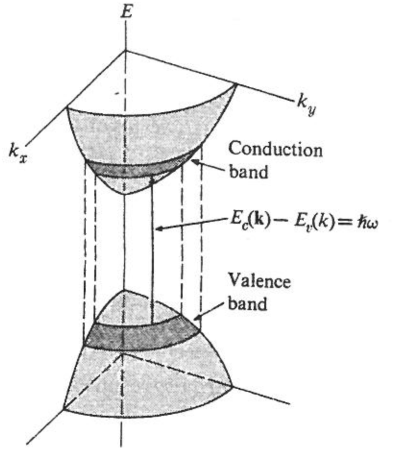


Fig. 8.22 The various states in **k**-space involved in the absorption process at light frequency ω.

When expression (8.84) is applied to bands of more complicated shapes, the integration may become exceedingly complex. In general, the integration contour is multiply connected, and consists of several distinct "pockets" in the Brillouin zone, each of which satisfies Eq. (8.85). But note also that the largest contribution comes from those points in the zone at which $E_c(\mathbf{k})$ and $E_v(\mathbf{k})$ have the same slope, because such points, known as the *critical points*, produce singularities in the integrand of Eq. (8.84).

Figure 8.23 shows $\epsilon_r''(\omega)$ for Ge, and correlates the various "shoulders" in the curve with the critical points responsible for the high absorption values. One can see that studies of optical absorption can be highly useful in the determination of band structure, and particularly in delineating the various critical points in the zone.

The real component of the dielectric constant $\epsilon_r'(\omega)$ describes the polarization aspects of the electronic system (Section 4.11). Although ϵ_r'' and ϵ_r' describe physically distinct phenomena, they are, in fact, mathematically related by an important theorem known as the *Kramers-Kronig relation* (Brown, 1967). In particular, the static dielectric constant may be written as

$$\epsilon_r(0) = \epsilon_r'(0) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\epsilon_r''(\omega)}{\omega}\, d\omega, \tag{8.87}$$

where P implies that the principal part of the integral is to be taken. Thus we may evaluate $\epsilon_r(0)$ by substituting $\epsilon_r''(\omega)$ from (8.84) and carrying out the frequency integration which illustrates that, like $\epsilon_r''(\omega)$, $\epsilon_r(0)$ is also directly dependent on the band structure of the solid. Note in particular that a significant correlation between $\epsilon_r(0)$ and the energy gap of the solid exists; since $\epsilon_r''(\omega) = 0$ for $\hbar\omega < E_g$, we may write Eq. (8.87) as

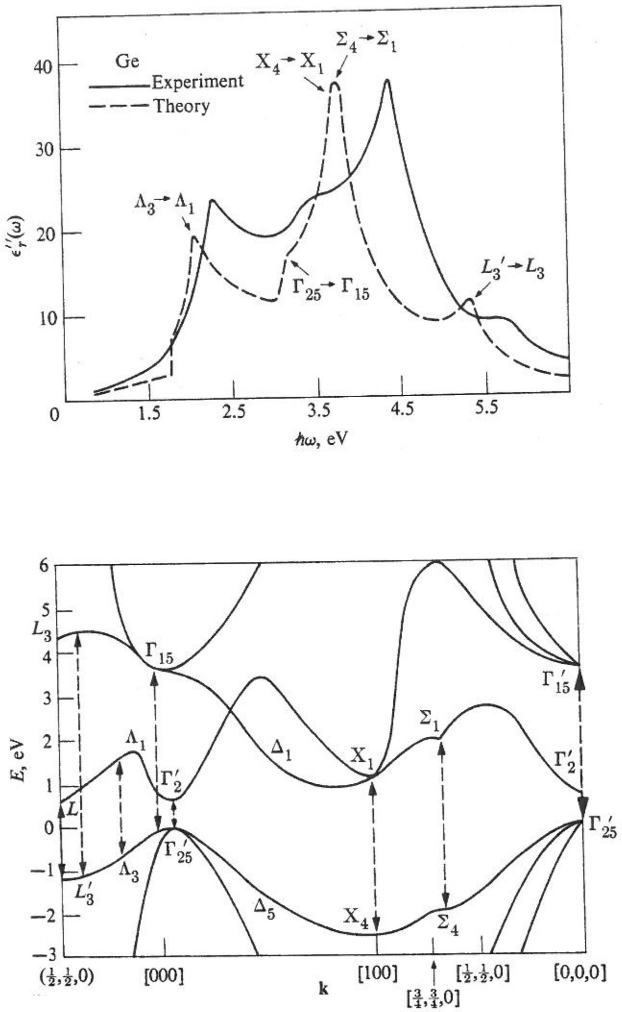


Fig. 8.23 (a) Imaginary dielectric constant $\epsilon_r''(\omega)$ versus photon energy $\hbar\omega$ for Ge. (b) The band structure of Ge. Dashed arrows indicate various critical points. [After Phillips, 1966]

$$\epsilon_r(0) = 1 + \frac{2}{\pi} \int_{\omega_0}^\infty \frac{\epsilon_r''(\omega)}{\omega}\, d\omega, \tag{8.88}$$

where $\omega_0 = E_g/\hbar$ is the frequency at the absorption edge. Clearly, the smaller the gap, the smaller ω_0, and the greater $\epsilon_r(0)$, because of the factor ω^{-1} in the integrand. This explains why $\epsilon_r(0) = 16$ in Ge, whose $E_g \simeq 1$ eV, while $\epsilon_r(0) = 5.6$ in NaCl, whose $E_g = 7$ eV.

Interband electronic polarizability and its associated dielectric constant are responsible for the optical properties of solids, particularly insulators and semiconductors, in the visible and ultraviolet ranges, because only such polarizability is effective at high frequency ranges. Also of importance in insulators and semiconductors is exciton absorption (Section 6.14).

As pointed out, the critical points assume a particularly significant role in the interpretation of interband-transition spectroscopic data. Since these points usually occur at symmetry points or along symmetry direction in the BZ, a knowledge of the interband energy difference $E_c(\mathbf{k}) - E_v(\mathbf{k})$ and the symmetry character (i.e., the location in the zone) of these points are highly useful in elucidating the band structure of the solid. Although the energy difference may be determined from the curve of $\epsilon_r''(\omega)$ versus ω (for example, Fig. 8.23), the accuracy is limited due to the background absorption associated with the noncritical regions of the zone. A special technique, known as *modulation spectroscopy*, has been developed in recent years to overcome this difficulty. The technique consists basically of devising an experimental procedure for extracting the first (or higher) derivative, $d\,\epsilon_r''(\omega)/d\omega$, as a function of ω. The reader can readily see that one can locate the critical points more readily on the derivative curve than on the original curve. Experimentally, this is achieved by superposing on the solid, in addition to the signal, an external time-dependent perturbation varying with a modulation frequency ω_m, and measuring the relative change in the dielectric function $\Delta\epsilon_r''/\epsilon_r''$ induced by the perturbation. Many different types of perturbations have been used, e.g., temperature and hydrostatic pressure. The symmetry character of the critical point is determined by applying a vector perturbation, like an electric field, or a tensor perturbation as a uniaxial pressure. For a brief review, see J. E. Fischer and D. E. Aspner, *Comments on Solid State Physics*, IV, 131; IV, 159. For a thorough treatment, see M. Cardona, 1968, *Modulation Spectroscopy*, New York, Academic Press.

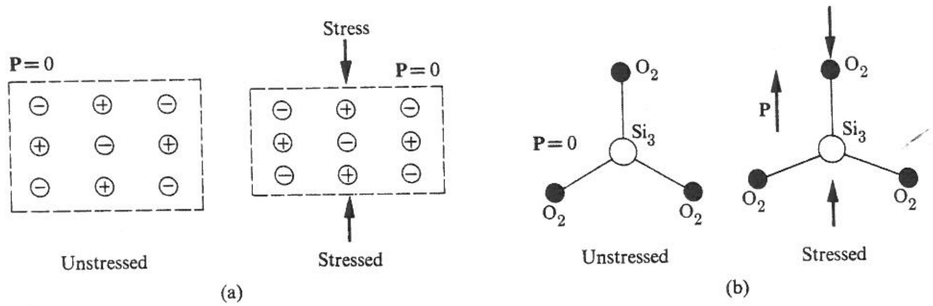
8.10 PIEZOELECTRICITY

In this and the following sections we turn to certain phenomena associated with ionic polarization. The term *piezoelectricity* refers to the fact that, when a crystal is strained, an electric field is produced within the substance. As a result of this field, a potential difference develops across the sample, and by measuring this potential one may determine the field. The inverse effect—that an applied field produces strain—has also been observed. (It was discovered in about 1880.)

The piezoelectric effect is very small. A field of 1000 V/cm in quartz produces a strain of only 10^{-7}. That is, a rod 1 cm long changes its length by 10Å. Conversely, even small strains can produce enormous electric fields.

The piezoelectric effect is often used to convert electrical energy into mechanical energy, and vice versa; i.e., the substance is used as a *transducer*. For instance, an electric signal applied to the end of a quartz rod generates a mechanical strain, which consequently leads to the propagation of a mechanical wave—a sound wave—down the rod. (One can reconvert the mechanical energy into electrical energy at the other end of the rod, if desired, by picking up the electric field produced there.) Quartz is the most familiar piezoelectric substance, and the one most frequently used in transducers.

The microscopic origin of piezoelectricity lies in the displacement of ionic charges within the crystal. In the absence of strain, the distribution of the charges at their lattice sites is symmetric, so the internal electric field is zero. But when the crystal is strained, the charges are displaced. If the charge distribution is no longer symmetric, then a net polarization, and a concomitant electric field, develops. It is this field which operates in the piezoelectric effect.



(a) (b)

Fig. 8.24 Crystal with center of inversion exhibits no piezoelectric effect. (b) Origin of piezoelectric effect in quartz: crystal lacks a center of inversion.

It follows that a substance can be piezoelectric only if the unit cell *lacks a center of inversion*. Figure 8.24(a) shows this, and demonstrates that if a center of inversion *is* present, it persists even after distortion, and consequently the polarization remains zero. However, when there is no center of inversion, as in Fig. 8.24(b), distortion produces a polarization. We can now understand, for example, why no regular cubic lattice can exhibit piezoelectricity.

Table 8.5

Some Piezoelectric Crystals (in Decreasing Value of Piezoelectric Coefficient)

Crystal	Chemical formula	Relative strength
Rochelle salt	$NaKC_4H_4O_6 \cdot 4H_2O$	Very strong
ADP	$NH_4H_2PO_4$	Strong
KDP	KH_2PO_4	Moderate
α-Quartz	SiO_2	Weak

Of the 32 crystal classes, 20 are noncentrosymmetric, and these are candidates for piezoelectric materials. The lack of inversion center, however, is not sufficient to guarantee piezoelectricity, and only relatively few substances, some of which are listed in Table 8.5, exhibit this phenomenon.

Another common application of piezoelectrics, in addition to their use in transducers, is in delay lines. When an electric signal is converted into a mechanical wave, it travels through a quartz rod at the velocity of sound, which, since it is much less than the velocity of light, leads to considerable delay of the signal .[Also piezoelectrics and related electro-optic crystals are now widely used in the fields of laser technology and modern optics. For instance, the cavity length of a laser may be varied continuously in a controlled manner by the application of a voltage to a piezoelectric crystal situated at one end of the cavity.]

8.11 FERROELECTRICITY

We have often commented that ionic susceptibility is not sensitive to variations in temperature. Although this is true for most substances, there is a class of materials which exhibits a marked departure from this rule: the *ferroelectric* materials. In these substances, the static dielectric constant changes with temperature according to the relation

$$\epsilon_r = B + \frac{C}{T - T_C}, \qquad T > T_C, \tag{8.89}$$

where B and C are constants independent of temperature. This relation is known as the *Curie–Weiss law*, and the parameters C and T_C are called the *Curie constant* and *Curie temperature*, respectively.

This behavior is valid in the temperature range $T > T_C$. In the range $T < T_C$, the material becomes *spontaneously* polarized, i.e., an electric polarization develops in it without the help of an external field. (This phenomenon is analogous to the spontaneous magnetization which takes place in ferromagnetic materials.)

A *phase transition* occurs at the temperature T_C. Above the transition temperature, the substance is in the *paraelectric phase*, in which the elementary dipoles of the various unit cells in the crystal are oriented randomly. The dielectric constant is given by (8.89), whose form is illustrated in Fig. 8.25a.

Below the transition temperature, the elementary dipoles interact with each other, and this gives rise to an internal field, which lines up the dipoles. The direction of this field and the associated polarization lie in a certain favorable orientation in the crystal. Figure 8.25(b) shows the variation of the spontaneous polarization P_s with temperature for $T < T_C$. This polarization increases gradually as the temperature is lowered.

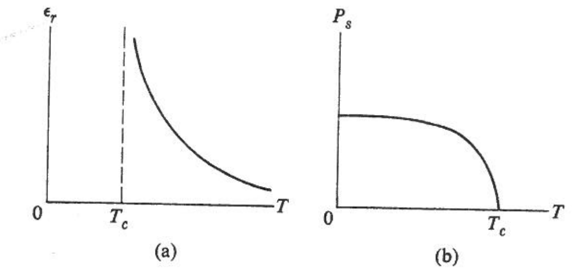


Fig. 8.25 (a) Dielectric constant ϵ_r versus T in a ferroelectric substance. (b) Spontaneous polarization P_s versus T in a ferroelectric substance.

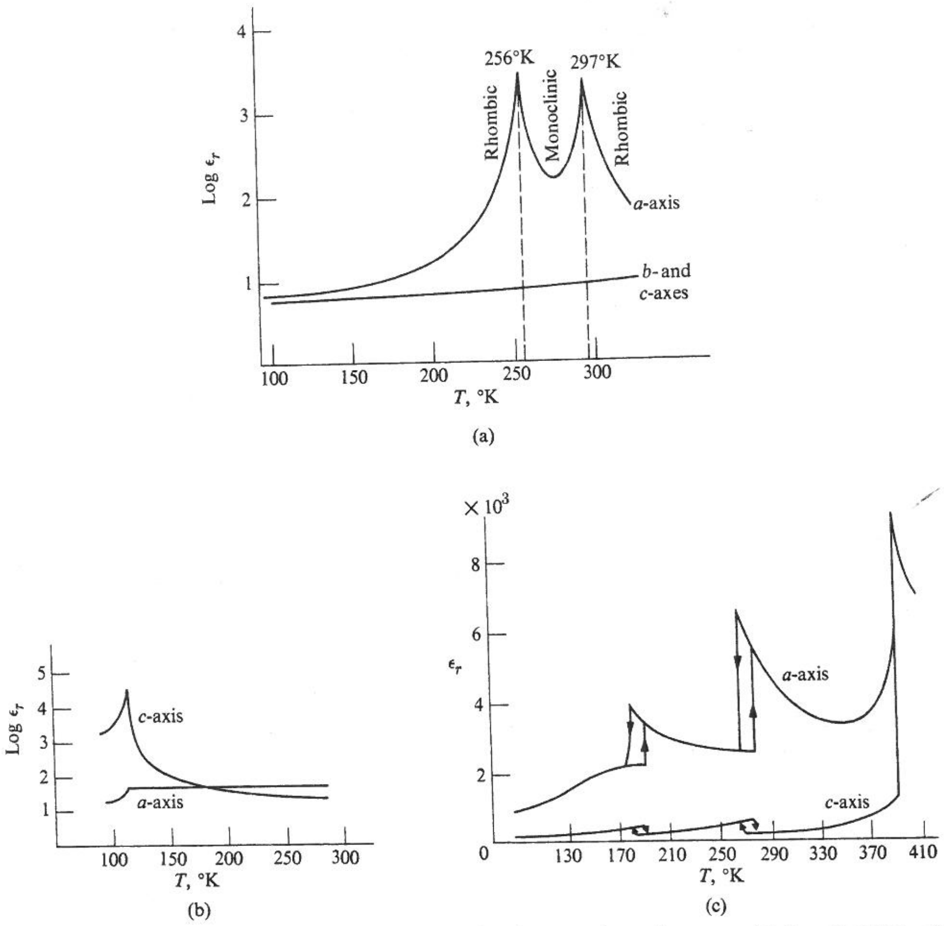


Fig. 8.26 (a) Log ϵ_r versus T for Rochelle salt along a-, b- and c-axes. (After Halblützel) (b) Log ϵ_r versus T for KDP along a- and c-axes. (After Busch) (c) ϵ_r versus T for $BaTiO_3$. (After Merz)

The second term in (8.89) is usually much larger than the first. Thus, although typically $B \simeq 5$, $\epsilon_r \simeq 1000$ or even larger near the transition temperature. We may therefore ignore B, and write to a good approximation

$$\epsilon_r = \frac{C}{T - T_C}. \tag{8.90}$$

There are three major ferroelectric groups: The Rochelle salt group, the KDP (potassium dihydrogen phosphate) group, and the perovskites group, headed by barium titanate. Table 8.6 gives data on these substances, and Fig. 8.26 presents the variation of temperature of the dielectric constants. Note in particular the enormous value of the dielectric constant in barium titanate, for which $\epsilon_r \simeq 10^5$ near the transition temperature.

Table 8.6

Ferroelectric Data

Crystal	Chemical formula	T_C(°K)	C, °K	P_s, coul/m^2	
Rochelle-salt group	$NaK(C_4H_4O_6) \cdot 4H_2O$	297 (upper) 255 (lower)	178	267×10^{-5}	[at 278°K]
	$LiNH_4(C_4H_4O_6 \cdot H_2O$	106		220	[95]
KDP group	KH_2PO_4	123	3100	5330	[96]
	KD_2PO_4	213		9000	—
	RbH_2PO_4	147		5600	[90]
	CsH_2AsO_4	143		—	—
Perovskites	$BaTiO_3$	393	1.7×10^5	26,000	[296]
	$SrTiO_3$	32		3000	[4]
	WO_3	223		—	—

The microscopic model

Let us now inquire into the microscopic source of ferroelectricity. The most obvious explanation is to assume a dipolar substance and use the Lorentz local field correction obtained in (8.30). This leads to a dielectric constant

$$\epsilon_r = \frac{1 + \frac{2}{3}\chi}{1 - \frac{1}{3}\chi}. \tag{8.91}$$

If we set $\chi \simeq \chi_d$, thus neglecting electronic and ionic contributions, which is appropriate in dipolar substances, and substitute for χ_d from (8.43), we find that

$$\epsilon_r = \frac{T + C}{T - T_C}, \tag{8.92}$$

where $C = 2Np^2/9\epsilon_0 k$ and $T_C = Np^2/9\epsilon_0 k$. If we ignore the term T in the numerator, it is evident that Eq. (8.92) has the same form as (8.90). In particular, the dipolar model predicts that ϵ_r diverges as T approaches T_C from above, and consequently one expects the system to become unstable and make a transition to a new phase, the "ferroelectric phase." The divergence at T_C is referred to as the *polarization catastrophe.*

Despite the fact that the dipolar model seems to lead naturally to ferroelectricity, the model is inadequate to account for observations. If we apply this model to water, for instance, for which $N \simeq \frac{1}{3} \times 10^{29}$ m^{-3} and $p = 0.62$ debye, it predicts that water would become ferroelectric at $T_C = 1100$°K. In fact, however, water never becomes ferroelectric, not even below its freezing point.

Another fact which underscores the failure of the model is its prediction that any dipolar substance should become ferroelectric at a sufficiently low temperature. Instead, however, all known ferroelectrics are *nondipolar* in nature. We must therefore look elsewhere for the explanation of ferroelectricity.

Ferroelectricity is associated with ionic polarizability. To see this, let us consider an ionic substance. The ac dielectric constant is given by

$$\epsilon_r(\omega) = n^2 + \frac{A}{\omega_t^2 - \omega^2}, \tag{8.93}$$

where we have used (8.74), and denoted $\chi_i(0)\omega_t^2$ by the constant A. The static dielectric constant, according to (8.93), is given by

$$\epsilon_r(0) = n^2 + \frac{A}{\omega_t^2}. \tag{8.94}$$

This expression shows that $\epsilon_r(0)$ increases as ω_t decreases, and indeed $\epsilon_r(0)$ diverges as $\omega_t \to 0$.

But why should ω_t decrease? We shall now show that the inclusion of the local field does indeed lead to a reduction in the value of this frequency. According to Eqs. (3.83 and 3.84), the transverse motion for the unit cell is governed by the equation

$$\mu \frac{d^2 u}{dt^2} + 2\beta u = 0, \tag{8.95}$$

where μ is the reduced mass of the unit cell, u the relative displacement between the ions, and β the force constant between the ions† (Section 3.6). This expression leads to a mode of oscillation with a frequency

$$\omega_t^2 = \frac{2\alpha}{\mu}, \tag{8.96}$$

which is the frequency of the long-wavelength optical phonon.

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† The force constant is denoted here by β rather than α, as in Chapter 3, in order to avoid any confusion with polarizability.

The equation of motion (8.95), however, requires modification if we consider the local field correction, because there is a polarization $P = Ne^*u$ associated with the displacement u, and hence a Lorentz electric field

$$\mathscr{E} = \frac{P}{3\epsilon_0} = \frac{Ne^*u}{3\epsilon_0}, \tag{8.97}$$

where e^* is the effective charge on the ion. Because of this field there is now an electric force acting on the unit cell given by $2e^*\mathscr{E}$, which modifies the equation of motion (8.95) to

$$\mu \frac{d^2u}{dt^2} + 2\beta u = 2e^*\mathscr{E}.$$

If one substitutes for $\mathscr{E}$ from (8.97), and rearranges the equation, one finds that

$$\mu \frac{d^2u}{dt^2} + \left(2\beta - \frac{2Ne^{*2}}{3\epsilon_0}\right) u = 0,$$

which is the equation for a harmonic oscillator of frequency ω_t^* given by

$$\omega_t^{*2} = \frac{2\beta}{\mu} - \frac{2Ne^*}{3\epsilon_0\mu}$$

or

$$\omega_t^{*2} = \omega_t^2 - \frac{2Ne^*}{3\epsilon_0\mu}, \tag{8.98}$$

where we have used Eq. (8.96).

The frequency ω_t^* is less than ω_t, the frequency obtained by neglecting the local field. It is easy to see the reason for this reduction: When the lattice is displaced, a local field is created in the same direction as u. The effect of this field is to reduce the restoring force, and consequently the oscillator frequency. The origin of the force constant β lies in the short-range elastic forces between the ions, while the local field is due to the familiar long-range Coulomb forces between these ions.

The expression (8.94) for the dielectric constant should now be replaced by

$$\epsilon_r(0) = n^2 + \frac{A}{\omega_t^{*2}}. \tag{8.99}$$

The effect of the local field is to increase the dielectric constant. If the second term on the right of (8.98) is large enough to cancel the first term, then $\omega_t^* \to 0$, and the dielectric constant becomes infinite. What happens, in fact, is that the system feels the *instability* and makes an adjustment to avoid the divergence, i.e., undergoes a transition to the ferroelectric phase. It is thus expected that the system would also undergo a simultaneous transition into a more stable crystal structure. This is indeed found to be the case in all ferroelectric transitions.

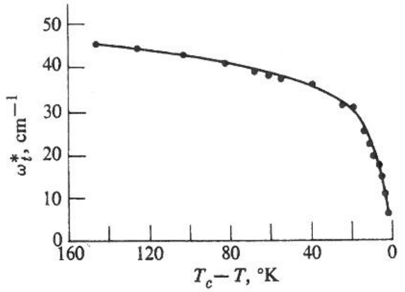

Fig. 8.27 Transverse frequency ω_t^* versus ($T_C - T$) in antimony sulphoiodide (SbSI). (After Perry and Agrawal, *Solid State Comm.* **8**, 225, 1970)

Figure 8.27 illustrates the observed decrease in phonon frequency as the temperature approaches the Curie temperature. Note that the frequency here is about 10 cm^{-1}, or $\nu = 3 \times 10^9$ Hz, considerably smaller than a typical optical phonon frequency of 10^{13} Hz.†

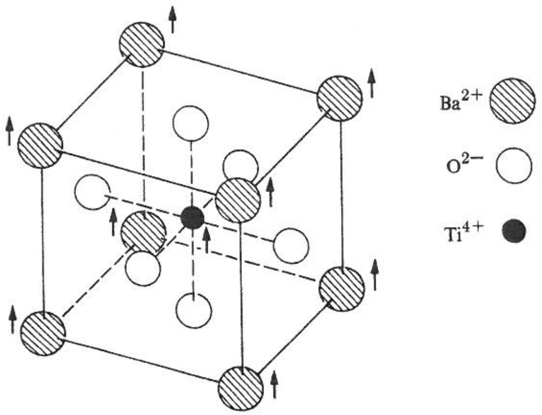

Fig. 8.28 Structure of BaTiO$_3$ in cubic phase (above T_C).

As a concrete example of ferroelectric structure transformation, Fig. 8.28 shows the appropriate structure for BaTiO$_3$. Above the Curie temperature the structure is cubic, but as the temperature is lowered to T_C, the Ba^{2+} and Ti^{4+} ions are displaced as shown, producing a slightly compressed cubic structure. Although the displacement is small—only about 0.15 Å—it is enough to give the

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† The mode whose frequency vanishes at the Curie temperature is called the *soft* mode.

observed polarization. It is this relative displacement of the internal structure which gives the model its name: the *displacive model*.

We have shown that the Lorentz calculation of the local field is misleading when applied to dipolar substances; yet we have used the same procedure for evaluating this field when it is associated with the ionic polarization. There is no contradiction here, because Onsager showed, many years ago, that while the Lorentz procedure is valid in evaluating the field associated with electronic and ionic polarizabilities, the procedure is inapplicable when one is dealing with orientational polarizability. Onsager demonstrated that the actual local field associated with the dipolar polarizability is much smaller than that provided by the Lorentz procedure, and it is this overestimation which leads to the erroneous conclusions concerning ferroelectricity. You can find a detailed discussion of this point in Frölich (1958).

Ferroelectricity, like piezoelectricity, can occur only in noncentrosymmetric crystals. The requirements of ferroelectricity are, however, more stringent, requiring the existence of a favorable axis of polarity. Only 10 crystal classes have sufficiently low degrees of symmetry to permit the occurrence of ferroelectricity.

Ferroelectric domains

A substance which is in its ferroelectric phase undergoes spontaneous polarization, but the *direction* of the polarization is not the same throughout the sample. The material is divided into a number of small *domains*, in each of which the polarization is constant. But the polarization in the different domains are different, so that the net total polarization of the whole sample vanishes in the equilibrium situation (Fig. 8.29).

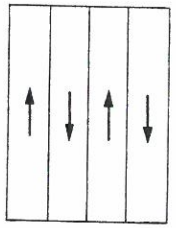

Fig. 8.29 Domain structure in an unpolarized ferroelectric sample.

When an external field is applied, the domains whose polarization is parallel to the field grow, while the domains of opposite polarization shrink. These growing and shrinking processes continue as the field increases until, at a sufficiently high field, the whole of the sample is polarized parallel to the field.

We shall discuss the concept of domains, and the associated hysteresis loop, in detail in connection with ferromagnetic materials (Section 9.11).

SUMMARY

The dielectric constant and molecular polarizability

The dielectric constant ϵ is defined by the equation

$$\mathbf{D} = \epsilon \mathscr{E},$$

where **D** is the electric displacement and $\mathscr{E}$ the average field inside the dielectric. In terms of the polarization **P**, the displacement vector **D** is

$$D = \epsilon_0 \mathscr{E} + \mathbf{P}.$$

The polarization **P** arises as a result of the polarization of the molecules, and is given by

$$\mathbf{P} = N\mathbf{p},$$

where N is the concentration of molecules and **p** the electric moment of each of these molecules. The electric moment is proportional to the field, and is given by

$$\mathbf{p} = \alpha \mathscr{E},$$

where α is the *molecular polarizability*. Substituting this into the above equations, we may express the relative dielectric constant in terms of the polarizability,

$$\epsilon_r = 1 + (N\alpha/\epsilon_0).$$

This result, which ignores the local-field correction, holds well in gases. In liquids and solids, however, the local-field correction is appreciable, and must be included. We then find the local field to be

$$\mathscr{E}_{\text{loc}} = \mathscr{E} + (\tfrac{1}{3}\epsilon_0)\,\mathbf{P},$$

which leads to the Clausius–Mosotti relation,

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N\alpha}{3\epsilon_0}.$$

Dipolar polarizability

Molecular polarizability is, in general, the additive result of dipolar, ionic, and electronic contributions. Statistical treatment of dipolar polarization gives the following expression for dipolar polarizability,

$$\alpha_d = p^2/3kT,$$

which decreases as the inverse of the temperature. The dielectric constant is

$$\epsilon_r = 1 + N\alpha_{ei}/\epsilon_0 + Np^2/3\epsilon_0 kT.$$

By plotting ϵ_r versus $1/T$, one may determine both the permanent moment p and the electronic-ionic polarizability α_{ei}. This information sheds light on the geometrical structure of the molecules.

The ac dipolar polarizability may be calculated by assuming that the dipole does not follow the field instantaneously, but with a certain relaxation time τ. One then finds the frequency-dependent dielectric constant

$$\epsilon_r(\omega) = n^2 + \frac{\epsilon_r(0) - n^2}{1 - i\omega\tau},$$

where n is the optical index of refraction and $\epsilon_r(0)$ the static dielectric constant. As the frequency ω increases from the range $\omega \ll 1/\tau$ to the range $1/\tau \ll \omega$, the dipolar contribution decreases from the value $[\epsilon_r(0) - n^2]$ to 0, because at high frequencies the dipoles no longer follow the field. The imaginary part of the dielectric constant is related to the energy absorbed by the dielectric from the field.

Ionic polarizability

Ionic crystals exhibit dispersion in the infrared region, as a result of the strong interaction of the electromagnetic wave with the optical phonons of the substance. The dielectric constant is

$$\epsilon_r(\omega) = n^2 + \frac{\epsilon_r(0) - n^2}{1 - (\omega^2/\omega_t^2)},$$

where ω_t is the optical phonon frequency. As ω varies from the range $\omega \ll \omega_t$ to the range $\omega_t \ll \omega$, the ionic contribution decreases from $[\epsilon_r(0) - n^2]$ to 0, because the ions no longer follow the field at high frequencies.

Electronic polarizability

A simplified classical treatment of static electronic polarizability yields

$$\alpha_e = 4\pi\epsilon_0 R^3,$$

where R is the atomic radius. The classical ac electronic polarizability, obtained by treating the electron as a classical particle bound to the remainder of the atom by a harmonic force, is

$$\alpha_e(\omega) = \frac{e^2/m}{\omega_0^2 - \omega^2},$$

where ω_0 is the natural oscillation frequency of the bound electron. This yields an optical dielectric constant n^2 given by

$$n^2 = 1 + \frac{NZe^2/\epsilon_0 m}{\omega_0^2 - \omega^2}.$$

Quantum treatment leads to a similar result.

In solids, dielectric and optical properties are related directly to the structure of the energy band of the substance.

Piezoelectricity

In noncentrosymmetric ionic crystals, the mechanical straining of a substance produces an internal electric field, and vice versa. This property is widely utilized in transducers, i.e., devices which convert electrical into mechanical energy, and vice versa.

Ferroelectricity

A ferroelectric substance is one which exhibits spontaneous polarization below a certain temperature. Above this *Curie temperature* T_C the dielectric constant is given by the *Curie–Weiss* law,

$$\epsilon_r = B + \frac{C}{T - T_C}.$$

The ferroelectric property can be explained by the *displacive model*: As the temperature approaches T_C from above, one of the optical phonon modes becomes so soft—due to the local-field correction—that $\epsilon_r \to \infty$, causing a structural phase transition and a concomitant spontaneous polarization.

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QUESTIONS

1. Let A and B refer to two different atoms. Using symmetry arguments, determine whether the following types of molecules are dipolar or not: AA, AB, ABA (rectilinear arrangement), ABA (triangular arrangement), AB_3 (planar arrangement with A at center of triangle), AB_4 (tetrahedral arrangement). Give one example of each type.
2. The static dielectric constant of water is 81, and its index of refraction 1.33. What is the percentage contribution of ionic polarizability?
3. For a typical atom, estimate the field required to displace the nucleus by a distance equal to 1% of the radius. [Refer to Eq. (8.79).]
4. Explain physically why ionic polarizability is rather insensitive to temperature. Do you expect a slight change in temperature to lead to an increase or a decrease in the polarizability as T rises? Explain.
5. Referring to Table 6.4, one notes that the polarizabilities of the alkali ions are consistently lower than those of the halide ions. Give a physical, i.e., qualitative, explanation of this fact.
6. In the classical treatment of electronic ac polarizability, the restoring force on the electron is assumed to have a harmonic form. How do you justify this in view of the fact that the force due to the nucleus has a coulomb form which is very different from the harmonic form? Give an expression for the natural frequency ω_0 in terms of the properties of the atom.
7. If one sets ω_0 equal to zero in (8.85), one obtains the same electron dielectric constant found in Section 4.11. Explain why.

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8. Suppose that a light beam passing through a semiconductor is absorbed either by electrons excited from the valence band to the conduction band (fundamental absorption), or by excitons. Describe an experimental electrical procedure for testing which of these two mechanisms is the operative one.

PROBLEMS

1. Using Coulomb's law, derive the expression (8.2) for the field of an electric dipole. Assume that $d \ll r$.
2. a) Derive Eq. (8.3), that is, show that the torque exerted on a dipole $\mathbf{p}$ by a uniform field $\mathscr{E}$ is given by

$$\boldsymbol{\tau} = \mathbf{p} \times \mathscr{E}.$$

   b) Derive Eq. (8.4), that is, show that the potential energy of a dipole in a field is given by

$$V = -p\mathscr{E}\cos\theta,$$

   where θ is the angle between the dipole and the field.
3. The dipole moment for a general distribution of charges is defined as the sum

$$\mathbf{p} = \sum_i q_i \mathbf{r}_i,$$

   where q_i and $\mathbf{r}_i$ are the charge and position, respectively, of the i^{th} charge, and the summation is over all the charges present. The choice of the origin of coordinates is arbitrary.
   a) Show that the above reduces to expression (8.1) for the special case of two equal and opposite charges. (Take an arbitrary origin.)
   b) Prove that if the charge system has an overall electrical neutrality, then the dipole moment is independent of the choice of origin.
4. Determine the dipole moment for the following charge distributions: 1.5 μcoul each at the points (0,3), (0,5), where the coordinate numbers are given in centimeters.
5. A parallel-plate capacitor of area 4×5 cm^2 is filled with mica ($\epsilon_r = 6$). The distance between the plates is 1 cm, and the capacitor is connected to a 100-V battery. Calculate:
   a) The capacitance of this capacitor
   b) The free charge on the plates
   c) The surface charge density due to the polarization charges
   d) The field inside the mica. (What would the field be if the mica sheet were withdrawn?)
6. Prove that when a molecule is polarized by a field $\mathscr{E}$, a potential energy is stored in this molecule. The value of this energy is $\frac{1}{2}\alpha\mathscr{E}^2$, where α is the molecular polarizability. What is the value of this energy for an Ar atom in a field of 10^3 volt/m? The polarizability of this atom is 1.74×10^{-40} farad-m^2.
7. a) Show that the surface charge density of the polarization charges on the outer surface of a dielectric is given by

$$\sigma_p = \mathbf{P} \cdot \hat{\mathbf{n}},$$

   where $\hat{\mathbf{n}}$ is a unit vector normal to the surface.

b) Prove Eq. (8.25). That is, show that the depolarization field in an infinite slab, in which the field is normal to the slab, is given by

$$\mathscr{E}_1 = -\frac{1}{\epsilon_0}\mathbf{P}.$$

c) The depolarization field $\mathscr{E}_1$ depends on the geometrical shape of the specimen. When the shape is such that the polarization inside is uniform, the depolarization factor L is defined such that

$$\mathscr{E}_1 = -\frac{L}{\epsilon_0}\mathbf{P}.$$

Show that the depolarization factor for an infinite slab with field normal to the slab is 1, while for a slab in which the field is parallel to the face, $L = 0$. Also show that $L = \frac{1}{3}$ for a sphere, and $L = 0$ or $\frac{1}{2}$ for a cylinder, depending on whether the field is parallel or normal to the axis of the cylinder, respectively. Put these results in tabular form.

8. a) Prove Eq. (8.28), showing that the field $\mathscr{E}_3$ due to the dipoles inside a spherical cavity vanishes in a cubic crystal.
   b) Suppose that the Lorentz cavity is chosen to have a cubic shape. Calculate the field $\mathscr{E}_2$ due to the charges on the surface of this cavity.
   c) Does this new choice of cavity modify the value of the local field? Explain. Use your answer to evaluate the field $\mathscr{E}_3$ due to the dipoles inside the cavity. (You may take the crystal to be cubic.)
9. The field $\mathscr{E}_3$ of Eq. (8.24) due to the dipole inside a cavity depends on the symmetry of the crystal, and in general does not vanish in a noncubic crystal. Assuming that this field has the form

$$\mathscr{E}_3 = (b/\epsilon_0)\,\mathbf{P},$$

where b is a constant, calculate the dielectric constant ϵ_r in such a substance.

10. Show that Eq. (8.33) reduces to (8.18) in gaseous substances, i.e., substances in which $N\alpha/\epsilon_0$ is very small.
11. Establish Eq. (8.40) by carrying out the necessary integration.
12. a) Expand the Langevin function $L(u)$ of (8.41) in powers of u up to and including the third power in u, and show that

$$L(u) = u/3 - u^3/45 + \cdots, \quad u \ll 1.$$

   b) Calculate the field required to produce polarization in water equal to 10% of the saturation value at room temperature.
13. a) Using Fig. 8.13 and Table 8.1, calculate the molecular concentration of $CHCl_3$, CH_2Cl_2, and CH_3Cl at which the measurements reported in the figure were made.
   b) Calculate the electronic-ionic polarizability α_{ei} in each of these substances.
14. The molar polarizability of water increases from 4×10^{-5} to 6.8×10^{-5} m^3 as the temperature decreases from 500°K to 300°K. Calculate the permanent moment of the water molecule.
15. Calculate the real and imaginary parts of the dielectric constant $\epsilon_r'(\omega)$ and $\epsilon_r''(\omega)$ for water at room temperature. Plot these quantities versus ω up to the frequency 10^{12} Hz. (Use semilogarithmic graph paper.)

16. We expressed the absorption in dipolar substances in terms of the imaginary dielectric constant, $\epsilon_r''(\omega)$. It is also frequently expressed in terms of the so-called *loss angle* δ, which is defined as

$$\tan\delta = \frac{\epsilon_r''}{\epsilon_r'},$$

where the quantity $\tan\delta$ is called the *loss tangent*.

   a) Show that the electric displacement vector is

$$D = \epsilon_0[\epsilon_r'^2 + \epsilon_r''^2]^{1/2}\, e^{i\delta}\,\mathscr{E}.$$

   b) Calculate the loss tangent as a function of the frequency, and plot the result versus $\omega\tau$.
   c) Show that the power absorbed by a dielectric (per unit volume) is

$$Q = \tfrac{1}{2}\,\epsilon_0\epsilon_r'\omega\tan\delta\,\mathscr{E}^2.$$

   Express the loss angle $\tan\delta$ in terms of the ratio of the dissipated energy to the energy stored in the dielectric.
   d) Calculate the loss tangent in water at room temperature at frequency 10 GHz. Also calculate the energy dissipated per unit volume, given that the field strength is 5 volts/m.
17. Assuming that the jumping period τ decreases exponentially with temperature as in (8.73), explain how the real and imaginary parts of the dielectric constant ϵ_r' and ϵ_r'' vary with temperature. Plot the results versus $1/T$. (Assume that all quantities other than τ are independent of temperature.) Does the loss tangent increase or decrease with temperature? Explain.
18. In deriving the result (8.74) for the dielectric constant involving ionic polarizability, it was assumed that the ions experience no collision or loss during their motion. Postulate the existence of a collision mechanism whose time is τ_i, and reevaluate the (complex) dielectric constant. Plot the real and imaginary parts $\epsilon_r'(\omega)$, $\epsilon_r''(\omega)$ versus ω, and compare with Fig. 8.20.
19. The crystal NaCl has a static dielectric constant $\epsilon_r(0) = 5.6$ and an optical index of refraction $n = 1.5$.
   a) What is the reason for the difference between $\epsilon_r(0)$ and n^2?
   b) Calculate the percentage contribution of the ionic polarizability.
   c) Use the optical phonon for NaCl quoted in Table 3.3, and plot the dielectric constant versus the frequency, in the frequency range $0.1\,\omega_t$ to $10\,\omega_t$.
20. Using the data in the previous problem and Table 8.4, calculate the nearest distance between Na and Cl atoms. Calculate the lattice constant of NaCl, and compare the result with the value quoted in Table 1.2. (Sodium chloride has an fcc structure.)
21. Calculate the static polarizability for the hydrogen atom, assuming that the charge on the electron is distributed uniformly throughout a sphere of a Bohr radius. Also calculate the natural electron frequency ω_0.
22. Show that expression (8.80) leads to a static susceptibility equal to that given by (8.77). Use elementary electrostatic arguments to find ω_0 in terms of atomic characteristics.

23. Modify expression (8.80) for the electronic polarizability to include the presence of a collision mechanism of time τ. Evaluate the high-frequency dielectric constant, both real and imaginary parts.
24. Carry out the steps leading to the expression (8.86) for $\epsilon_r''(\omega)$ due to interband transition in solids.
25. The Kramers-Kronig relations, which lead to (8.88), are derived in Brown (1966). Read the discussion there and present your own summary.
26. a) An acoustic oscillator is made of a quartz rod. Explain why the resonant frequency of this oscillator is given by

$$\nu = \frac{v_s}{2l},$$

where l is the length of the rod and v_s the velocity of sound in the specimen.

b) Show that this frequency is also given by the expression

$$\nu = \frac{1}{2l}\sqrt{\frac{Y}{\rho}},$$

where Y is Young's modulus and ρ the mass density of the rod.

c) Taking $Y = 8.0 \times 10^{11}$ dyne/cm^2 and $\rho = 2.6$ g/cm^3 for quartz, calculate the length of a 5-kHz-oscillator.

d) Calculate the potential difference across the rod for a strain of 2×10^{-8}. The piezoelectric coefficient $P/S = 0.17$ coul/m^2.

27. Many applications of piezoelectric crystals are discussed in Mason (1950). Make a summary of these.
28. In evaluating the local field correction in (8.97), we neglected the electronic contribution. Reevaluate the correction including this contribution, and calculate the new optical phonon frequency ω_t^* and the dielectric constant.
29. A dielectric has a very small electrical conductivity. However, if a very strong electric field is applied, the conductivity suddenly increases as the field reaches a certain high value. This phenomenon, known as *dielectric breakdown*, is due to the fact that a strong field ionizes the electrons from their atoms, and as these electrons are accelerated they ionize other atoms, etc. Read the discussion of dielectric breakdown presented in N. F. Mott and R. W. Gurney (1953), *Electronic Processes in Ionic Crystals*, second edition, Oxford University Press, and write your own review of this phenomenon.
30. The discussion of dielectric and optical properties in the text was limited to the *linear* region, i.e., the field is sufficiently small that polarization is a linear function of the field. Nonlinear effects become important at high fields, which are now conveniently available from laser sources. Read the discussion of such effects given in A. Yariv (1971), *Introduction to Optical Electronics*, Holt, Rinehart, and Winston, and write a brief summary.

CHAPTER 9 MAGNETISM AND MAGNETIC RESONANCES

Where order in variety we see,
and where, though all things differ, all agree.
Alexander Pope